The Effect of Colorants on the Content of Heavy Metals in Recycled Corrugated Board Papers

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Recycled paper is an important raw material to provide sustainability of natural resources and reduce the environmental impact of the use of paper from recycled pulp in the packaging industry. Hence, recycled paper production is higher in terms of volume and utilization. Recycled paper products are used in the packaging industry partially or fully. Such usage leads to the presence of heavy metals due to recycled and chemical additive sources. The present study aims at determining the amounts and also identifying the sources of heavy metals such as Pb, Cd, Zn, Ni, and Cu contained in recycled testliner (TL) and fluting (FLT), which are main products used in production of corrugated cardboard. The metals in the structure of the paper used in packages directly or indirectly in contact with foods are heavy metals. Mean values of 2.6 mg kg^{-1} Pb (lead), 2.8 mg kg^{-1} Zn (zinc), 0.094 mg kg^{-1} Cd (cadmium), 1.8 mg kg^{-1} Ni (nickel), and 25.4 mg kg^{-1} Cu (copper) were detected in test liner and fluting papers using inductively coupled plasma optical emission spectrometry (ICP-OES). The main sources of heavy metals are colorants, mainly consisting of conventional paint and pigments as well as spot and Pantone Matching System (PMS) colorants.

Keywords: Heavy metals; Migration; Paper and cardboard; Food packaging; Ink

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INTRODUCTION

In Turkey and across the world, paper and cardboard are manufactured through recycling. Such re-use of materials helps to protect the environment and the natural resources and to ensure the sustainability of these raw materials. The proportion of waste paper used for paper production is as high as 71% in Turkey (SKSV 2013). For this reason, it is desirable to minimize levels of air emissions, which may result when the ash created by the burning of recycled paper waste contains harmful and toxic substances. Another goal is to minimize levels of harmful leachate generated by landfills.

Secondary fiber obtained from waste paper has, as some of its major ingredients, additives such pigments, dyes, starch, and adhesive chemicals. After manufacturing of the recycled base paper, it is also common to add dyes, pigments, and mineral products to improve surface, optical, and printing characteristics, as well as to adjust color, according to the intended usage (Conti 2008). Recovered paper and cardboards are likely to contain heavy metals, such as zinc, lead, cadmium, and chromium, because these metals are present in the raw materials as a seconder fiber and the chemical additives particularly colorants used for the production and finishing of pulp and paper (Ginebreda *et al*. 2012).

The pigments that are being used in paper applications, as well as their chemical composition, cover a broad range. Some pigments are used to give high opacity to the paper, and thus, to improve the structure and the surface qualities of the paper; they may contain zinc and cadmium. They are also used for filling materials and coating formulations in the form of zinc oxide, zinc sulphide, or lithopone (resulting from the combination of barium sulphate with ZnS for high-pressure laminated paper, cardboard products, and wall paper). Certain zinc oxide compounds provide photoelectrical properties for photo reproduction papers. Zinc and cadmium pigments are additives that provide fluorescent properties to the paper and increase the cohesive strength in certain coating applications on paper surfaces (Conti 2007). Moreover, other chemicals are used to improve the cohesive strength and other process properties of recycled paper.

Besides these, yellow and green color dyes and pigments used in the packaging result include compounds such as lead chromate, lead sulphate, and lead oxide (Kim *et al*. 2008).

The diversity of the inks in the last printing process varies according to the printing base materials and printing methods. The main components contained in the inks are pigments (5% to 30%), binders (15% to 30%), additives (1% to 10%), solvents (20% to 70%), and water (Conti 2007).

The values presented in Table 1 show by how many times the pigments and dyes increased or decreased (+/-); calculations are based on the data of Sutter (1994), and show the before and after changes in color formulations in order to improve the heavy metal contents in printing ink pigments.

Table 1. Changes of Heavy Metal Content of Pigments

Metal (times)	Blue[1]	Green	Red[2]	Yellow
Cd	+3.25	-0.58	+5.85	+2.5
Cr	+5	+1.85	+3.26	-5.71
Cu	-128	-311	+2.04	-34.14
Pb	-0.66	+2.00	+29.67	+7.2
Hg	-2	+4.31	2.22	-1.51
Ni	-3.75	+1.42	-2.81	-60.8
Zn	+2.34	-15.95	+2.43	0
[1]Reflex blue, [2]Warm red				

Reflex blue is deep blue-violet hue and warm red (red Lake C) is both alkali pigments with similar printing properties as is used commonly in the PMS system (J2 dizayn 2016)

As shown in Table 1, each color pigment consists of mixtures of many, different heavy metals. Additionally, after some improvements were carried out in the formulation of printing inks, changes in the heavy metal content of the ink pigments decreased in some, increased in others, and did not change at all in some others (Sutter 1994).

