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Chromium Concentrations in Automotive Paints from Retail Stores in Kenya

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Chromium (Cr) is among the heavy metals that are added to automotive paints to provide protection against corrosion and reflective properties. However, exposure to hexavalent chromium Cr(VI), which is the toxic form of Cr is associated with adverse health effects such as lung cancer. The study, therefore, assessed Cr levels in the automotive paints commonly used by spray painters in informal settings in Nairobi City. Chromium concentrations were determined in triplicates in the three sets of automotive paint samples in red, blue and green colours. The same samples were also used for the determination of lead content and the findings of the study were published elsewhere. The automotive paint samples were procured from 8 formal and informal retail stores. The Cr concentrations was also analyzed using Atomic Absorption Spectrophotometry. The mean ± standard deviation (SD) of Cr levels obtained from informal retail shops ranged from 120.5±10.6 to 2771.9±35.6 parts per million (ppm). On the contrary, those from the formal retail stores were significantly lower ($p < 0.05$), and were in the range of 39.3±7.0 to 461.9±11.1 ppm. The Cr levels in automotive paints varied greatly across different colours and retail shops. Substantial levels were

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observed in almost all paint samples purchased from the informal retail shops except one retail shop. The elevated Cr levels in various colours of automotive paints used by spray painters in the informal sector call for a comprehensive assessment of Cr in these settings along with health-driven policies to address related health impacts.

Keywords: Chromium-based paints; automotive repair; spray painting; retail stores.

1. INTRODUCTION

"Chromium (Cr) is among the heavy metals that are extensively added to paints because of their useful properties" [1-11]. Hexavalent chromium [Cr(VI)] pigments are essentially used to manufacture paints to prevent corrosion [1,4,7,8]. Green chromium (III) oxide is more stable and forms long-lasting pigments [7]. Furthermore, the pigments are resistant to both alkaline and acidic conditions with excellent covering and hiding power. Additionally, most Cr compounds form coloured pigments as a result of the excitation of an electron from a lower energy of the d-orbital to a higher energy level [7,8]. It is for this reason that a wide array of colours are achieved in the painting industries ranging from yellow to dark red [6-9].

"Chromium (VI) peroxide is formed by the addition of acidified hydrogen peroxide solutions to sodium chromate or potassium dichromate" [2,8,11]. In most cases, the yellow chromates or orange dichromates can turn to the dark blue colour of chromium (VI) peroxide whereas chromic sulfate is dark green. The yellow lead chromate paint pigment is composed of pure lead chromate. Lead sulfochromate is in a mixed phase of pigments, it is usually a combination of lead chromate and lead sulphate while lead chromate molybdate sulphate consists of lead chromate, lead sulphate and lead molybdate but in varying proportions [8,11].

"Chromium exists in two stable oxidation states, the trivalent (III) and hexavalent (VI) forms" [12,15]. The latter has more toxicological effects than Cr(III) due to its high solubility, mobility and strong oxidizing abilities [12-19]. Although the mechanism of Cr(VI) induced toxicity is not clear, it appears that oxidative stress may play an important role [14,15]. The Cr(VI) form is usually the product of anthropogenic activities [12,15]. It is therefore widely studied in occupational exposure, and is a potentially known irritant, corrosive and carcinogen associated with lung, nasal, and sinus cancers [12,14,19,21]. It is also genotoxic and mutagenic [22]. "Chronic exposure to Cr(VI) compounds through inhalation results in health impacts on the respiratory tract, with perforations and ulcerations of the septum" [12,17-24]. "Bronchitis, decreased pulmonary function, pneumonia, asthma, nasal itching and soreness are some of the adverse health effects that have also been reported. Moreover, Cr(VI) is capable of damaging the skin and eyes causing irritations due to its high penetration power and ability to form free radicals" [14,15,16].

As discussed in details in the previous publications, much of these exposures are through brazing, soldering, welding, cutting; coating and painting activities, and metal treatment, which are typical of auto repair and spray painting operations in the informal settings [25-31]. Chromium also has ability to persists in the environment for a long time and is commonly non-biodegradable in nature [32-34]. In this way, the concentrations gradually reach its critical level over time. It pollutes the soils, water and air, thereby posing a significant health risk to humans [19,26,32-34]. Untreated industrial effluents in paint-related activities have been identified as the main sources of Cr (VI) pollution in the environment [34].

