West Indian Journal of Engineering Vol. 27, No. 1, (July 2004) Technical Paper (Adewuyi & Oladunjoye) 10 - 17

Corrosion of Tin Plate by Malic Acid Containing Colourants and Sweetening Agents

B.O. Adewuyi
& O.A. Oladunjoye*

The corrosion of tin in aqueous solution of malic acid containing various food colourants (Sunset Yellow, Carmosine, Tartazine and Poncreau 4R) and/or sweetening agents (Glycerol, Saccharin, Glucose and Sucrose) has been studied. In general, the corrosivity of the acid containing various colourants increases with acid concentration and colourant concentration in the order: Sunset Yellow < Carmosine < Poncreau 4R. However, at constant colourant concentration with increasing acid concentration, corrosivity was in the order: Carmosine < Sunset Yellow < Poncreau 4R < Tartazine. The sweetening agents inhibit corrosion rate. Their inhibition efficiency was in the order: Glycerol < Saccharin < Glucose < Sucrose. In solution containing colourants, the corrosion rate increases in the order: Glycerol < Sucrose < Saccharin < Glucose and Glycerol < Saccharin < Glucose < Sucrose in Carmosine and Sunset Yellow respectively.

Keywords: Corrosion, sweetening, colouring agent, tin.

1. Introduction

The history of food packaging goes back to the dawn of human civilisation. Packaging and containers have become tools for subdivision and transportation of food. Food packaging and containers are made from different materials: paper and paper boards, glass, plastics and metals, (**Kishimoto 1990**); (**Matsubayashi 1990**).

Various food preparations may contain, among other things, some acids, sweeteners, colourants and other additives that may impart organoleptic qualities to food (**Patel** and **Talati 1987**). Food is canned in either plain tin plate or lacquered tin-free steel, although some food processing industries prefer to use lacquered tin plate which is very expensive but offers a longer shelf life. The quality of can is a major factor in the operations of food-processing industries. The toxic effect of some packaging material on food has made the selection of food cans very critical. Tin is considered to be quite resistant to attack by organic acids but undergoes corrosion if oxygen is present in the solution. In such cases, the food product may pick up corroded tin, which will affect the colour and taste. With prolonged exposure, it may also have toxic effect on the quality of the food (**Kadoya 1990**).

The electrochemical relationship between tin and iron is a complicated one. Tin can be regarded as being anodic to iron when in contact with such products as fruit juices, meat and meat derivations and mild in solutions of citric, tartaric, oxalic and malic acids and their salts (**DeMan 1990**); (**Shreir 1976**). Fruits such as pineapples and apples used for fruit juice contain 4 -10% malic acid. The attack on tin by fruit juices depends very largely on the formation of complexes in fruit acid such as oxalic, citric and malic acids. Organic acids present in foodstuff act as electrolytes. Complexing anions can influence the relative position of Sn, Fe and Sn-Fe alloy, hence the corrosion mechanism. According to **Ulick (1976)**, the presence and decomposition of fungicide can cause pitting of steel by acid food due to the hydrogen overvoltage of tin which leads to the reduction in cathodic protection. Addition of food additives such as colourants, flavour, sweeteners and preservatives, affects the characteristic

* Metallurgical and Materials Engineering Department, Federal University of Technology, Akure, Africa.

Pertinent discussion will be published in January, 2005 West Indian Journal of Engineering if received by November, 2004.

of the food. In studying the corrosivity of food colourants (monoazo dyes), **Patel** and **Talati (1987)** discovered that the colourants affect the corrosion of copper by food acids. Their corrosivity may be attributed to the fact that they contain two or more sulphuric acid groups that form soluble compounds. Another possibility of increase in corrosion rate is the presence of hydroxyl group in the O-position to the azonitrogen that forms complexes. **Vogel (1977)** confirms that organic compounds like sugar and glycerol contain hydroxyl groups that form complexes with metal ions that inhibit corrosion. Some sweeteners, according to **Fox** and **Cameron (1984)** had been found to be detrimental to health. For example, the high-energy values of sugar make it unsuitable for slimming products and contributes to obesity and also act as major causes of dental problems and are related to coronary heart disease. A sweetener generally provides flavour appeal and frequently, texture through crystallinity, **Hough *et al.* (1978)**. Its taste, appearance and smell rather than its food value determine appeal of food. Some colourants are found to contain organic acids. These acids slow down bacteria spoilage (**Walford 1972**). This study is carried out to determine the corrosive effect of plain malic acid of different concentration on tin plate and the effect of food dyes and sweetening agents. This becomes necessary for effective qualitative and quantitative data collation.

