A Study of the Corrosion of Tin Plate by Can Washing Compounds

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Introduction

Although the problem of corrosion of producers' milk cans by cleaning materials has been recognized for many years, few specific investigations relating to the problem have been presented in the literature. General studies dealing with the attack on a variety of dairy metals by numerous alkalies, strong and weak acids, and other materials have been conducted by Hunziker, Cordes, and Nissen (1929), Prucha (1930), and Parker (1940, 1942). Unfortunately, only a limited amount of data directly related to the factors affecting corrosion of tin plate were presented by these investigators.

For the most part, experiments specifically concerned with corrosion of tin and tin plate have been limited primarily to those performed by the English workers, Kerr (1935, 1940), Hoar (1934, 1937), and MacNaughtan and Hedges (1936). Kerr (1935) observed that the rate of corrosion of tin and tin plate was influenced more by the temperature and dissolved oxygen content of an alkaline solution than by the concentration of alkali. He also revealed that the use of a reducing agent, such as sodium sulfite, greatly minimized alkaline corrosion of tin.

In view of the scarcity of information relating to milk can corrosion, the object of this investigation was to obtain additional data on the relative corrosiveness of can washing compounds and to review the role of oxygen in alkaline corrosion of tin.

Experimental Methods

While consideration was given to several methods for making the corrosion tests, no attempt was made to duplicate actual conditions encountered in mechanical can washers. Laboratory reproduction of actual operating conditions would have been too time consuming and tedious to be practical. The method selected was one which was easily controlled and which would yield reproducible, relative corrosion values. Justification of the procedure lies in the fact that relative corrosion values, when interpreted as such, can be equally as informative as absolute corrosion values.

Strips of hot-dipped tin plate, each having a total surface area of ten square inches, were used for the tests. The bare edges of the strips were coated by dipping them into pure molten tin. The tin strips were thoroughly washed, degreased with ether and finally dried to constant weight. Duplicate tin strips were used in the various concentrations of each cleaner tested, both for total immersion and partial immersion tests. Partial immersion tests were made to determine the combined action of oxygen and the cleaner at the air-solution interface.

Various concentrations of each cleaner were employed so that the concentration recommended by the manufacturer would fall within the test range. Eight commercial alkaline
cleaners, two commercial acid cleaners and four alkalies were subjected to test. The four alkalies were sodium carbonate (soda ash), sodium metasilicate (metasilicate), tri-sodium phosphate (t.s.p.) and sodium hydroxide (caustic soda). All of the alkaline cleaners contained at least one of these basic alkalies.\(^2\)

Since some of the cleaners, when used in hard water, precipitated lime salts, distilled water was used in preparing the test solutions, in order to prevent deposition of the salts on the tin strips. Beakers of 250 ml. capacity, containing 200 ml. and 100 ml. amounts of the solutions, were used for the total and partial immersion tests respectively. In the partial immersion tests the tin strips were placed so that approximately one half of each strip was in contact with the solution and the remaining half exposed to air. In determining the exposure time it was estimated that a can would remain in contact with the wash solution for about 12 seconds in the standard 12 can per minute can washer. Thus the equivalent of one year's washing was found to be about 73 minutes, assuming that the can was washed each day in the year. The temperature of 160°F. was used for the tests, since it was the highest temperature recommended for use in the wash tank with any of the commercial cleaners. The solutions were heated to 160°F. before immersing the tin strips and this temperature was maintained by means of a thermostatically controlled oven. After 73 minutes exposure to the solutions at 160°F. the strips were removed, rinsed with tap and distilled water, and then dried to constant weight. The solutions were neither agitated nor aerated during the tests.

To determine the influence of oxygen on the corrosion of tin in alkaline solutions, corrosion tests were made, according to the method described previously, using sodium hydroxide solutions ranging in concentration from 0.0 percent to 30.0 percent. Sodium hydroxide was selected because it was considered the most corrosive alkali. Oxygen determinations of the sodium hydroxide solutions, selected from the lowest to the highest concentrations, were made, using the method described by Van Slyke and Neill (1924) for the determination of gases in blood and other solutions. Inasmuch as the Van Slyke-Neill method made it necessary to run the oxygen determinations at room temperature, the sodium hydroxide solutions after preparation were heated to 160°F. and subsequently cooled under a layer of mineral oil to room temperature. This made it possible to determine the oxygen solubility of the solutions at the temperature employed in making the corrosion tests. The mineral oil layer (about one-half inch in depth) was used on the solutions to prevent re-absorption of air by the solutions during the cooling process.