During chemical analysis, Cr(VI) and Cr(III) are capable of inter-conversion to either species, which is an impediment for quantitative determination and establishment of the regulatory restriction of hexavalent chromium [11,16]. Besides, Cr(VI) is easily reduced to a more stable Cr(III) in the presence of reducing agents or oxidizable agents. This also implies that the availability of Cr (III) is a health risk due to possible conversion to hexavalent chromium [12,34]. There is hence an environmental health concern over the availability of Cr in the paint products and its related adverse health effects. This study was therefore undertaken to determine the concentrations of Cr in automotive paint that is frequently used by spray painters in the informal settings. The investigation is part of a recently published article by Mwai et al. [30], that assessed lead (Pb) content in the automotive paint samples purchased at formal and informal outlets in Kenya

2. METHODS AND MATERIALS

2.1 Study Area

The automotive paint samples were procured from formal and informal retail shops that were in close proximity to spray painting activities that were clustered within a one km radius [30]. A detailed map was published that describes the study area where the paint samples were purchased along with the clustered spray painting operations within different land use in densely populated residential areas and commercial sites [30].

2.2 Sampling Procedure

The sampling procedures for the automotive paints have further been discussed and published [30]. It involved the procurement of three sets of 250 mL and 100 mL cans of automotive paints that consisted of red, blue and green colours from each of the eight formal and informal retail shops, respectively. The samples were randomly selected. The paint samples were coded as follows, those from the: Formal Industrial Area shops-1 and 2 were coded as FIA 1 and FIA 2, Formal Kariobangi North shops-1 and 2 were coded as FKN 1 and FKN 2, Informal Kariobangi South shops-1 and 2 were coded as IKS 1 and IKS 2 and Informal Kamukunji shops-1 and 2 were coded as IK 1 and IK 2. The Supplementary Material, S1 in Fig. 2 summarizes the coding of the paints [30].

2.3 Laboratory Preparation of Samples

The coded samples were subsequently transferred to the analytical laboratories and were subjected to the chemical preparation including digestion of the samples prior to metal analysis [30].

2.4 Analysis of Chromium Levels

The digested samples in triplicates were thereafter analyzed using the Atomic Absorption Spectroscopy (AAS) Shimadzu ASC 7000 (auto-sampler) equipped with an appropriate mono-elementary hollow cathode lamp for chromium [35]. The deuterium (D2) arc-background corrector was used for the quantification of total chromium. A series of standards of 1, 2, 4, 6, 8 and 20 parts per million (ppm) for Cr calibration curves were freshly prepared by serial dilution in 0.01 M nitric acid (1% (v/v) from 1000 ppm commercial stock for the AAS.

The Cr levels in the digested paint and blank samples were assayed using AAS at optimized operational conditions (Table 1). The concentration was then obtained directly from the standard calibration curves after correction of the absorbance using appropriate reagent blanks. The samples were diluted in cases where their absorbance was higher than that of the standard solution, All the automotive paint samples were measured in triplicates and the mean values were expressed in parts per million (ppm).

2.5 Quality Control and Assurance

Quality control and assurance were maintained as published elsewhere [30]. The Inter-laboratory comparisons were also carried out by randomly subjecting 10 selected samples to similar analytical procedures at the Analytical Laboratory at the Mines and Geological Department under the Ministry of Mining and the Department of Chemistry of the University of Nairobi. The Pearson correlation coefficient at $P = 0.05$ gave a positive correlation coefficient of $r = 0.9997$. Furthermore, the analyzed samples were randomly spiked with the addition of varying amounts of Cr in the standard solutions. Spike recovery values were between 95 and 105% and this was within the expected AAS performance. The validity of the method was further ascertained by cross-method checks and replication analysis. The averages of all analyzed samples in triplicates were considered when the relative standard deviation (RSD) values were less than 5%, indicating a high precision.

2.6 Data Analysis

The coded raw data of Cr levels in parts per million (ppm) of three sets of colours of automotive paints from eight formal and informal retail shops were subjected to appropriate statistical analysis. The Cr concentrations were analyzed in triplicate ($n = 3$) and expressed as arithmetic means with a standard deviation (±SD). Descriptive analyses were applied to all variables. One-way analysis of variance (ANOVA) and the Student’s t-test were used for the comparison of different colours in automotive paint samples purchased from formal and informal retail stores. All the tests were done at the 5% significance level.