2. Experimental Procedure

Uniformly high tin-coated plates used for canning pineapple juice were used. The composition of the steel base plate is given in **Table 1**.

Thirty-eight (38) test specimens were cut into sizes of approximate dimensions 4.56 x 2.65 x 0.022cm. The initial tin-coating thickness on the surface of the test materials was 0.375 microns. Pre-experimental treatment that can affect the texture and expose the steel surface, like grinding, was avoided. The materials were subjected to thorough cleaning by washing in acetone to remove dirt and any grease or oil. The sharp edges were smoothened using abrasive paper to prevent misleading corrosion results.

2.1 Preparation of Corrosive Media

The range of malic acid concentration used for the investigations varied between 0.01M (1.34gm^{-3}) and 0.5M (67gm^{-3}). To study the effect of colourants on the corrosion of tin plates, four (4) different colourants were used namely:Tartazine, Carmoisine, Sunset Yellow and Poncreau 4R. The colourants' concentration was varied from 0.01%-0.05%. Also, to study the effect of sweetening agents, Glycerol, Saccharin, Glucose and Sucrose, sweeteners were used. The concentrations were maintained at 10%. These concentrations were adopted because they are within the normal industrially acceptable levels.

2.2 Test Procedure

Corrosion study was carried out by total immersion test specimens in the corroding media. Each test-piece of the tin plate was suspended in the corrosive media by attaching the test piece to a wooden label using a PVC thread. The following experimental variants were subsequently performed:

Variant 1.

Samples were immersed in four (4) different containers (marked I-IV) containing plain malic acid solution with concentration varying from 0.01-0.5M. This was used as the control.

Variant 2.

Samples were immersed in different containers (marked V-VIII) for Tartrazine; IX-XII for Carmoisine; XIII-XVI for Sunset Yellow and XVII-XX for Poncreau 4R) in varying malic acid concentration (0.01-0.5M). The colourant concentrations were kept constant at 0.025%.

Variant 3.

Samples were immersed in four (4) different containers (marked XXI-XXIV) in 0.1M malic acid with sweeteners. In each solution, different sweeteners at 10% concentrations, (Saccharin at 0.3%, being the normal industrial acceptable levels) were added.

TABLE 1: *Chemical Composition of Steel-Coated Plate*

C	Mn	Si	P	S	Cu	Ni	Cr	Mo	Al	Fe
0.13	0.60	0.03	0.05	0.05	0.2	0.15	0.1	0.05	0.02-0.1	Others

TABLE 2: *Inhibitive Tendency of Sweetening Agents in Malic Acid*

	% Inhibition in 0.1M Malic Acid containing Colourants and Sweeteners					
	Acid only		Solution with Carmoisine		Solution with Sunset Yellow	
Solution	% Inhibition	Weight loss ($mgdm^{-2}$)	% Inhibition	Weight loss ($mgdm^{-2}$)	% Inhibition	Weight loss ($mgdm^{-2}$)
Acid only			8.0	285.501	25.33	231.711
Sacharin	42.67	177.921	52.00	148.957	58.67	128.269
Glycerol	12.00	273.088	21.33	244.124	36.00	198.610
Sucrose	76.00	74.749	49.33	154.233	90.67	28.964
Glucose	46.67	165.508	73.33	82.754	73.33	82.754

Variant 4.
Samples were immersed in different containers (marked XXV-XXXII) containing sweeteners and colourants in constant malic acid concentration (0.01M) solution.

Variant 5.
Samples were immersed in different containers (marked XXXIII-XXXVIII) containing colourant in constant malic acid concentration solution. The colourants' concentrations were varied from 0.01-0.05% while the acid concentration was kept constant.

