Eco-friendly conversion coating for the protection of aluminium alloys in the food/beverage canning industries

M Oki¹, A A Adediran¹, N Egiebor², I Olaofe¹, C S Awiaka¹ and O Dawodu¹

¹Mechanical Engineering Department, Landmark University, Omu-Aran, Kwara State, Nigeria.
²Department of Environmental Resource Engineering, College of Environmental Science and Forestry New York State University, Syracuse, NY 13210, USA.

Corresponding Author: makanjuola.oki@lmu.edu.ng

Abstract: In view of environmental and health challenges associated with conversion coatings derived from heavy metal ion compounds, this work reports the development and performance of water extracts of Hibiscus sabdariffa (HS) calyces (Hibiscus flower), as a starting green inhibitor in the development of environment friendly, non-carcinogenic conversion coating on aluminium alloy for application in the canning and food packaging industries. Gravimetric analyses revealed that the coating developed sluggishly, a coating weight of about 3 mg was attained after 30 mins of treatment in the coating bath. Fourier transform infrared spectroscopy (FTIR) analyses showed that the coating solution and the coating materials stripped from the aluminium alloy substrate had identical functional groups which were either shifted down or upfield in the FTIR spectra of the coating. However, scanning electron microscopy (SEM) examination revealed that the thin coating developed on aluminium mapped the grain and sub-grain boundaries of the substrate. Whereas, within the detection limits of the EDS, the coating is composed essentially of carbonaceous compounds of aluminium and its oxides as well as those of the other elements present in the substrate and in the coating solution. These compounds are probably hydrated. The corrosion performance and adhesion characteristics of the HS coating were better than for the ‘bare’ aluminium alloy substrate.

1. Introduction
Conversion coating on aluminium and its alloys in any application is a sine-qua non in terms of paint/lacquer adhesion in order to maintain aesthetic values and corrosion resistance. In the metal finishing industry chromate in coating baths as starting materials have pride of place albeit in the high technical spectrum as in the aerospace and building industries. However restrictions have been placed on the use of chromium containing coatings in various other sectors as in white goods, electronics and more stringent restrictions have been put in place in the food and beverage sector. This sector has a zero-tolerant for chromium in its entirety. Chromate as in Cr(VI) has been labeled as carcinogenic, however, others have espoused that Cr(III) being less toxic could be an alternative. Thus chromate phosphate came into being because it is largely composed of CrIII phosphate which Asami et al. [1] during electrochemical spectroscopy for chemical analysis (ESCA or XPS) later showed to contain some Cr VI species. However, it has been revealed that Al being a strong oxidizer converted Cr(III) to Cr(VI) in
coatings developed from baths containing Cr(III) and Zr [2]. Patented Zirconium conversion coatings are in use in the canning industry, however, Zr, being a heavy metal, its ions, may in the nearest future become a source for health concern to the public in general.

The search for replacements for Cr(VI) and other heavy metal ions in conversion coating baths has been wide, far and continuous, however coatings developed from potassium permanganate have been tipped to be a good replacement as regards its use in the canning industry [3-8]. Mn either in oxidation state of +2 or higher may also be a source for health and environmental concern in the nearest future although presently being employed in small dosages for treatment of skin afflictions for humans and fishes.

It has been proved beyond par adventure that the extracts of the calyx of Hibiscus sabdariffa have medicinal values [9-11] and are employed as colorants in the food industry [12]. In addition, it has been affirmed by various researchers [9,12-14] to be a versatile corrosion inhibitor of aluminium alloys and other metals. Conversion coating baths are usually composed of corrosion inhibitors, mostly inorganics. However, glycerol coupled with other components in solution has been employed to form a conversion coating on aluminium [15]. Thus, this investigation sought to develop, examine the corrosion and adhesion characteristics of a conversion coating developed from a corrosion inhibitor which is eco-friendly and of medicinal value, the calyx of Hibiscus sabdariffa. Hibiscus sabdariffa is a tropical plant that is grown and used widely for multiple purposes ranging from pharmaceutical to industrial applications. The plant is typically reared for its flower and the red calyces have always been resources for medicinal treatment of many chronic and degenerative diseases like diabetes, kidney and urinary bladder stone, cancer etc. The extracts of these calyces are composed of an array of compounds with –OH functional groups ranging from flavonoids, phenol to anthocyanin [16-19]. The extracts are also good sources of inorganic components present in vitamin supplements such as iron, phosphorus, calcium, magnesium, manganese, aluminium, sodium, potassium, nickel, zinc etc [20].