Table 1. Optimized AAS conditions for analysis of chromium in automotive paints

Operating conditions for chromium analysis	Wavelength (nm)	Lamp current (ma)	Measurement time (s)	Fuel	Slit width/ bandwidth (nm)	Flow rate (l/min)	Sensitivity (ppm)	The detection limit (ppm)	linear equation	R^2
Parameters	357.9	10	1.0	air-acetylene	0.7	2.8	0.0550	0.0050	y = 0.0033x-0.0004	0.9997

Table 2. Mean ±SD, chromium levels (ppm) in various colours of automotive paint from informal and formal retail stores formal retail stores

Sampling Sites		Mean ± SD Cr levels (ppm) in various paint colours		
		Blue	**Red**	**Green**
Informal Retail Shops	IKS1	120.5±10.6[a]	235.9 ±12.8[a]	146.6±3.4[a]
	IKS2	319.0±9.9[b]	2380.5±6.2[c]	406.9±1.8[b]
	IK1	2771.9±35.6[d]	489.4±14.0[b]	543.6±4.5[b]
	IK2	1793.2±21.7[c]	575.1 ±1.1[b]	1350.6±38.0[c]
Overall mean ± SD Cr levels (ppm)		1251.2±58.8[c]	920.2±14.1[c]	611.9±19.3[c]
Formal Retail Shop	FIA1	39.3±7.0[a]	94.8±8.1[a]	187.8±2.1[b]
	FIA2	225.3±1.5[b]	280.3 ±3.0[b]	258.5±13.1[b]
	FKN1	338.4±1.3[b]	373.4±7.3[b]	404.2±6.6[b]
	FKN2	406.4 ±3.1[b]	430.9±1.1[b]	461.9±11.1[b]
Overall mean ± SD Cr levels (ppm)		252.4±160.5[b]	294.9±147.1[b]	328.1±126.8[b]
p-value		<0.001	<0.001	<0.001

Note ±SD=Standard deviation from the mean, and the mean values followed by the same small letter within the same column do not differ significantly (α=0.05, SNK-test)

3. RESULTS AND DISCUSSION

3.1 Chromium Levels in Automotive Paints

Table 2 presents the results of chromium (Cr) levels in automotive paints in various colours purchased from informal retail stores that were coded IKS1, IKS2, IK1 and IK2 and formal retail shops (FIA1, FIA2, FKN1 and FKN2).

From Table 2, the informal retail stores had mean levels of Cr in various colours of automotive paints that ranged from 120.5±10.6 to 2771.9±35.6 parts per million (ppm). On the other hand, the formal retail store had significantly ($p<0.05$) low mean levels of Cr in the range of 39.3±7.0 to 461.9±11.1 ppm. Nonetheless, irrespective of the paint colours, the informal outlets had the highest overall mean Cr levels when compared to the formal retail shops. It was also observed that the paint samples from the Informal Kamukunji, shop 1 (IK 1) had generally the highest mean values of Cr. On the contrary, the first shop in Informal Kariobangi South (IKS 1) had the lowest mean Cr levels. In almost all cases, the levels were much higher in the samples that were procured from informal retail shops with the exception of those from the IKS 1 that had significantly ($p<0.05$) low levels. Interestingly, comparably low lead (Pb) levels were also reported in the automotive paints purchased from the IKS 1 shop. These levels were comparable with those of formal retail shops [30]. This suggests that the IKS 1 shop could be using lower levels of heavy metals during production processes compared to the other informal retail stores. It also seems like Pb and Cr-containing compounds were added to paints in varying amounts during production processes.

The red paint from the Informal Kariobangi South Shop 1 (IKS 1) had the highest Cr levels of 235.9±2.8 ppm whereas the blue paint had the lowest concentration of 120.5±10.6 ppm. Although there was no significance in the levels. The same trend was observed in paints from the Informal Kariobangi South shop 2 (IKS 2) which had an elevated concentration of 2380.5±6.2 ppm in red paint and 319.0±9.9 ppm in blue. Even though the difference in the levels was significant. The Cr levels in red paints could be a contribution from the use of raw materials such as chromium (VI) oxide that mostly gives red colouration. Additionally, the first shop in Informal Kamukunji (IK 1) had significantly ($p<0.05$) higher Cr level of 2771.9±35.6 ppm in blue paint whereas the lowest level of 489.4±14.0 ppm was in red paint. In the second shop in the Informal Kamukunji (IK 2), the highest Cr level was 1793.2±21.7 ppm in blue paint while red paint had the lowest level of 575.1±11.1 ppm. Overall, differing levels of Cr across various colours were observed. This is expected because Cr compounds are used as pigments in paints and when they are added in higher amounts they result in elevated Cr levels.