The experiment was carried out for 26 days, after which there was complete de-tinning and an appearance of pitting corrosion on the steel plate.

Corrosion rate was assessed by the conventional weight-loss method as well as visual observation of test pieces. CRISON pH 200 microprocessor controlled pH meter was used to monitor and measure the pH variation with time and the potential drop of the corroding media. The data obtained are used in the assessment of experimental results.

The test pieces were weighted on an electronic digital weighing balance. The weight loss of a test piece is taken to be equal to the initial weight of the test piece less the final weight of the specimen:

$$W_1 = w_k - w_{k-1},$$

where W_1 = weight loss, (mg);
w_k = initial weight and
w_{k-1} = final weight.

Hence, Corrosion rate (mpy) was calculated using the following equation:

$$C.R. = 534W_1/DAT,$$

where D = density;
A = Area of exposure of specimen and
T = exposure time in hours.

(The total area of exposure of each specimen was calculated to be on the average of $0.24168dm^2$).

It is assumed that corrosion rate is slowed down by the presence of sweetening agents. Hence, the inhibition efficiency of the sweetening agents is expressed using the earlier method by **Patel** and **Talati** in calculating the percentage inhibition, (Pi). This is calculated by:

$$Pi, (\%) = (w_u + w_i)/w_u \cdot 100;$$

where w_u and w_i are the weight loss in acid with or without colourant and acid with containing sweetening agents with or without colourant respectively.

3. Results and Discussion

The results are given in **Table 2** and also in **Figures 1-6**. **Figure 1** shows the effect of malic acid without any addition of colourants or sweeteners but of different concentrations on tin plates. **Figures 2** and **Figure 3** show the variation of pH with potential (mV)

