

Chromium Concentrations in Automotive Paints from Retail Stores in Kenya

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 4 sets of automotive paint samples in red, blue and green colours. These samples were also used for the assessment of lead content that was published elsewhere. The samples were procured from formal and informal retail stores. The mean \pm standard deviation (SD) of levels of Cr 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 low ($p < 0.05$), and were in the range of 39.3 ± 7.0 to 461.9 ± 11.1 ppm. The Cr levels varied greatly across different paint colours. Substantial levels were 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 possible exposures.

Key Words:

Chromium-containing paints; automotive repair; spray painting

1. Introduction

Chromium (Cr) compounds among other metals are extensively added to paints because of their useful properties [1-11]. For example, hexavalent chromium [Cr(VI)] compounds are essentially used to manufacture paints to prevent corrosion [1,4,7,8]. Chromium oxide is more stable and forms a long-lasting pigment in automotive paints [7]. Furthermore, it is resistant to both alkaline and acidic conditions with excellent covering and hiding power. Additionally, most Cr compounds form coloured pigments due to the excitation of an electron from a lower energy of the d-orbital to a higher energy level [7,8]. A wide array of colouration from green to brown has been used by artists in painting activities [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 pigment in the paint is composed of pure lead chromates. Lead sulfochromate is in mixed phases of pigments in paints and comprises lead chromate and lead sulphate while lead chromate molybdate sulphate consists of lead chromate, lead sulphate and lead molybdate 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 ability [12-19]. Hexavalent Cr is widely studied in occupational exposure, a potentially known carcinogen associated with lung, nasal, and sinus cancers [12,14,19,21]. It is also genotoxic, and mutagenic [22]. Exposure to Cr(VI) through chronic inhalation results in

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 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 earlier publications, much of these exposures are through brazing, soldering, welding, and cutting; coating and painting activities, and metal treatment, which are typical of auto repair and spray painting operations in the informal sector [25-31]. Chromium also persists in the environment for a long time and is frequently non-biodegradable in nature, and capable of polluting the soils, water and air and thereby posing a significant health risk to humans [19,26,32-34]. Untreated industrial effluents in paint-related activities are the main sources of Cr(VI) pollutants in the environment (34).

During chemical analysis Cr(VI) and Cr(III) are capable of inter-converting, which is an impediment for both quantitative determinations of Cr and regulatory policies for the restriction of Cr [11,16]. Hexavalent chromium 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 Cr(VI) [12,34]. There is thus a health and environmental concern over the toxic effects of Cr due to its availability and persistence in the environment. The present study is part of the recently published work by Mwai et al. [30] that assessed lead (Pb) content in automotive paint samples frequently used by spray painters purchased at formal and informal outlets in Kenya. This study was undertaken to assess levels of Cr in automotive paints.

2. Method 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 clustered within a one km radius [30]. A detailed map was also published that describes the study area where the paint samples were purchased along with the clustered spray painting activities and other land use [30].

2.2 Sampling procedure

The sampling procedures for the automotive paints has further been published [30], and it involved the procurement of sets of cans of automotive paints that consisted of red, blue and green colours of 250 mL and 100 mL from each of the eight formal and informal retail shops, respectively that were randomly selected. The paints were coded as follows: those that were purchased from Formal Industrial Area shop-1 and 2 were coded as FIA 1 and FIA 2, Formal Kariobangi North shop-1 and 2 (coded as FKN 1 and FKN 2), the Informal Kariobangi South shop-1 and 2 (coded as IKS 1 and IKS 2) and the Informal Kamukunji shop-1 and 2 (coded as IK 1 and IK 2). Fig. S1 (Supplementary material) by Mwai et al. [30] summaries the coding of the automotive paints.

2.3 Laboratory preparation of samples

The coded samples were subsequently transferred to the analytical laboratories and were subjected to the chemical preparation 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).

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 1: Optimized AAS conditions for analysis of chromium in automotive paints

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 ($\pm SD$). Descriptive analyses were applied to all variables. One-way variance of analysis (ANOVA) was applied for the different colours in automotive paint samples purchased from formal and informal retail stores. All the tests were done at the 5% significance level.

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 coded IKS1, IKS2, IK1 and IK2 and formal retail shops (FIA1, FIA2, FKN1 and FKN2).

Table 2: Chromium levels (ppm) in automotive paint samples from informal and formal retail stores in different colours.