For the cases of automotive paints purchased from the formal retail shops, the first (FIA 1) and second (FIA 2) retail shops in the Industrial area had relatively lower overall Cr mean levels than those from the first (FKN 1) and second (FKN 2) retail shops in Kariobangi North. The study established that the amount of Cr-based pigments that were used to manufacture the automotive paints differed across the line of production. The blue and the red paints from the Formal Industrial Area shop 1 (FIA 1) had significantly ($p<0.05$) low Cr concentration of 39.3±7.0 ppm and 94.8±8.1 ppm, respectively. This was then followed by the green paints with concentrations of 187.8±12.1 ppm. For instance, chromium (III) oxide that is mostly used as a green pigment may contribute to substantial levels of Cr in paints when added in large amounts during manufacturing processes. The second Formal Industrial Area shop (FIA 2) had the highest mean levels of 280.3±13.0 ppm in red and the lowest level of 225.3±10.5 ppm in blue paint. Although the difference among Cr levels was not significant ($p>0.05$).

Earlier studies have also shown increased use of chromate-based paints as anti-corrosion pigment for spray painting activities [1,4,7,8]. The Cr(VI)] is usually applied as a first-coat primer onto auto-metallic surfaces to protect them from associated corrosion. During manufacturing of anti-corrosive paints, diverse chromate pigments are often added in differing proportions [4,7,8]. They may include a combination of basic zinc chromate/alkali chromate, basic potassium zinc chromate, basic zinc chromate, strontium chromate, calcium chromate, and lead chromate [8]. Using any of the aforementioned pigments suggests that the manufactured paints will ultimately have Cr in varied amounts in the paints. Restricting the amount of heavy metals that are added to paint during manufacturing processes is the best way to ensure that the paints are free from toxic metals [30].

Spray painting activities using Cr-based paints are a direct source of occupational exposure to Cr(VI) in the auto-repair industry. The adverse health effects as a result of inhaled Cr(VI) based particles' are strongly influenced by the site of deposition within the respiratory system and the overall concentrations [12,17-20]. It is worth noting that exposure to Cr(VI) poses a significant risk of cancer to the respiratory system [12,14,19,21]. "This is based on several cases involving laryngeal cancer that have been reported in paint sprayers. Cancer of the nasal cavities and paranasal sinuses was commonly reported in users of chromate paints whereas buccal cavity and pharynx cancers were observed in painters" [19,21].

3.2 Chromium Levels in Different Paint Colours

The overall mean ± SD chromium levels in each of the red, blue and green paints purchased from formal and informal retail shops is given in Fig. 1.

The blue paints purchased from the informal retail shops had the highest overall mean ± standard deviation*SD) Cr levels of 1251.2±125.8 ppm while the green paints had a relatively lower level of 611.9±519.3 ppm (Fig. 1). The latter had also Cr levels that varied greatly as indicated by a high standard deviation (±SD) from the mean. In contrast, when comparing the mean Cr levels in various paint colours from the formal retail shops, the green paint had the highest level of 328.1±126.8 ppm whereas the blue paint had the lowest level of 252.3±160.5 ppm, although the difference is not significant (p>0.05).

It should be noted that most Cr compounds are coloured due to the excitation of an electron from a lower energy of the d-orbital to a higher energy level [7,8]. These paints clearly exhibit different colours such as green, blue, red, yellow, orange and black [6-9]. Lead (II) chromate which is also referred to as chrome yellow and green chromium (III) oxide is commonly added to paints as pigments [11]. The continual use of these compounds in the manufacture of the paints results in elevated concentrations of Cr in paint which could have adverse health effects to human and environment [34].

In developing countries, atypical automobile repair sites mainly consist of auto mechanics, spray painters, panel beaters and welders who are usually engaged in related activities [27,28-31]. High levels of heavy metal including Cr contaminations on the environment have been reported as a result of due to above-mentioned operations that are not regulated [26,30]. The workers are thereby exposed to substantial amounts of particulate matter through sanding and panel beating before re-painting or remodeling. Furthermore, the spray-painting gun often atomizes the paint into aerosols, some of which form overspray that can be inhaled [30]. The aerosols also get dispersed in the air and have great potential to contaminate the environment. Chromium that is released into the environment from sanding processes is usually in the hexavalent form and occupational and environmental exposure usually results in multi-organ toxicity [13,14,17,23].