The packaging papers' coloring pigments and dyes and printing ink pigments had mostly red colors, followed by yellow and green colors which may be understood to be caused by some of heavy metals (Table 1).

In addition to the pigments used in coloring processes, fluorescent and metallic inks, which contain high amounts of heavy metals, constitute an obvious environmental risk. Fluorescent inks contain almost all color pigments.

High color intensity (or saturation) is an important property for printing quality (Sonmez 2017). Spot colors are widely used to obtain highly saturated colors in the packaging printing. Spot colors are created with a Pantone Matching System (PMS). PMS offers a higher degree of threat than the conventional coloring process. Many formulations containing PMS colors contain very large quantities of copper and barium and also both these metals, and each of them contain more than 40 different metals (Zalewski 1994; Pekarovicova *et al.* 2008). The Pantone Matching System (PMS) color scale is used from light (PMS 721C) through dark (PMS 725C) in the printing industry (Keenan 1997).

The chemicals used during the production or finishing of papers used as packaging for food have a significant role in the interaction between the packaging and the food, which are in direct contact. The term migration signifies transfer of the chemical compounds within the structural body of the paper and cardboard packages to the food. However, packages that are in direct contact with the food can be subject to migration of contaminants. In this type of migration, the ink compounds inadvertently migrate from the exterior surface (printed outside of the package) towards the interior surface (which is in direct contact with the food) on the bobbin or during stacking (*e.g.*, a stack of imprinted paper cups) or storage.

The present study aims at determining the amounts and sources of heavy metals such as Zn, Pb, Cd, Ni, and Cu contained in recycled test liner (TL) and fluting (FLT), which are main products used in production of corrugated cardboard; this study also determines the suitability of the food packaging to the relevant legislation.

EXPERIMENTAL

Materials

Five pieces of each recycled test liner and fluting paper manufactured from paper and cardboard, used in corrugated food packaging, were used as materials in this study and were supplied from a factory in Istanbul, Turkey.

Test liner (TL)

Linerboard was used as a carrier paper for corrugated cardboard. Carrier cardboard or paper typically ranges between 125 gm^{-2} and 350 gm^{-2}. Carrier papers in the range of 100 gm^{-2} are sufficient in small boxes. Liners obtained from recycled fiber are called test liners (Paulapuro 2000).

In the market, TL papers are mostly known as imitation craft paper and differing from FTL, during base paper production colorant pigments are added which is believed to be the reason for increase in Cd, Pb, Zn, and Cu values (Tutus *et al.* 2014).

Fluting (FLT)

Fluting is a type of paper produced from all kinds of waste paper and used as an intermediate layer in corrugated paper by a fluting machine. Fluting is not treated with any chemical additives or processes. Compared with other papers, its strength is lower, and it is a paper of 95 gm^{-2} to 200 gm^{-2} (Leblebici 2007).

Methods

The moisture content of each sample was based on a dry basis after using the oven-drying method at 105 °C for 4 h (ISO 287 2009). The weight of the paper samples was determined using a digital balance (Scaltec 31, Istanbul, Turkey) with a 0.1-mg accuracy as gsm (g/square meter).

The content of heavy metals from recycle paper was evaluated. The weight of each recycled TL and FLT paper specimen, corresponding to an area of about 1 dm^2 was determined. These were then cut into small pieces by hand using polyethylene gloves and then dried on dry weight basis.

Digestion with strong mineral acids (HCl, H_2SO_4, HNO_3) is considered a form of pseudo-total analysis. These acids are strong enough to dissolve the heavy metals, which is the normal case for the heaviest metal pollutants (Mantylahti and Laakso 2002) The samples prepared for analysis were kept for three hours at a fixed temperature of 50 °C in 12 mL of concentrated HNO_3 and 4 mL of H_2O_2 water bath in order to implement the process of "digestion," based on extraction, to transfer the heavy metal components into the solution. The samples were allowed to rest in the solution at room temperature for 24 h for total digestion. The cure and the solutions were also prepared under the same laboratory conditions. The measurements were made using in an inductively coupled plasma optical emission spectrometry ICP-OES device (Perkin Elmer Optima 7000 DV, Istanbul, Turkey).

