

MIGRATION OF TOXICANTS FROM PLASTICS INTO DRINKING WATER DURING STORAGE

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ABSTRACT

In this study, migration of toxicants, such as, manufacturing additives and previously adsorbed materials into drinking water stored inside plastic containers was investigated. The study considered virgin containers as well as those previously used to store sulphuric acid, calcium hypochlorite, methyl ethyl ketone (MEK) and ethanol.

The results showed that drinking water stored in virgin containers desorbed 0.047mg/l of lead, 0.001mg/l of cadmium, and 4.68mg/l of phosphate within 35 days of storage. Lead and cadmium were therefore within FEPA's specifications of <0.05mg/l, while phosphate was outside the FEPA's range of <0.1mg/l. When ethanol was stored in virgin containers for 18 weeks, benzene and hexane were detected in the ethanol as migrants from the plastic showing that ethanol degraded the plastic thereby causing the release of such components. Tests carried out on reused containers showed that for containers used previously to store sulphuric acid, pH decreased from 7.14 for tap water to 2.23 for stored water after two weeks and sulphate concentration increased from 0.1mg/l in tap water to 2.94mg/l in water stored for two weeks. Iron, lead and cadmium were also above their respective upper limits for drinking water.

KEYWORDS: Migration, Toxicants, Plastics, Water, Storage.

INTRODUCTION

Bottles, drums, jars, and cans made of High Density Polyethylene (HDPE) have become accepted for the packaging of many industrial solvents and chemicals because of their high stiffness to weight ratio and excellent resistance to attack by most chemicals at normal temperatures (Bever, M.D, 1986; ASTM, 1991). Household use of polyethylene plastic containers in Nigeria is mainly in the storage of drinking and cooking water, alcoholic beverages such as palm-wine, palm oil, and other liquid consumables such as honey and herbs. Generally plastic cans are reused for the storage of these liquid foods after they have been used previously for the storage of solvents and chemicals.

The most popular commercial process for the production of HDPE is the Du Pont-Sclairtech's, which involves catalyst preparation, polymerization, polymer separation, extrusion, finishing and solvent and monomer recovery. The catalyst consists of a mixture of vanadium oxychloride and titanium tetrachloride using triethylaluminum as co-catalyst (Mills, N. J., 1986; Donnelly, P. & Asbey, B. 2000; Perry, R. H., 1984). During catalyst preparation, cyclohexane is used as recirculating solvent and butane-1 as co-monomer with ethylene. At polymer separation, acetyl acetone is added as catalyst deactivator. After separation of the polymer from un-reacted monomers, resins are added as anti-oxidants, anti-static and anti-blocking agents. In addition, hindered phenols and phosphates are used as stabilizer. The above additives are toxic to man if ingested, causing diarrhea and tremor (Finar, I. L, 1980; Muscilik, H. 1995). In addition, colorants used may be cadmium, chromium or lead based pigments. Drinking water containing 0.1 ppm of cadmium produces cadmium accumulation in the kidney; Chromium though an essential diet element as a component of vitamins and mineral supplements is a suspected carcinogen as a chromate in the oxidized state; while lead is toxic with a threshold limit value of 0.05mg/l (Rosa F, (1985).

This study focuses attention on the level of migration of components of the pigments into drinking water stored in virgin plastic containers as well as on the adsorption and subsequent

release of materials earlier stored when a plastic container is reused. Of particular interest in this study are containers previously used to store sulphuric acid, calcium hypochlorite, methylethyl ketone and ethanol. Effects of colour of the plastic container, if any, on the pattern of pigment migration was similarly investigated.

MATERIALS AND METHODS

Materials

HDPE containers used previously for storing sulphuric acid, methylethyl ketone (MEK) and calcium hypochlorite were obtained from a local chemical store, while the virgin cans of red, blue, white and yellow colours were brought from Mile-3 market, Diobu, Port-Harcourt, Nigeria. Water was obtained from the Port-Harcourt municipal supply while all other chemicals used were of general purpose grade.

Methods

Chemical Analysis

For all the analyses, a sample of drinking water was tested immediately after collection from a tap. The water was then stored for two weeks in two thoroughly washed HDPE containers that were previously used for the storage of sulphuric acid and calcium hypochlorite respectively. Further samples were then taken from the containers for analysis. The chemical analyses were carried out as follows:

Alkalinity

Alkalinity of water was measured using a radiometer auto-titrator using standard Hydrochloric acid (0.02N) and standard sodium hydroxide (0.02N) with phenol-phthalein as indicator.

pH Measurement

The pH was taken with a laboratory pH meter (Corning Model 340) fitted to a flow-through sample chamber and temperature compensator.