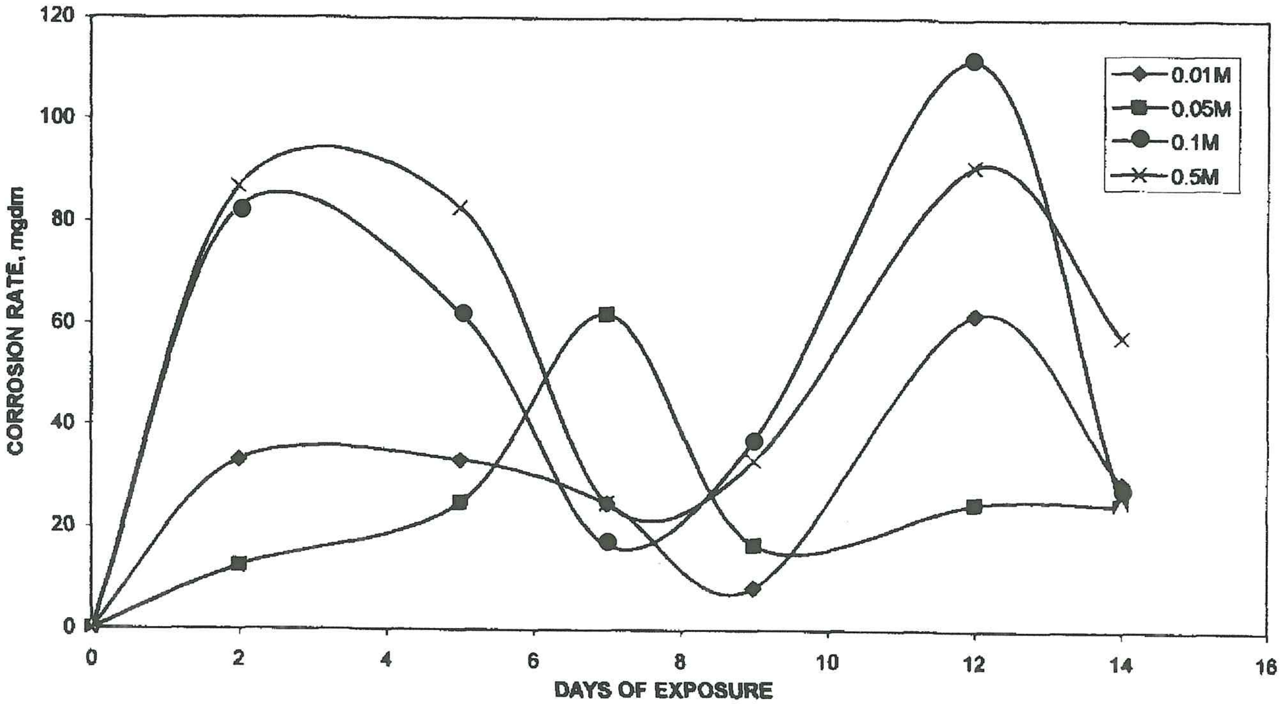

FIGURE 1: *Effect of Plain Malic Acid on Tin Plate*

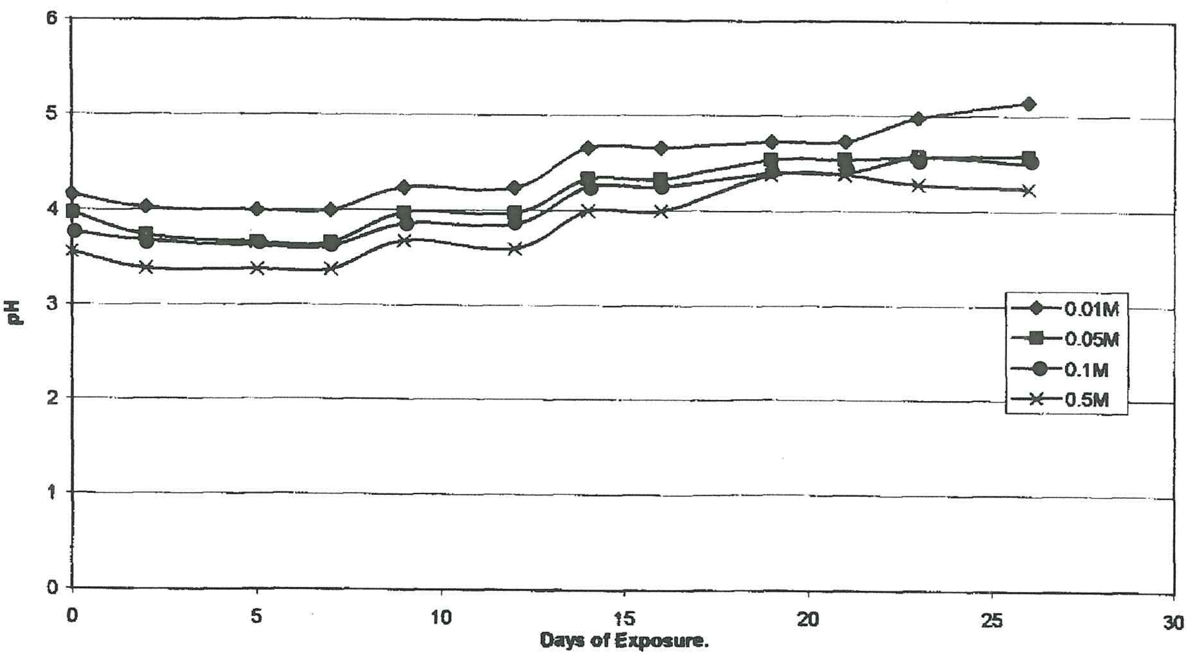