Standard Solutions and Reagents

All reagents used were of analytical reagent grade. The standard solutions of the analyses for calibration were prepared as $mgkg^{-1}$, as can be seen in the Table 2

Table 2. Standard Solutions of the Analytes for Calibration

	Pb	**Cd**	**Ni**	**Zn**	**Cu**	**Cr**	**Al**
Wave length (nm)	**220.353**	**228.802**	**231.604**	**206.200**	**327.393**	**267.716**	**396.153**
Calib. 1 ($mgKg^{-1}$)	[0.005]	[0.005]	[0.005]	[0.05]	[0.005]	[0.005]	[0.1]
Calib. 2	[0.01]	[0.01]	[0.01]	[0.1]	[0.01]	[0.01]	[0.5]
Calib. 3	[0.05]	[0.05]	[0.05]	[0.5]	[0.05]	[0.05]	[1]
Calib 4	[0.1]	[0.1]	[0.1]	[1]	[0.1]	[0.1]	[5]
Calibration 5	[0.4]	[0.4]	[0.4]	[5]	[0.4]	[0.4]	[10]

The standard reference material (SRM) used to compare the accuracy of the method was NIST (National Institute Standards and Technology) SRM 1575a Trace Elements in Pine Needles (*Pinus taeda*) Denver, CO, USA.

RESULTS AND DISCUSSION

The quantities of heavy metal in the recycled TL and FLT paper samples at different weights, which are used as intermediate material by corrugated cardboard manufacturers, are shown in Table 3. The quantities of analyzed heavy metal elements are given as mg per dm^{-2} paper (Q_a).

The amounts of heavy metals were estimated as presented by CEPI and CITPA (2012), using Eq. 1,

$$Q_m = Q_a*100000/G \quad (1)$$

where Q_a is the concentration of the substance in the paper as $mgdm^{-2}$, Q_m is the concentration of the substance in paper as mg kg^{-1}, and G is the grammage (gm^{-2}) of the paper.

According to Council of Europe (2002) and the European Council 94/62 EC (2015), the maximum limit of heavy metals (*e.g.* Pb and Cd) identified in the packages of recycled papers produced out of primary pulp and secondary pulp obtained from waste paper used in food packages should not exceed 100 mg per each kg of package material. According to this regulation, the migration of package materials to the food cannot exceed 100 ppm by weight for up to five years. In addition, according to the Turkish Food Codex, lead and arsenic cannot exceed 20 mg kg^{-1} and 2 mg kg^{-1}, respectively, in egg boxes and packages containing vegetable fibers.

As shown in Table 1, each color pigment consists of mixtures of many diverse heavy metals. Additionally, after some improvements were carried out in the formulation of printing inks, changes in the heavy metal content of the ink pigments decreased in some, increased in others, and did not change at all in some others (Sutter 1994). Table 2 shows the heavy metal analysis results of the recycled test liner and fluting paper samples at different weights used as raw material by corrugated cardboard manufacturers. The analyzed heavy metal elements were Zn, Pb, Cd, Ni, and Cu.

According to the European Council 94/62 EC (2015), the maximum limit of heavy metals identified in the packages of recycled papers produced out of primary pulp and secondary pulp obtained from waste paper used in food packages should not exceed 100 mg per each kg of package material for elements like Pb and Cd. According to this regulation, the migration of package materials to the food cannot exceed 100 ppm by weight up to five years. In addition, according to the Turkish Food Codex, lead and arsenic cannot exceed 20 mg kg^{-1} and 2 mg kg^{-1}, respectively, in egg boxes and packages containing vegetable fibers.

Table 3. Heavy Metal Analyses for Packaging Papers (mg kg^{-1})

Samples	gm^{-2}	Zn	Pb	Cd	Ni	Cu
TL	100	3.7	2.4	0.096	1.5	29.9
TL	115	3.7	3.2	0.106	1.8	33.6
FLT	100	2.3	2.1	0.040	1.6	24.5
FLT	112	2.6	2.8	0.067	2.8	24.5
FLT	140	3.8	4.9	0.181	2.4	44.8

Pb Concentrations

As shown in Table 3, the Pb values detected in the TL and FLT papers had a minimum and maximum of 2.4 mg kg^{-1} and 4.9 mg kg^{-1}, respectively, and they had an average value of 3.1 mg kg^{-1}. According to 94/62/EC (European Parliament and Council Directive 2015), these values mostly were lower than the limit values (3 $mgkg^{-1}$), and they were also similar to some literature values (Castle *et al.* 1997; Duran *et al.* 2013).

Lead is commonly used in the white inks. Substitute materials that have similar qualities may reduce the use of lead as pigment. Red, yellow, and green colored pigments may be the source of the Pb heavy metal (Table 1-3; Zalewski 1994; Keenan 1997; Kim *et al*. 2008).

When average Pb quantities are compared with the data from the literature (Duran *et al.* 2013), it has been determined that FLT samples with high levels of Pb values have higher weight and that since it is used in intermediary curled paper in corrugated cardboard production, it is of different height than the layer of paper contacting with the food. It is estimated that when the food packaging is composed partially or wholly of secondary fibers, this will reduce the possible risk.

Cd Concentrations

The basic structure of cadmium red and cadmium yellow, which are widely used as they have brighter colored pigments than other dyes used in fine arts, is constituted by cadmium heavy metal. It is highly preferred for printing inks; yet there are many pigments with qualities to replace it, and these are already used in many other applications (Zalewski 1994).