Metal Ion Measurement

Iron, cadmium and lead were measured by Flame Atomic

Table 1: Desorption of components into water stored for two weeks in re-used black containers formerly used to store sulphuric acid (301) and calcium.

Chemical Component	Sulphuric acid container	Calcium hypochlorite container	Fresh water	Standard values
pH	2.23	6.42	7.14	6.5-8.0
Iron(mg/l)	0.158	0.059	0.052	0.1
Lead (mg/l)	0.064	0.027	<0.01	0.05
Cadmium (mg/l)	0.084	0.01	<0.01	0.1
Sulphate (mg/l)	2.940	0.01	<0.1	3.5
Chlorine (mg/l)	3.20	7.47	1.06	5.1

Table 2: Desorption of components into stored water from virgin plastic containers of different colours.

Chemical Parameter	Plastic Colour	DAYS						Standard
		0	7	14	21	28	35	
pH	Blue	6.87	7.61	7.45	7.35	7.32	7.28	6.5-8.0
	White	6.87	7.58	7.54	7.42	7.25	7.00	..
	Yellow	6.87	7.56	7.31	7.00	6.98	6.98	..
Iron (mg/l)	Blue	0.052	0.016	0.034	0.039	0.06	0.74	0.1
	White	0.052	0.019	0.021	0.021	0.04	0.053	0.1
	Yellow	0.052	0.003	0.047	0.048	0.048	0.054	0.1
Phosphate (mg/l)	Blue	<0.01	<0.01	<0.01	<0.01	0.17	3.22	0.1
	White	<0.01	<0.01	<0.01	<0.01	0.35	4.68	0.1
	Yellow	<0.01	<0.01	<0.01	<0.01	0.11	3.49	0.1
Lead (mg/l)	Blue	<0.001	<0.001	0.021	0.028	0.047	0.047	0.05
	White	<0.001	<0.001	0.021	0.05	0.05	0.05	0.05
	Yellow	<0.001	<0.001	0.034	0.034	0.034	0.034	0.05
Cadmium (mg/l)	Blue	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.05
	White	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.05
	Yellow	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.05

Absorption Spectrophotometry using a Perkin Elmer Model 400 instrument after appropriate calibration. No digestion was required.

Determination of Anions

Chlorine was determined by colorimetric method using ferric ammonium sulphate and mercuric thiocyanate at the wavelength of 463nm on a Spectronic (Bausch & Lomb). The

total phosphate was determined by the Kurita method (Harris, E. W and Byran, K. C., 1982) using a photometer (Corning Scientific Instruments, England), while sulphate was assayed by spectrophotometric method using Spectronic 20.

Ethanol Determination

Ethanol was analyzed using a Shimadzu 17A Gas chromatograph fitted with a split injection system and a 30m fused silica capillary column of 0.32mm inner diameter and 0.50µm film thickness of bonded phase using a Flame ionization Detector (FID) and helium as carrier gas. The column was run at the initial temperature of 35°C, programmed at 5°C/min and then left for 15 minutes at the final temperature of 180°C. Detector was kept at the temperature of 250°C and injection port at 200°C. Prior to use the GC was calibrated with solutions of known ethanol concentrations using 0.5µl sample size throughout.

RESULTS AND DISCUSSION

Desorption from used plastics

The results are presented in Table 1. The results show that for the container used to store sulphuric acid, pH decreased from

7.14 for fresh water to 2.23 for the stored water. It is clear that any or all of the following phenomena may have come into effect (a) absorbed hydrogen ions have migrated into the water (b) absorbed hydrogen ions have de-sorbed into the water (c) permeated hydrogen ions have de-sorbed into the water. The observations therefore show that sulphuric acid get bonded chemically or absorb physically with HDPE when the two gets in contact and that the sulphuric acid can easily desorb into water from the surface of the HDPE container. The results also show that within the two weeks that the water was stored, there was migration of iron, lead, cadmium, sulphate and chlorine. Their concentrations in the water increased in different proportions as follows; iron (increased in concentration from 0.052 - 0.158mg/l), lead (increased in concentration from 0.01 - 0.064mg/l), cadmium (increased in concentration from 0.01-0.084mg/l) sulphate (increased concentration from 0.01-2.94mg/l) and chlorine (increased concentration from 1.06 - 3.20 mg/l) though all were within acceptable limits for domestic water as shown by standard values in Table 1.