2. Methodology

Aluminium alloy specimens were made out into spade like electrodes, etched in 10% NaOH solution, de-smutted in 50% vol/vol Nitric acid, rinsed in acetone, allowed to dry in air and stored in desiccator prior to further use. Dried samples of Hibiscus sabdariffa (HS) were collected from a local market at Omu-Aran, Kwara State Nigeria. 200 g of the dried calyces was added to 1litre of distilled water and allowed to stand overnight in order to avoid thermal extraction which may increase the carbon-foot print of the conversion coating procedures. The liquid extract, which was filtered into a beaker containing 1g of NaF was employed as the conversion coating solution. The pH of the extract was about 3.5.

Cleaned and weighed aluminium specimens were severally immersed in the conversion coating baths for periods of time ranging from 30 s to 30 mins, rinsed in distilled water and allowed to dry in air. The specimens which were made in triplicates per immersion time were reweighed. The mean weight for each immersion time was taken as the final weight.

2.1 Material Processing

A Shimadzu FTIR spectrometer was employed to determine the functional groups in the coating solution and the conversion coating stripped from aluminium alloy substrate to determine their possible participation in the conversion coating formation. The spectrometer run was performed in the transmission mode from 400 to 4000 cm\(^{-1}\).

Conversion coated specimens was done for 5 mins in a triplicate sequence for reproducibility. Some were further coated with lacquer while others were left ‘bare’. These specimens were cross-hatched and a set was exposed to the atmosphere while the other set was exposed to 3.5g/l sodium chloride solution over a period of 168 hrs. Prior to exposure, the photographs of the specimens were taken and monitored visually and with photography over the immersion period. At the end of the exposure period, Japanese industrial adhesion test [11] was applied on lacquer coated specimens using cello-tape that was firmly
applied unto the specimens and was rapidly pulled off against itself. The surfaces were then examined with photography.

3. Results and Discussions

The coating development was sluggish; however, after 30 mins of immersion, a slightly golden coloured coating had developed over the macroscopic alloy surface. Coating weight changes between 30 s and 30 min was low in the order of 0.003 g, suggesting that the conversion coating was very thin and coatings developed in between the two periods were transparent. These were expected since the conversion coating solution contained basically organic functional groups of -OH as in phenols, flavonoids, anthocyanin and glycosides which are the main constituents of water extract of HS calyx. Other electron-rich centers identified were S-H Stretching of thiols, N-O Stretching of nitro compounds, C=O Stretching of anhydrides and C-O Stretching of esters.

Figure 1. FTIR spectra of water extract of Hibiscus Sabdariffa calyx

Fig 1 displays the spectra for the water extracts of HS calyx where, C=O and C-O from anhydrides and esters predominate at 1818.1 cm⁻¹ for acid anhydrides and 1207.9 for ester and at 1135.2 cm⁻¹ for tertiary alcohol. Other notable peaks ascribed in the FTIR analysis are displayed in Table 1 which compares the peaks in the extract and in the stripped Zobo coating.

Table 1. Assignment of FTIR peaks in water extract of HS calyx, Zobo coating and conversion coating stripped from Al.

| S/No | Bands (cm⁻¹) | Band assignments for HS Calyx & zobo coating | Band assignments for coating stripped from Al |
|------|--------------|---------------------------------------------|---------------------------------------------|
| 1    | 3688.8       | -                                           | O-H Stretching of alcohol                    |
|      | 3081.5       | C-H Stretching alcohol                      | C-H Stretching alcohol                      |
|      | 3089.6       | C-H Stretching alcohol                      | C-H Stretching of alkene                    |
|      | 3004.1       | -                                           |                                             |
| 2    | 2968.1       | C-H Stretching alkane                       | C-H Stretching alkane                       |
|      | 2457.8       | -                                           | S-H Stretching of thiol                     |
|      | 2143         | -                                           | C≡C Stretching of alkyne                    |
| 3    | 1763.3       | -                                           | C=O Stretching of anhydride                 |
| Wavenumber (cm⁻¹) | Functional Group                        |
|------------------|----------------------------------------|
| 1818.1           | C=O Stretching anhydride               |
| 1509.0           | N-O Stretching nitro compound          |
| 1207.9           | C-O Stretching ester                   |
| 1135.2           | C-O Stretching tertiary alcohol         |
| 912              | S=O Stretching of sulfonates           |
| 901.7            | C=C bending alkene                      |

Figure 2 displays the FTIR spectra generated from the HS coating stripped from the aluminium alloy substrate. The various peaked observed are as described in Table 1.