As shown in Table 3, the Cd values detected in the TL and FLT papers had a minimum and maximum of 0.040 mg kg^{-1} and 0.181 mg kg^{-1}, respectively, and they had an average value of 0.098 mg kg^{-1}. According to the 94/62/EC Directive (2015), these values mostly are much lower than the limit values (2 $mgkg^{-1}$), and they are also similar to some literature values (Conti *et al*. (1996, 1997); Castle *et al.* 1997; Duran 2013). It may be the red, yellow, and blue colors affected the presence of the Cd as well (Table 1; Zalewski 1994; Keenan 1997; Kim *et al*. 2008).

Zn Concentrations

Some of the Zn-based compounds used in paper production are zinc oxide and zinc sulfate. Zinc sulphate is used to increase the opacity of special papers, whereas zinc-oxide is used partially for production of photocopy paper (Erkan and Malayoglu 2001). This metal is also engraved on many packaging as metal embroidery along with copper and aluminum (Zalewski 1994).

The maximum, minimum, and average values for Zn in the TL paper were 2.3 mg kg^{-1}, 3.8 mg kg^{-1}, and 3.2 mg kg^{-1}, respectively. The identified values were below the limit values according to 94/62/EC (Directive 2015), although zinc heavy metal has fluorescence and many other similar sources in filling and coloring materials, the waste paper forming the waste paper pulp did not appear to contain too much of these additives. Also, the red and blue colors affected the formation of zinc at the about same rate. It is considered that the difference between Zn values of TL and FTL papers is caused by the additional chemicals used in coloring and production of TL (Table 1; Erkan and Malayoglu 2001; Zalewski 1994; Keenan 1997; Kim *et al*. 2008).

Cu Concentrations

Although copper is quite toxic to aquatic life, it provides very important printing colorants. In the color printing process, phthalocyanine blue, which mostly gives a standard color as cyan, is an essential ingredient. It also helps in the formation of many green tones. Despite the negative effect of copper, there is no comparable option in printing (Zalewski 1994).

The minimum and maximum values of Cu in the TL papers were found to be 19.9 mg kg^{-1} and 44.8 mg kg^{-1}, respectively. The average Cu value in the test liner (100 gm^{-2}) papers was 29.5 mg kg^{-1}. According to 94/62 EC, these values are well below the limit values (Conti 2007). The FLT papers exhibited large values with a remarkable difference from the test liner paper values, as shown in Table 3. The red pigment, as with other heavy metals formation (Pb, Cd, Cr, Zn) was observed to contribute in the formation of Cu metal (Table 1; Zalewski 1994; Keenan 1997; Kim *et al*. 2008).

Ni Concentrations

The TL average Ni value was 1.7$mgkg^{-1}$ and the FLT paper average Ni value was 2.3 $mgkg^{-1}$. This may be the result of the presence of multiple colorants in the waste paper pulp (Table 1; Zalewski 1994).

According to EN 13428 (2004), the presence of noxious substances and other hazardous materials as constituents of packaging material or of any of the packaging components needs to be minimized with regard to their presence in emissions, ash, or leachate when packaging or residues from management operations or packaging waste are incinerated or landfilled. The values observed in this study are below the limit values that have been identified in food legislation.

CONCLUSIONS

1. The heavy metals in recycled paper and cardboard packaging used to produce corrugated cardboard and in the overall packaging industry were examined relative to their appropriateness of food packaging used in the sector. The results showed that the use of recovered paper could increase heavy metals during the recycling process.
2. This increase in heavy metals is obviously caused by chemical additives used in the process of pulp and paper manufacturing, as well as the finishing operations of paper. The heavy metal amounts of FLT and TL papers with high grammage were higher than the those of low grammage papers. Also, the heavy metal values of the TL papers were much greater than the FTL paper values. These differences are believed to be generating from the use of colorant and imprinting ink originated pigment and dyes with usually 100% waste raw materials content of the FTL used in the intermediary layer of the corrugated cardboard.
3. In the market, TL papers are mostly known as imitation craft paper and, differing from FTL, during base paper production colorant pigments are added. Such addition of colorants is understood to be the reason for increase in Cd, Pb, Zn, and Cu contents.
4. Colored pigments have different sources of heavy metals. In a scale of lighter to darker colors, red chiefly, as well as green, blue, yellow and white, are included. Based on this study, it can be said that these colors were the primary sources of Pb, Cd, Zn, and Cu. Such colorants included fluorescence pigments, spot, and PMS colors.
5. Minimizing heavy metals in the recycled paper also may be a key way to minimize heavy metals in emissions, ash, and leachate, when packaging or residues from management operations or packaging waste are incinerated or landfilled.

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