\[\text{RESULTS}\]

The results of the corrosion tests on all of the alkaline and acid cleaners as well as the alkali components appear in Table 1. In the first column, the letters A to H inclusive were used to represent the eight commercial alkaline cleaners, and the letters J and K were used to represent the two commercial acid cleaners. The four basic alkalies were identified by their chemical names. All of the commercial alkaline cleaners were found to attack tin quite readily. As was to be expected, the pure alkalies were somewhat more corrosive than the majority of the commercial cleaning mixtures. Negligible attack on tin was noted in the tests using two commercial acid cleaners.

Manufacturers of cleaning mixtures have generally referred to concentrations in terms of ounces per
<table>
<thead>
<tr>
<th>Cleaner or Compound</th>
<th>Alk. as % Na₂O</th>
<th>Concentration ounces/gallon</th>
<th>Ave. wt. loss-mg.</th>
<th>Average % loss of tin</th>
<th>Corrosion rate mg./dm.²/day</th>
<th>Ave. wt. loss-mg.</th>
<th>Average % loss of tin</th>
<th>Corrosion rate mg./dm.²/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.03-.12</td>
<td>0.22-.89</td>
<td>2.65</td>
<td>3.19</td>
<td>81.0</td>
<td>1.59</td>
<td>3.80</td>
<td>97.2</td>
</tr>
<tr>
<td>B</td>
<td>0.05-.20</td>
<td>0.42-1.66</td>
<td>3.38</td>
<td>4.07</td>
<td>103.3</td>
<td>2.04</td>
<td>4.91</td>
<td>124.7</td>
</tr>
<tr>
<td>C</td>
<td>0.07-.15</td>
<td>0.40-.90</td>
<td>3.52</td>
<td>4.24</td>
<td>107.6</td>
<td>2.08</td>
<td>5.02</td>
<td>127.2</td>
</tr>
<tr>
<td>D</td>
<td>0.05-.20</td>
<td>0.37-.50</td>
<td>3.60</td>
<td>4.34</td>
<td>110.1</td>
<td>2.19</td>
<td>5.27</td>
<td>135.0</td>
</tr>
<tr>
<td>E</td>
<td>0.10-.25</td>
<td>0.61-.52</td>
<td>3.68</td>
<td>4.43</td>
<td>112.5</td>
<td>2.14</td>
<td>5.15</td>
<td>133.9</td>
</tr>
<tr>
<td>F</td>
<td>0.07-.15</td>
<td>0.35-.75</td>
<td>3.82</td>
<td>4.60</td>
<td>116.8</td>
<td>2.63</td>
<td>6.34</td>
<td>160.8</td>
</tr>
<tr>
<td>G</td>
<td>0.10-.25</td>
<td>0.64-.60</td>
<td>4.10</td>
<td>4.94</td>
<td>125.4</td>
<td>2.99</td>
<td>7.20</td>
<td>182.8</td>
</tr>
<tr>
<td>H</td>
<td>0.16-.22</td>
<td>0.70-.10</td>
<td>4.72</td>
<td>5.68</td>
<td>144.3</td>
<td>4.05</td>
<td>9.76</td>
<td>247.7</td>
</tr>
<tr>
<td>I</td>
<td>pH 4.0 -5.5</td>
<td></td>
<td>0.22*</td>
<td></td>
<td></td>
<td>0.19*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>pH 4.0 -5.5</td>
<td></td>
<td>0.05*</td>
<td></td>
<td></td>
<td>0.05*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>0.05-.20</td>
<td>0.23-.91</td>
<td>5.50</td>
<td>6.63</td>
<td>168.2</td>
<td>3.53</td>
<td>8.50</td>
<td>215.8</td>
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<tr>
<td>Sodium metasilicate</td>
<td>0.05-.20</td>
<td>0.23-.93</td>
<td>5.68</td>
<td>6.84</td>
<td>173.7</td>
<td>3.60</td>
<td>8.74</td>
<td>220.1</td>
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<tr>
<td>Tri-sodium phosphate</td>
<td>0.05-.20</td>
<td>0.29-1.18</td>
<td>5.78</td>
<td>6.96</td>
<td>176.7</td>
<td>4.28</td>
<td>10.30</td>
<td>261.4</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>0.05-.20</td>
<td>0.09-0.36</td>
<td>6.30</td>
<td>7.59</td>
<td>192.6</td>
<td>4.35</td>
<td>10.48</td>
<td>266.0</td>
</tr>
</tbody>
</table>