FIGURE 2: *Variation of pH with Days of Exposure*

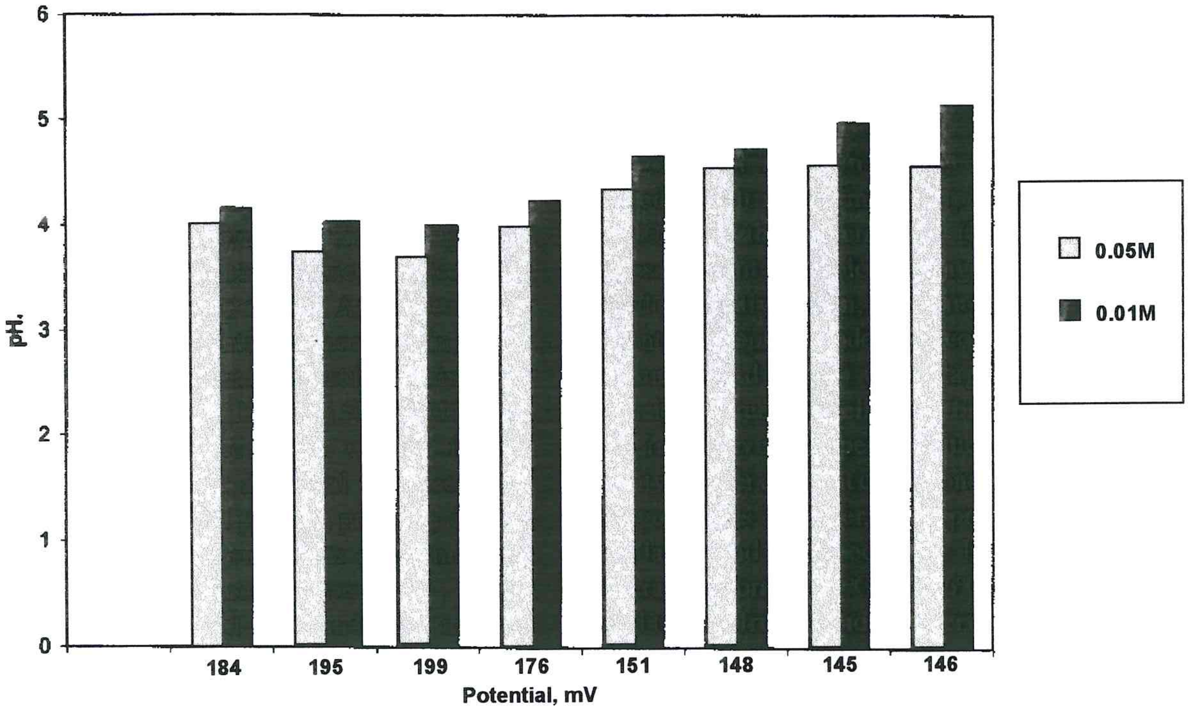

FIGURE 3: *Variation of pH with Potential of Tin Plate on 0.01 and 0.05M Malic Acid*