It is generally agreed in FTIR studies and interpretation that consequent upon interactions among functional groups and other reactants, if bond length decreases, the peak wave number will shift to higher values on the other hand, if the values decrease, the bond length increased. Thus comparing the spectra and peaks in the extract and the HS coating, all the functional groups of interest either had their peaks either shifted down field or up field. These suggested that reactions between the molecules of the extract and aluminium substrate. An important peak at between 912 cm⁻¹ and 928 cm⁻¹ was identified in the spectra for the coating which has been described by Ehab Alshamaileh et al. [28] as peak for Al-OH clearly indicated reactions between the myriads of –OH in the HS extract with aluminum substrate.

The SEM micrograph for aluminium alloy treated for 5 minutes in the HS coating solution and

Figure 3. (a) SEM micrograph for HS coating and (b) EDS spectra HS coating developed for 5 min.
its corresponding EDS analysis are displayed in Figs 3 a and b respectively. From Fig 3 a, it is obvious that the coating mapped the grain and sub-grain boundaries of the aluminium alloy substrate with islands of thicker coating sections which may be associated with other metal inclusions which are usually cathodic to the aluminium matrix.

For conversion coatings to develop on aluminium substrate, it is generally held that fluoride species in the coating solution activate the substrate with the release of 3 electrons thus,
\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \ldots \ldots (1)
\]

In the absence of easily reducible ions in solution, the electron-rich centers such as OH, NO, C=O, -SH etc will now react with the activated aluminium alloy substrate to form various carbon containing compounds along with oxides and/or hydroxides of aluminium and other metallic ions which are likely to be hydrated.
\[
\text{Al}^{3+} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 \quad \ldots \ldots (2)
\]

As time of immersion increased, the various species in the solution are adsorbed and/or occluded within the growing coating which resulted in the light golden coloration after 30 mins of immersion. Within the detection limits of the EDS, the elemental compositions of the coating are Al, O, C, Mg, Zn, Si, K, Ca and Fe. K was strongly indicated in the coating, this may have been derived from the extract which is known to contain about 0.46 mg/g of the HS calyx [21], and thus K must have reacted in one manner or the other in formation of the growing thin coating on the substrate.

To the naked eyes on examination of specimens after the natural exposure tests over 168 h, the adhesion and corrosion protection characteristics of the HS conversion coating were better than for bare aluminium alloy.

![Figure 4](image)

**Figure 4.** (a) HS and lacquer coated specimen and (b) lacquer coated ‘bare’ specimen after exposure to NaCl solution for 168 h and adhesively tested. X10

However, a clearer distinction was revealed after exposure of lacquer coated ‘bare’ aluminium alloy and those coated in HS coating solution prior to being over coated with lacquer were exposed to 3.5% NaCl solution for 168 h. On examination of the ‘bare’ lacquer specimen displayed in Fig 4b, there was clear paint delamination over its surface and corrosion pits were revealed. However, the HS coated specimen displayed in Fig 4a revealed a yellowish lacquer coating without paint delamination and corrosion pits. The colour change in the lacquer may have resulted from the interaction of NaCl with components of the lacquer. Thus it can be safely inferred that the HS coating outperformed the ‘bare’ specimen both in terms of corrosion resistance and paint adhesion characteristics.

**Conclusions**

The HS conversion coating developed over the aluminium alloy substrate in a manner that mapped the grains and sub-grain boundaries of the substrate. From the EDS analysis the coating is composed of elements derived from the HS water extract and those of the substrate aluminium alloy. These are likely to oxides/hydroxides and carbon containing compounds of aluminium, magnesium, zinc, potassium and
calcium infiltrated with organic components of the HS extracts. The coating outperformed the ‘bare’ specimen in terms of improved corrosion resistance and paint adhesion capabilities.

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