*Within range of experimental error for the exposure time employed.
Corrosion of Tin Plate
gallon. Therefore, the solution concentration ranges were expressed in those units for all corrosion tests. The alkalinity ranges of the solutions were expressed as percent Na₂O, the solutions having been titrated to a phenolphthalein end-point. Exception was made in the use of the acid cleaners; the reactions of these solutions were determined in terms of pH using a Beckman pH-meter.

The deviations in weight losses of the strips from different concentrations of the same cleaner were for the most part small. Therefore, average weight losses were determined for all totally immersed strips and for all partially immersed strips exposed to each cleaner. While only half as much surface area was exposed to the test solution in the partial immersion tests as in the total immersion tests, the percentage loss of tin and the corrosion rates were higher for partial immersion. This was probably due to the increase in the corrosive activity of the solution by oxygen at the solution surface. The percentage loss of tin was calculated from the average weight of tin per unit area for the type of tin plate used.

McKay and Worthington (1936) expressed corrosion rates in terms of milligrams of metal lost per square decimeter per day (mg./dm.²/day). Inasmuch as these investigators considered corrosion rates near or above one hundred milligrams per square decimeter per day to be "serious," all corrosion rates appearing in table 1 would thus be considered "serious." McKay and Worthington advised, however, that when using these or other units consideration must be given to the "form of corrosion" and to the relative effect on corrosion by the experimental conditions as compared to conditions encountered in commercial practice.

Corrosion data and oxygen solubilities on sodium hydroxide solutions ranging from 0.0 percent to 30.0 percent concentration appear in table 2 and figure 1. While it was to be expected that increasing alkali concentrations would result in decreasing oxygen solubilities of the solutions, it was interesting to note that oxygen influenced tin corrosion to a greater extent than did the alkali content. Increasing the sodium hydroxide concentration caused increased corrosion only in the 0.0 percent to 0.01 percent concentration range. Further increases in alkali concentration had no apparent effect on the corrosiveness of the solutions except in lowering the oxygen solubilities of these solutions.

It was noteworthy that the can washing alkalinity range, 0.05 percent to 0.20 percent Na₂O, which is equivalent to 0.65 percent to 0.27 percent NaOH, fell precisely within the concentration range where maximum corrosion occurred.

An inspection of figure 1 reveals that at high sodium hydroxide concentrations, the oxygen content of the
solutions approached zero whereas the tin corrosion values approached a constant. This probably can be attributed to the dissolution of the oxide surface film on the tinplate by the alkaline solutions. Insufficient oxygen was present to reform the oxide film and thus further weight loss was prevented.

**Discussion**

Although the results indicate that the basic alkalies were somewhat more corrosive than commercial alkaline cleaners, corrosion rates for all the compounds tested were in the range considered "serious" by McKay and Worthington. It should be noted that the seriousness of can corrosion cannot be determined by visual inspection of cans in actual practice. No correlation was found in comparing the visual appearances or "spangling" with the weight losses of the tin strips.

It was shown previously that the acid cleaners in the concentrations employed did not appreciably attack tin. However, limited tests using iron revealed that the acid cleaners caused localized corrosion with the formation of pits. Iron, as it is used in can washers, is relatively immune to attack by the alkaline solutions, although in the presence of oxygen it is rapidly pitted by neutral or weakly acid solutions. Since the acid cleaners belong to the weakly acid group, the iron corrosion tendency should be considered.

Since the partial immersion tests revealed greater percentage losses of tin and greater corrosion rates than did the total immersion tests, the oxygen at the air-solution interface apparently caused the greater corrosive action. The importance of oxygen was again demonstrated by the corrosiveness of sodium hydroxide solutions through a wide concentration range. These results did not indicate that alkali concentration had any significant relation to tin corrosion except when the concentrations were very low. Furthermore, the data revealed that alkali concentrations low enough to produce negligible attack on tin would be too low to possess any detergency.