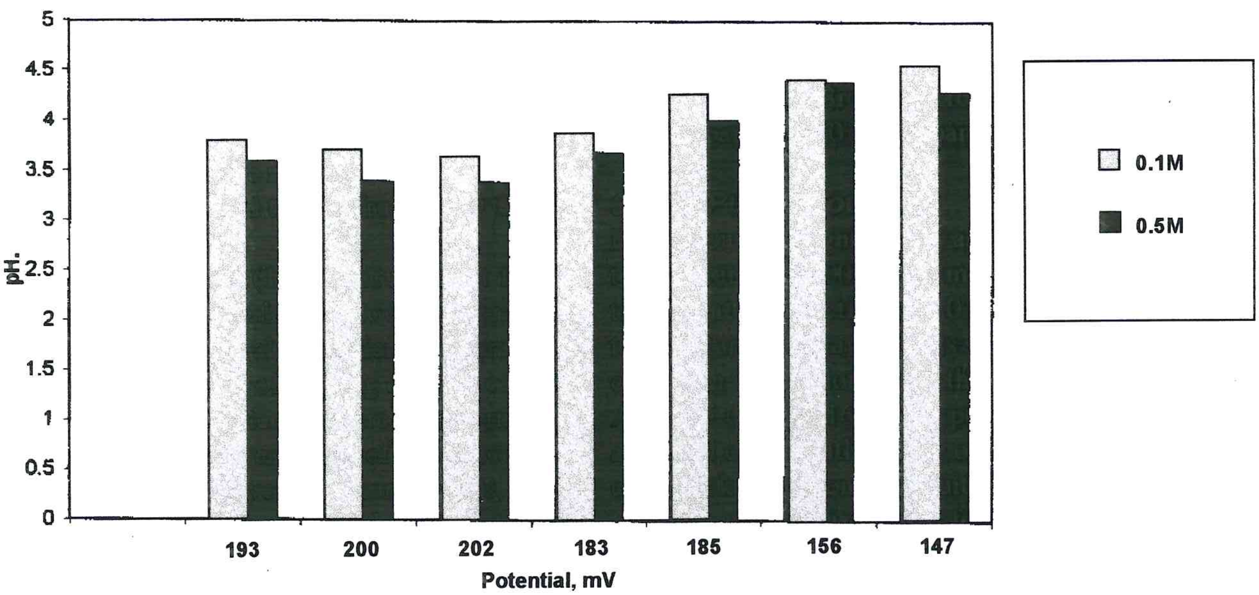

FIGURE 4: *Variation of pH with Potential of Tin Plate in 0.1M and 0.5M Malic Acid*

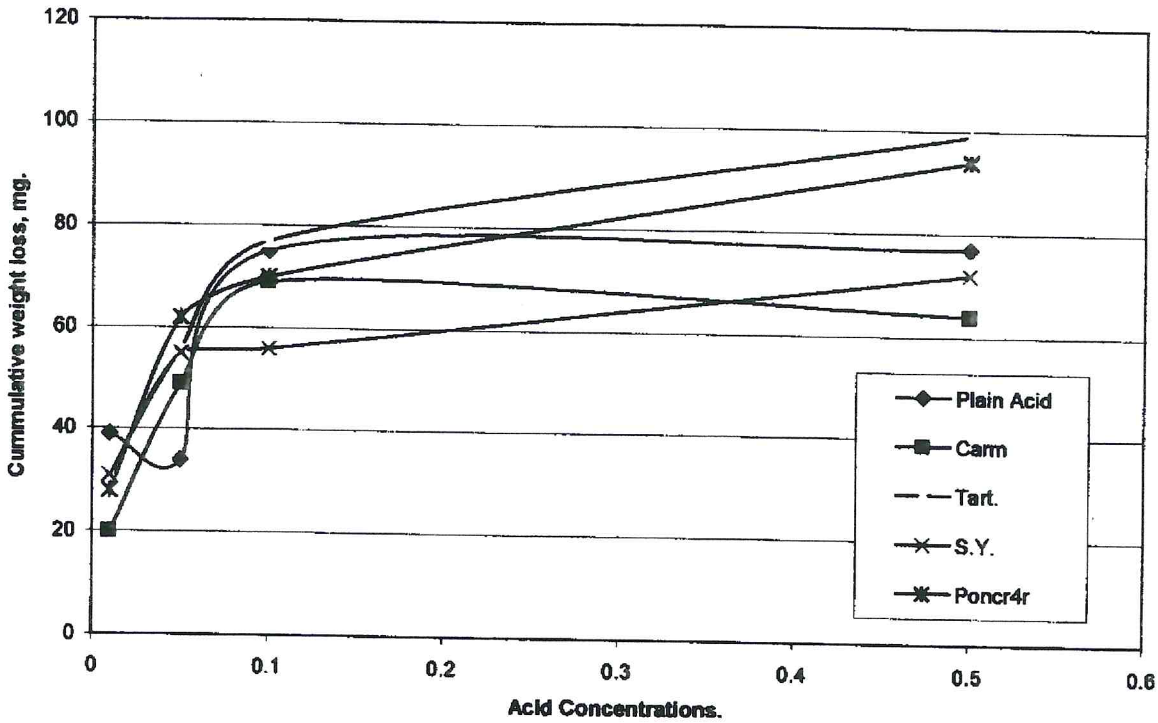

FIGURE 5: *Effect of Colourant Addition on Cumulative Weight Loss in Varying Acid Concentrations*