Migration from virgin containers

Water was stored in blue, red and yellow containers for 35 days during which the pH, as well as the concentrations of iron, phosphate, lead and cadmium were monitored every seven days. Table 2 shows the values obtained. Lead content which showed a wide variation with container colour has been further presented in Fig. 1.

The pH varied slightly within the 35 days increasing within the first seven days from 6.87 in fresh water to 7.61, 7.58 and 7.56 for water stored in blue, white and yellow containers

Table 3: Desorption of Components into stored water from plastic containers previously used for the storage of ethanol.

Chemical Parameter	Plastic Colour	DAYS						
		0	7	14	21	28	35	Standard
pH	Blue	6.87	6.86	6.87	6.87	6.87	6.87	6.5-8.0
	Red	6.87	6.87	7.06	7.06	7.06	7.06	..
	Yellow	6.87	6.52	6.93	7.02	7.02	7.02	..
Alkalinity	Blue		9.08	14.28	14.32	14.30	14.30	26.5
	Red		12.98	12.98	12.98	12.98	12.98	..
	Yellow		6.98	12.98	12.98	12.98	12.98	..
Iron (mg/l)	Blue	0.052	0.043	0.044	0.044	0.044	0.044	0.1
	Red	..	0.043	0.053	0.053	0.053	0.053	..
	Yellow	..	0.055	0.055	0.055	0.055	0.055	..
Lead (mg/l)	Blue	<0.01	0.049	0.05	0.05	0.05	0.05	0.05
	Red	..	0.045	0.05	0.05	0.05	0.05	..
	Yellow	..	0.032	0.049	0.049	0.049	0.049	..
Cadmium (mg/l)	Blue	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05
	Red	..	<0.01	<0.01	<0.01	<0.01	<0.01	..
	Yellow	..	<0.01	<0.01	<0.01	<0.01	<0.01	..

respectively. It then decreased at different rates for the different colours of container. The water stored in the yellow and white containers showed the same variation in pH of 0.58 units while the blue container registered a lower variation of 0.33. There is no immediate explanation for the difference in pH observed for various colours of the containers. However, the pigments used during manufacturing are different, for example, the blue pigment used include ferric ferrocyanide and ultramarine which contain sulphur and sodium compounds while kaolin, white lead and barium sulphate are used as white pigments. The sulphate usually increase acidity when they dissociate. However the pH obtained were in all cases within

the acceptable range of 6.5 – 8.0 for good drinking water for all the samples tested.

The iron and cadmium contents were well within specification. The little increase observed may be due to leaching or migration of components of the pigments which are usually iron or cadmium based. Lead content increased from less than 0.01mg/l to 0.034 mg/l, 0.047mg/l, and 0.05mg/l for yellow, blue and white containers respectively. These values are so close to the highest acceptable limit of 0.05mg/l that there is need for caution since lead has been associated with liver problems in man. Most of lead migration occurred during the second week of storage, suggesting that it is quite safe to

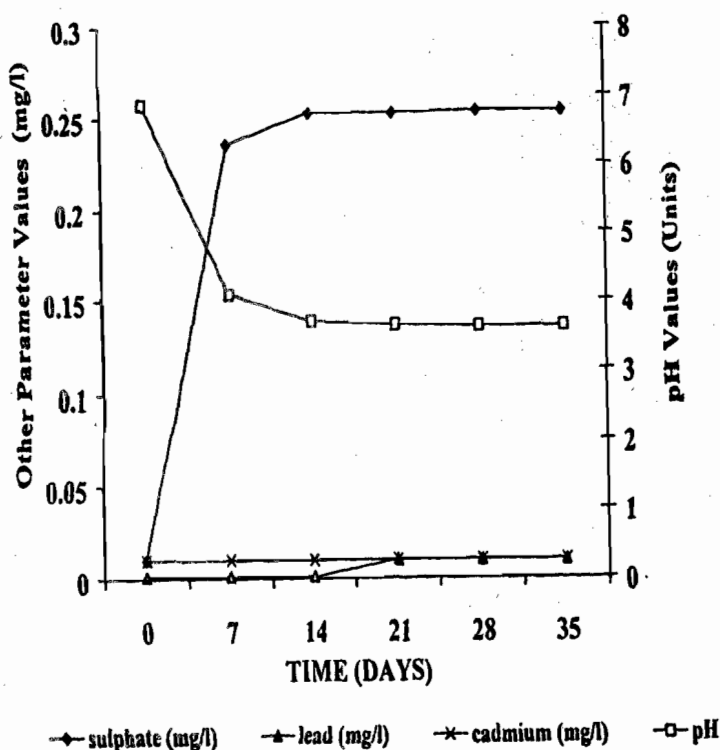


FIG 1: Parameter Values Obtained During Storage of Water in re-used Plastic Containers in which Sulphuric acid was Originally Stored.