It is doubtful if the problem of alkaline corrosion of milk cans can be solved by varying the combination of alkalies in commercial washing compounds or by raising or lowering the concentrations of these compounds in wash solutions. Apparently, elimination of oxygen from alkaline wash solutions is the best corrosion remedy. According to Kerr (1935) the reducing agent, sodium sulfite, was an effec-

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**Figure 1. Oxygen-Corrosion Relationships**

![Graph showing oxygen-corrosion relationships with curves for concentration of sodium hydroxide solutions and oxygen solubility curve.](http://meridian.allenpress.com/jfp/article-pdf/10/5/263/2393846/0022-2747_10_5_263.pdf)
tive corrosion inhibitor and it was most effective in alkali concentrations where maximum corrosion occurred. The results of a few tests in which sodium sulfite was added to the alkali solution were in close agreement with those of Kerr.

In view of the above results and the findings of Kerr, it appears that the prevailing idea regarding corrosion of tin by alkalies has been overemphasized. Although sodium hydroxide was considered so corrosive that it has been eliminated from most of the can washing compounds, its elimination has not appreciably decreased the corrosion rates of these compounds. The work of Levine and his associates (1927), Lowman et al. (1931), and Arnold and Levine (1942) indicated that sodium hydroxide exhibited more germicidal potency than any of the other alkalies. Therefore, it would seem that the use of a corrosion inhibitor, such as sodium sulfite, in alkali can cleaners would be beneficial not only in minimizing corrosion but also in permitting more effective use of the more germicidal alkalies.

**Summary**

1. An investigation was made to determine the relative corrosiveness of eight commercial alkaline cleaners, two commercial acid cleaners, and four basic alkalies on tin plate.
2. All of the commercial alkaline cleaners and basic alkalies readily attacked tin. The corrosion rates were within the so called "serious" range (near or above 100 milligrams per square decimeter per day). The two commercial acid cleaners did not appreciably attack tin during the time of exposure. These acid cleaners did cause localized corrosion of iron with the formation of pits.
3. A study of the corrosiveness of sodium hydroxide solutions through a wide concentration range revealed that concentration, except when very low, had relatively little effect on the corrosion of tin. The oxygen content of the alkali solution was found to be the primary factor affecting tin corrosion.
4. The alkalinity range, normally used in can washing (0.05 percent to 0.20 percent Na₂O, which is equivalent to 0.005 percent to 0.27 percent NaOH) fell within the sodium hydroxide concentration range where maximum corrosion occurred.
5. It seems logical from the results of this investigation that a satisfactory corrosion inhibitor, such as sodium sulfite, should be incorporated in alkaline can washing compounds. Such an inhibitor would not only minimize alkaline corrosion of milk cans but would also permit more effective utilization of the more germicidal alkalies in the cleaning compounds.

**Acknowledgments**

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**References**


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NEW YORK QUALIFICATIONS FOR SANITARIANS

Qualifications: The qualifications of assistant sanitarian, in addition to those prescribed for Grade I or Grade II dairy and milk inspector in section D of this chapter if such sanitarian performs the duties, respectively, of a Grade I or Grade II dairy and milk inspector, shall be:

(a) Graduation from a university or school of recognized standing with a degree in agriculture, veterinary medicine, or other branch of science, including successful completion of courses in chemistry, bacteriology, and biology, and two years of satisfactory experience in sanitation work related to milk, food or other phases of environmental sanitation; or,

(b) Graduation from a university or school of recognized standing with a bachelor’s degree, including successful completion of courses in chemistry, bacteriology, and biology, and four years of satisfactory experience in sanitation work related to milk, food or other phases of environmental sanitation; or,

(c) Any combination of education, experience and training which in the opinion of the public health council is the equivalent of either of the above qualifications.

Sanitary Inspector.

Duties: Environmental sanitation inspections of a subprofessional nature.

Qualifications: The qualifications of sanitary inspector, in addition to those prescribed for Grade III dairy and milk inspector in section D of this chapter if such sanitary inspector performs the duties of a Grade III dairy and milk inspector, shall be:

(a) Graduation from high school, including successful completion of courses in general science, mathematics and chemistry, and two years of satisfactory sanitary inspection experience; or,

(b) Six years of satisfactory sanitary inspection experience. Each year of a successfully completed high school or general college course shall be accepted in lieu of one year of satisfactory experience; provided, however, that in any case at least one year of satisfactory sanitary inspection experience is required; or,

(c) Any combination of education, experience and training which in the opinion of the public health council is the equivalent of either of the above qualifications.

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