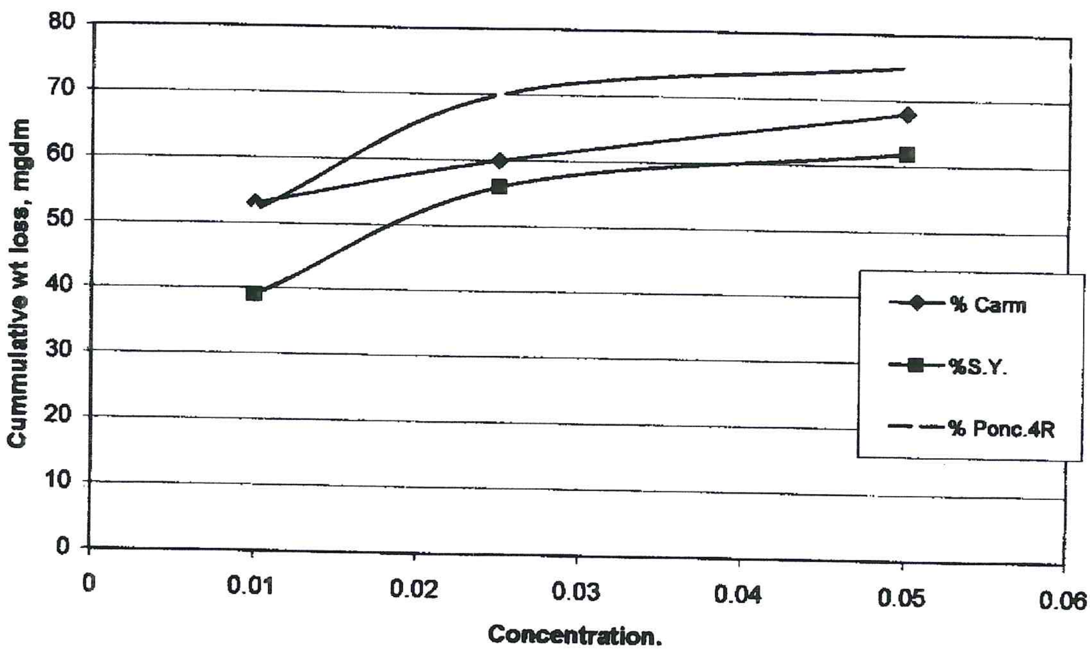

FIGURE 6: *Effect of Variation in Colourant Concentration on the Cumulative Weight Loss in 0.1M Malic Acid*

of tin plate in malic acid. **Figure 5** shows the effect of colourant addition on the cumulative weight loss in varying acid solutions and **Figure 6** is the effect of variations in colourant concentrations on the cumulative weight loss in 0.1M malic acid.

3.1 Effect of Plain Malic Acid

From **Figure 1**, three (3) main peaks are visible on the 3rd, 12th and 19th days. The first peak shows the rate of corrosion rising within the first three days and reduces after three days and reach minimum on the 6th and 7th days. This rising and falling tendency is repeated between the 9th and the 14th and also between the 16th and 21st days. The initial rise after three days is as a result of attack Sn-Fe alloy layer. This is followed by a temporary passivation due probably to the reduction in the pH of the system and formation of temporary protective oxide layers on the surface. Further de-tinning continues as a result of breakdown of passivation due mainly to dissolution of protective oxide layer and absorption of atmospheric oxygen into the solution. Complete removal of the Sn-Fe alloy layer and the total exposure of the surface of the steel to the corrosive media are responsible for the astronomical rise after the 16th day.

According to **Talati** and **Patel**, factors that influence corrosion rates are the pH of the solution, hydrogen over voltage of the metal, oxygen concentration of the solution and the solubility of the salts formed. This can also be used to explain the mechanism of the corrosion that occurs on the tin plate in malic acid. **Figure 2** confirms the pH dependence of the corrosion rate.

3.2 Effect of Sweetening Agents

The effects of sweetening agents, Saccharin, Glycerol, Glucose and Sucrose on the corrosion rate and inhibiting efficiency of sweetening agents in acid containing colourants are shown in **Table 3**.

From **Figures 3** and **4**, it is evident that the corrosivity of the media reduces as the pH increases, much lower than when compared to the plain acid media.

Vogel (1977) had earlier observed that organic compound like sugar and glycerol containing hydroxyl groups form complexes and that the metal ion replaces the hydrogen of the hydroxyl group. He further confirms that if the complex were insoluble, it would inhibit corrosion. Hence, the inhibiting tendency of the sweetening agents may be traced to complex formation of the compound through general adsorption on the metal surface.