Sampling Sites		Mean \pm SD Cr levels (ppm) in various paint colours		
		Blue	Red	Green
Informal Retail Shops	IKS1	120.5 \pm 10.6	235.9 \pm 2.8	146.6 \pm 3.4
	IKS2	319.0 \pm 9.9	2380.5 \pm 6.2	406.9 \pm 1.8
	IK1	2771.9 \pm 35.6	489.4 \pm 14.0	543.6 \pm 4.5
	IK2	1793.2 \pm 21.7	575.1 \pm 1.1	1350.6 \pm 38.0
Overall mean \pm SD Cr levels (ppm)		1251.2 \pm 158.8*	920.2 \pm 94.1*	611.9 \pm 519.3*
Formal Retail Shop	FIA1	39.3 \pm 7.0	94.8 \pm 8.1	187.8 \pm 2.1
	FIA2	225.3 \pm 0.5	280.3 \pm 3.0	258.5 \pm 13.1
	FKN1	338.4 \pm 1.3	373.4 \pm 7.3	404.2 \pm 6.6
	FKN2	406.4 \pm 3.1	430.9 \pm 1.1	461.9 \pm 11.1
Overall mean \pm SD Cr levels (ppm)		252.4 \pm 160.5	294.9 \pm 147.1	328.1 \pm 126.8

Note \pm SD=Standard deviation from the mean and * significantly high ($p < 0.05$) overall mean values in the informal retail stores

From Table 2, the informal retail stores had mean levels of Cr in various colours of automotive paints that ranged from 120.5 \pm 10.6 to 2771.9 \pm 35.6 parts per million (ppm). The formal retail store had significantly low mean levels of Cr in the range of 39.3 \pm 7.0 to 461.9 \pm 11.1 ppm.

Nonetheless, irrespective of the of colours of these paints, the informal outlets had the highest overall mean Cr levels when compared to the formal retail shops.

It is however observed that the paint samples from the Informal Kamukunji, shop 1 (IK1) had generally the highest mean values of Cr. On the contrary, the first shop in Informal Kariobangi South (IKS1) 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 IKS1. Interestingly, low lead (Pb) levels were also found in the automotive paints that were purchased from the IKS1 shop. These levels were comparable with those of formal retail shops [30]. This suggests that the IKS1 shop could be using lower levels of heavy metals during production processes compared to the other informal retail stores. It also appears that 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 (IKS1) 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. The same trend was observed in paints from the Informal Kariobangi South shop 2 (IKS2) which had an elevated concentration of 2380.5 ± 6.2 ppm in red paint and 319.0 ± 9.9 ppm in blue. 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 (IK1) had the highest 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 (IK2), the highest Cr level was 1793.2 ± 21.7 ppm in blue paint while red paint had the lowest level of 575.1 ± 1.1 ppm. Overall, differing levels of Cr across various colours were observed. Several Cr

compounds are used as pigments in paints and when they are in higher amounts they result in elevated Cr levels in paints.

For the cases of automotive paints purchased from the formal retail shops, the first (FIA1) and second (FIA2) retail shops in the Industrial area had relatively lower overall Cr mean levels than those from the first (FKN1) and second (FKN2) retail shops in Kariobangi North. The study established that the amount of Cr-containing pigments that were used to manufacture the automotive paints differed across the line production. The blue and the red paints from the Formal Industrial Area shop 1 (FIA1) had the lowest 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 ± 2.1 ppm. Green chromium (III) oxide is mostly used as a pigment in paints and therefore if added in large amounts during production processes it could contribute to substantial levels of Cr in paints. The second Formal Industrial Area shop (FIA2) had the highest mean levels of 280.3 ± 3.0 ppm in red and the lowest level of 225.3 ± 0.5 ppm in blue paint.

Previous studies have also shown increased use of chromate-containing paints as an 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. In the manufacture 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 implies that the manufactured paints will ultimately have the corresponding amounts of Cr 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 hence important and is 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) containing particulate matter 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 \pm SD chromium levels in each of the red, blue and green paints purchased from formal and informal retail shops is given in Fig. 1.



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

The blue paints purchased from the informal retail shops had the highest mean Cr levels of 1251.2 ± 125.8 ppm while the green paints had a relatively lower mean 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 (\pm 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.

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]. They 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 [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 due to aforementioned operations that are not regulated [26,30]. They are thereby exposed to substantial amounts of particulate matter through sanding and panel beating before re-painting or remodeling. Furthermore, the spray-painting gun 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 to it results in multi-organ toxicity [13,14, 17,23].

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. 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]. Hexachromium is in addition known to cause eye, skin, and respiratory irritation as well as gastrointestinal effects. Chronic exposure to Cr(IV) 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.

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 [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 these toxic metals they are

exposed to nor the deleterious effects they have on their health [25]. Several studies have also assessed the exposure of workers in the metal and paint industries to heavy metals, mainly Pb and Cr, during the scraping of old paints and spray painting [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 identified increased risks of bladder and lung cancer among these cadres of workers [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 will go a long way in curbing the substantial cancer risk that occurs even at a low exposure level of Cr(VI) [36].

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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