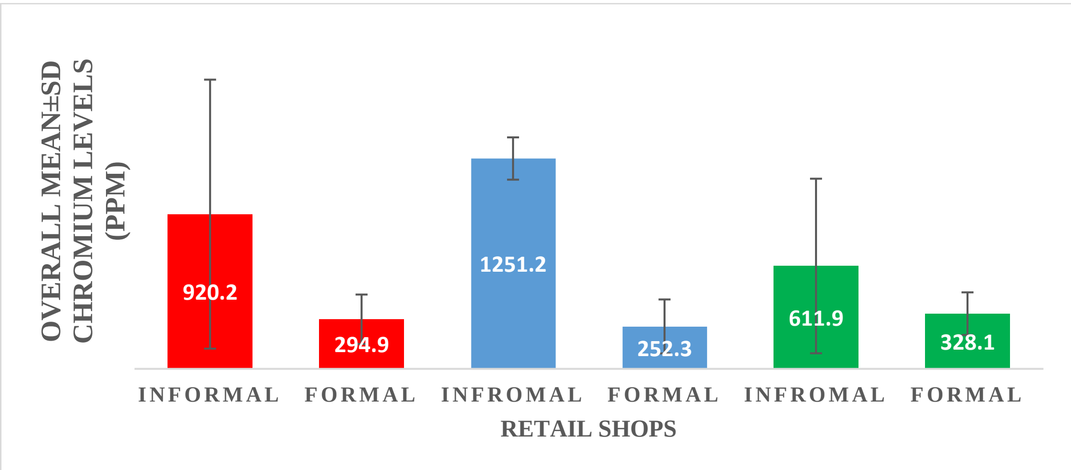

Fig. 1. Overall chromium mean± SD levels (ppm) in various automotive paint colours purchased from informal and formal retail shops

The spray painters have been observed to be at the greatest risk of exposure to Cr and Pb that emanate from automobile paints [26,28,29]. Welding of chromium-painted surfaces further results in excessive exposure to Cr(VI) since these metals are components of paints. Similarly, the fumes of Cr may be inhaled during auto-repair as a result of the panel beating operation [28-31]. "Some of the long-term effects of Cr exposure include degeneration of the central nervous system, anemia and renal failure" [13,14,23]. "Furthermore, chronic exposure to Cr can cause lung cancer and other adverse health effects involving the immune, respiratory, endocrine, renal, musculoskeletal, and cardiovascular systems. It has also been reported that long-term exposure to Cr can result in renal tubular dysfunction, disturbance of calcium metabolism, osteoporosis and osteomalacia" [13,14,17,23]. Hexavalent chromium is in addition known to cause eye, skin, and respiratory irritation.
Studies have reported higher blood Cr levels in auto repair workers than those of the controls [27,28-31]. Other studies have in addition shown higher values of serum Cr in spray painters. Chronic exposure to Cr(VI) has a health effect on the respiratory tract causing reduced respiratory function, perforations, and ulcerations of the nasal septum, bronchitis, and pneumonia [28-31]. "It can also have adverse consequences for the liver, kidneys, and the general immune system". [22]. The main route of exposure to Cr dust is via inhalation, and the lung is the primary target organ. Some Cr exposure has been observed to penetrate through the skin [15,17,24]. In most cases, auto repair workers are neither aware of the magnitude of Cr exposure nor the deleterious effects they have on their health [25]. Several studies have also assessed heavy metals exposure, mainly Pb and Cr, during the scraping of old paints and spray painting activities [27,28,30].

The report of the International Agency for Research on Cancer (IARC) classified Cr pigments as carcinogenic to painters due to epidemiological studies that pointed out increased risks of bladder and lung cancer among the painters and auto-repair [13,14]. It is nonetheless estimated that 99 % of the auto-body repair and refinishing facilities in the USA use Cr and Cd-free coatings [36]. This effort that need to be replicated by all countries will go a long way in curbing the substantial cancer risk that occurs even at a low exposure level to hexavalent chromium [36].

4. CONCLUSION

The study has established that chromium compounds are added to automotive paints in varying concentrations, however, chromate pigments have been listed as toxic and are restricted by European Union. Additionally, previous studies have found that workers in auto-repair activities and paint production have been found to have high risks of adverse health effects including developing various cancers. The study highlights the need for source control to limit chromium levels in automotive paints and calls for a comprehensive assessment of Cr exposure.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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