3.3 Effect of Acid and Colourant Concentration

From **Figure 5**, it is shown that at a constant colourant concentration, the corrosion rate increases with increasing acid concentration. At acid concentration up to 0.05M, corrosion rate increases in this order: Carmoisine < Poncreau 4R < Sunset Yellow < Tartazine, while at acid concentration above 0.05M, the corrosivity of Carmosine and Sunset Yellow show slight decrease. In general, the order of corrosivity of the acid containing the colourants is Carmoisine < Sunset Yellow < Poncreau 4R < Tartazine.

Figure 6 shows the effect of variation of the colourant concentrations on the cumulative weight loss. At all the colourant concentrations, the corrosivity of the acid is found to increase in the order: Sunset Yellow < Carmoisine < Poncreau 4R.

4. Conclusion

From the investigations, it was found that the pHs of the solution, hydrogen over voltage of the metal and oxygen concentration of the solution are the main factors that influence corrosion rate of tin plates. Also, additives and preservatives in the form of colourants affect the corrosion rates. While colourants increase the corrosion rate, sweeteners act as inhibitors through general adsorption on the metal surface. The following conclusions are therefore reached:

1. The corrosivity of the acid containing various colourants increases with acid concentration and colourant concentration in the order: Sunset Yellow < Carmosine < Poncreau 4R.

2. At constant colourant concentrations with increasing acid concentration, corrosivity was in the order: Carmosine < Sunset Yellow < Poncreau 4R < Tartazine.

3. The sweetening agents inhibit corrosion rate. Their inhibition efficiency was in the order: Glycerol < Saccharin < Glucose < Sucrose.

4. In the solution containing colourants and sweetening agents, the corrosion rate increases in the order: Glycerol < Sucrose < Saccharin < Glucose and Glycerol < Saccharin < Glucose < Sucrose in Carmosine and Sunset Yellow respectively.

The option of lacquered tin-can cannot be down-played because of the high level of corrosion resistance it offers compared to tin plate. It is recommended therefore that when canning food that contains malic acid, it is necessary to use properly coated steel-base plate with the appropriate tin film thickness. This will go a long way in avoiding food-poisoning that can emanate from corrosion of tin cans. Food products may pick up corroded tin, which will affect the colour and taste. Therefore, there is need to monitor the shelf life of canned foods since from the results, it is evident that prolonged exposure may have toxic effect on the quality of food caused by corrosion pollution.

Acknowledgement
The authors would like to thank Carnaud Metal Box Ltd., Ogba, Lagos, for their assistance.

References

[1] Patel, A.S. and Talati, J.D. (1987). *Corrosion of Copper by Food Acids containing Colourants and Sweetening Agents*. Part V. Corrosion by Acetic Acid. Paper presented at 10th International Congress on Metallic Corrosion (ICMC), Vol. iv. 16:3. Madras, India.

[2] Talati, J.D. and Patel, A.S. (1989). *Corrosion of Copper by Malic Acid containing Colourants and Sweetening Agents in Metal Abstract*. The Burlington Press, Cambridge, England.

[3] Kishimoto, A. (1990). *New Food Packaging Materials in Food Packaging*. Academic Press Inc., California.

[4] Matsubayashi, H. (1990). *Metal Containers in Food Packaging*. Academic Press Inc., California.

[5] DeMan, J.M. (1990). *Principle of Food Chemistry*, Von Nostrand Reinhold, New York, pp. 414.

[6] Kadoya, T. (1990). *Food Packaging*. Academic Press Inc., California, pp. 48 – 103.

[7] Shrier, L.L. (1976). *Corrosion*. Voli Newness Butterworths, London, pp. 14 – 20; 97.

[8] Ulick, R.E. (1976). *The Corrosion and Oxidation of Metals*. Vol. 2, Edward Arnold Ltd., London, pp. 308.

[9] Vogel, A.I. (1977). *Macro and Semi-Micro and Qualitative Inorganic Analysis*, Orient Longman Ltd., pp. 56. ■