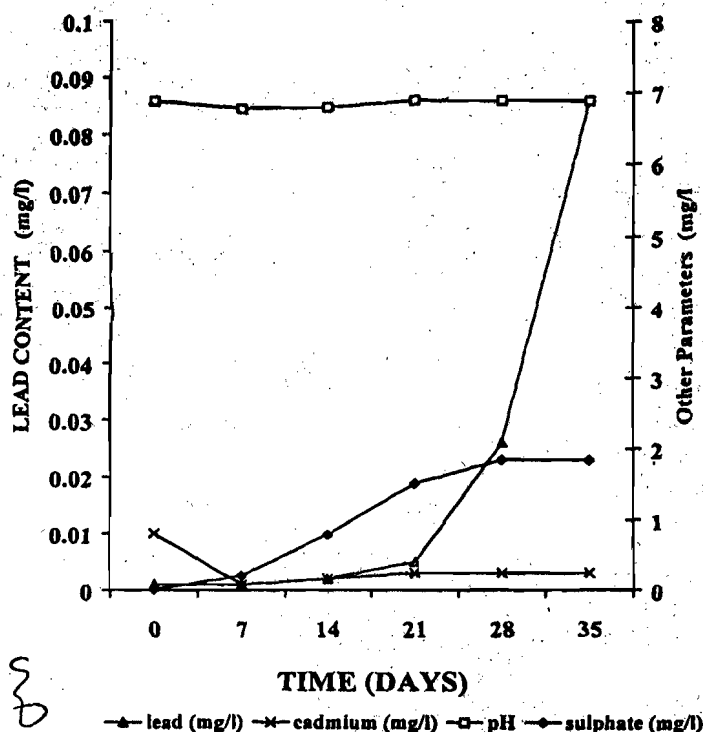


FIG 2: Parameter Values Obtained During Storage of Water in Re-used Plastics in which Methyl Ethyl Ketone was Originally Stored.

store water in these containers for about seven days on a continuous bases after which the contents much be used or discarded.

Cadmium concentration in all the cases was far below the toxic limit and there was no indication of migration of leaching or cadmium additives into the water. Cadmium sulphate is usually used in yellow pigment production. The observation shows that either cadmium-based pigment was not used or they are stable compounds exhibiting no tendency to dissociate and thence to migrate.

After three weeks of storage, phosphate level increased from below 0.01mg/l to as high as 4.68mg/l, which is about 500% of the upper safe limit in drinking water. Until the third week it was still below 0.01mg/l. The source of phosphate is the stabilizer. It is likely that due to the long period of storage some degradation of the plastic has taken place from reaction with the water resulting in the release of free phosphate, which migrated into the water. The observation suggests that it may be safe to store water in these containers for up to one week, without fear of intoxication from phosphate.

Degradation of plastic by stored solvent

Ethanol was stored continuously in blue, red, white and yellow plastic containers for 18 weeks and migration of plastic components monitored using GC equipped with FID detector. The results are shown in Table 3. From the results there was no migration until the fourth week. By the end of sixteen weeks it was clear that normal hexane was migrating from all the colours of plastic into the ethanol and benzene was observed for yellow plastic only after 18 weeks of contact. The hexane may have come from the cyclohexane used for the dilution of additives in polyethylene resin production. It is suspected that the ethanol has attacked the plastic, resulting in degradation and rearrangements in its internal structure thereby forcing

loose moieties to migrate. This observation agrees with the Chemical Resistance Chart published by Cole-Palmer International (Anonymous, 1995) which shows that ethanol has minor effect on LDPE.

CONCLUSION

The experiments carried out with virgin plastics showed that drinking water may be stored in such containers of whatever colour for up to two weeks without contamination by additives introduced during the manufacture of plastics. After two weeks migrations of such additives especially lead from the plastic into the water became evident. The results also showed that the surface of plastics such as the interior of containers is capable of adsorbing liquid materials such as sulphuric acid and methyl ethyl ketone when they come in contact during storage. Such adsorbed materials get de-sorbed subsequently into liquids stored in such containers during re-use. Indiscriminate re-use of plastic containers should therefore be discouraged especially for the storage of liquid food items as undesirable reactions may occur.

It also became evident that the colour of the plastic is important since the toxicant that migrated into the water was identified as components of the pigment. Ethanol was also observed to cause the breakdown of the plastic structure of HDPE after 18 weeks of contact thereby enhancing the migration of manufacturing components.

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