NYWGF RESEARCH - FINAL REPORT

Funding for fiscal year: 2022-23

SECTION 1:

Project title: Anticorrosive food ingredients to address the challenges of "Hard-to-Hold" canned alcoholic beverages

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New Research ☒ **Continued Research** ☐

Amount Funded **$** 94953

SECTION 2: (This section should be in depth and akin to an academic report)

Project Summary Impact Statement: The packaging of wine in cans is limited in corrosion of the can by sulfur dioxide (SO_2) to form hydrogen sulfide (H_2S, "rotten egg" off-aroma) and, in extreme cases, can leakage and failure. This work evaluating the use of approved wine additives as anticorrosives to limit H_2S formation and other potential problems. Preliminary work demonstrated that certain approved additives (e.g. carboxymethylcellulose) could limit H_2S formation when wines were exposed to bare aluminum. However, similar improvements in performance were not observed for storage of treated wines in lined beverage cans, likely because the liner prevented the anticorrosive additive from reaching the metal surface. Ongoing work is exploring ways to allow passage of these anticorrosive ingredients to the metal surface. Preliminary results from the work were included in a successful multi-year USDA-AFRI award. These results are being delivered to winemakers and beverage can producers through peer-reviewed and trade publications.

Objectives:

Objective 1: Using unlined aluminum coupons stored in representative "Hard-to-Hold" beverages, screen food ingredients (n=12) for their anticorrosive activity.

Objective 2: Using anticorrosive additives (n=3) selected following completion Objective 1, evaluate the efficacy of anticorrosive additives during long-term can storage of wine and related "Hard-to-Hold" beverages

Materials & Methods:

For Objective 1, Initial Screening of Anticorrosive Ingredients

1) Test beverages: evaluations of potential corrosion inhibitors will use a representative "hard-to-hold" alcoholic beverages with
   a. High molecular SO_2, representative of a white table wine (12% ABV, pH 3, molecular SO_2 = 2 mg/L)
   b. High alcohol distilled spirit (40% ABV, pH 4.5 grape brandy).
   c. High chloride RTD cocktails (12% ABV, pH 3.5, chloride = 2000 mg/L).

2) Corrosion inhibitors: Nine putative corrosion inhibitors were evaluated (Table 1). The list was drawn from existing literature on carbohydrate-based corrosion inhibitors (Umoren and Eduok 2016), and supplemented with other compound classes with antioxidant activity and/or surface activity (polyphenols, polypeptides). For initial screening, potential inhibitors were tested at concentrations close to their solubility limits, up to a maximum of 3 g/L.

Table 1: Anticorrosive Additives in Initial Screening

Compound class	Additive for initial corrosion inhibition trials
Polyphenol	1) Condensed tannin (grape-derived) 2) Hydrolyzable tannin (oak-derived)
Polysaccharide	3) Carboxymethylcellulose (CMC) 4) Pectin 5) Gum Arabic 6) Chitosan 7) Carrageenan 8) Corn fiber
Polypeptide	9) Yeast mannoprotein

3) Corrosion trials: A recently validated method was used for accelerated aging tests. Briefly, de-aerated and aerated beverages w/ or w/o inhibitors will be stored in 20 mL amber vials in the presence of 5 cm x 1 cm coupons (3004 Al alloy). In initial experiments, only positive and negative controls (no inhibitor and no coupon, respectively) will be run to determine appropriate storage times (3 and 14 d at room temperature and 50 °C) to achieve measurable corrosion. If necessary, storage conditions can be extended to allow for sufficient corrosion to occur in the positive control. After appropriate conditions are determined, the experiments can be repeated with addition of corrosion inhibitors.

4) Corrosion characterization: The extent of corrosion was quantitated by measuring dissolved Al by ICP-AES in all beverages. In the wine samples, H_2S formation was measured by a previously described gas detection method.

5) Data evaluation – inhibition efficiency: Inhibition efficiency (%IE) will be calculated as the normalized decrease in weight loss. The effectiveness of putative inhibitors as compared to the control will be determined by appropriate statistical tests.

For Objective 2, Evaluation of Anticorrosives during Long-term Canned Storage

i) Test beverages: evaluations of potential corrosion inhibitors used the representative "hard-to-hold" alcoholic beverages described in Objective 1.

ii) Anticorrosives: From Objective 1, carboxymethylcellulose (CMC) was selected as the most promising of evaluated anticorrosives. Two other putative anticorrosives (potassium polyaspartate (KPA) and ascorbic acid) were also included.

iii) Storage experiments – long-term and accelerated aerobic and anaerobic: Long-term storage experiments were performed for each beverage × inhibitor combination using aluminum cans with two different BPA-NI can liners provided by our industry cooperator. Canning will take place using a manual seamer using previous validated protocols at Cornell. During canning, cans were air saturated (aerobic) or sparged with inert gas to limit oxygen pickup (anaerobic). Cans were be stored at room temperature and sampled at 8 and 32 weeks. All experimental treatment timepoints were performed in triplicate.

iv) Corrosion characterization and data evaluation: The extent of corrosion was quantitated by measuring dissolved Al by ICP-AES and H_2S formation by a previously described GDT method, as described in Objective 1. Inhibition efficiency (%IE) is calculated as the normalized decrease in either Al dissolution or H_2S formation.

Results/Outcomes/Next Steps:

Experiment 1, Results and Outcomes

- Three hard-to-hold beverages (wine, RTD, brandy) were incubated at elevated temperature (50 °C, 3 d) in the presence of an unlined aluminum coupon along with one of nine different putative anticorrosives. Control samples containing no anticorrosives were also included.
- As expected, the control showed high levels of corrosion following accelerated aging at elevated temperatures, as was evidenced by high dissolved aluminum (>1 mg/L), along with high H_2S production (> 50 µg/L).
- Certain anticorrosives decreased corrosion metrics (Figure 2), especially carboxymethylcellulose (CMC). For example, CMC showed an inhibition efficiency of up to 40% (i.e. a 40% decrease in H2S and dissolved aluminum as compared to control samples).
- Several other trialed anticorrosives showed significant effects for some but not all beverages, including chitosan and gum Arabic.
- Notably, all effective treatments were negatively charged polysaccharides, which presumably could interact with positively charged Al(III) to act as an anodic corrosion inhibitor.

Experiment 2, Results and Outcomes

- The same three hard-to-hold beverages from Experiment 1 were used and canned with one of three anticorrosives (CMC, ascorbic, KPA). A control was also included.

- All beverages started with negligible dissolved aluminum (<0.1 mg/L).
- After eight weeks room temperature storage, increases in dissolved aluminum were observed in all beverages, especially the wine (up to 2 mg/L).
- In contrast to results with aluminum coupons in Experiment 1, no anticorrosive effect was observed for any of the additives as compared to the control (Figure 3, left)
- We hypothesized that anticorrosives are ineffective in lined cans as compared to unlined coupons because anticorrosives are unable to reach aluminum surface to provide anticorrosive effect

- Next Steps: We are evaluating alternative approaches to utilizing anticorrosive ingredients, in which cans are first incubated with anticorrosives at elevated temperatures to allow them time to penetrate the liner. After this, we will evaluate the performance of these treated cans with hard-to-hold beverages.

Technology Transfer Plan: If a successful strategy to utilizing anticorrosive ingredients is identified, we will share results through trade- and peer-reviewed publications. We also have several can and liner industry collaborators, and will ask them to share the findings with their customers.

Attachments:

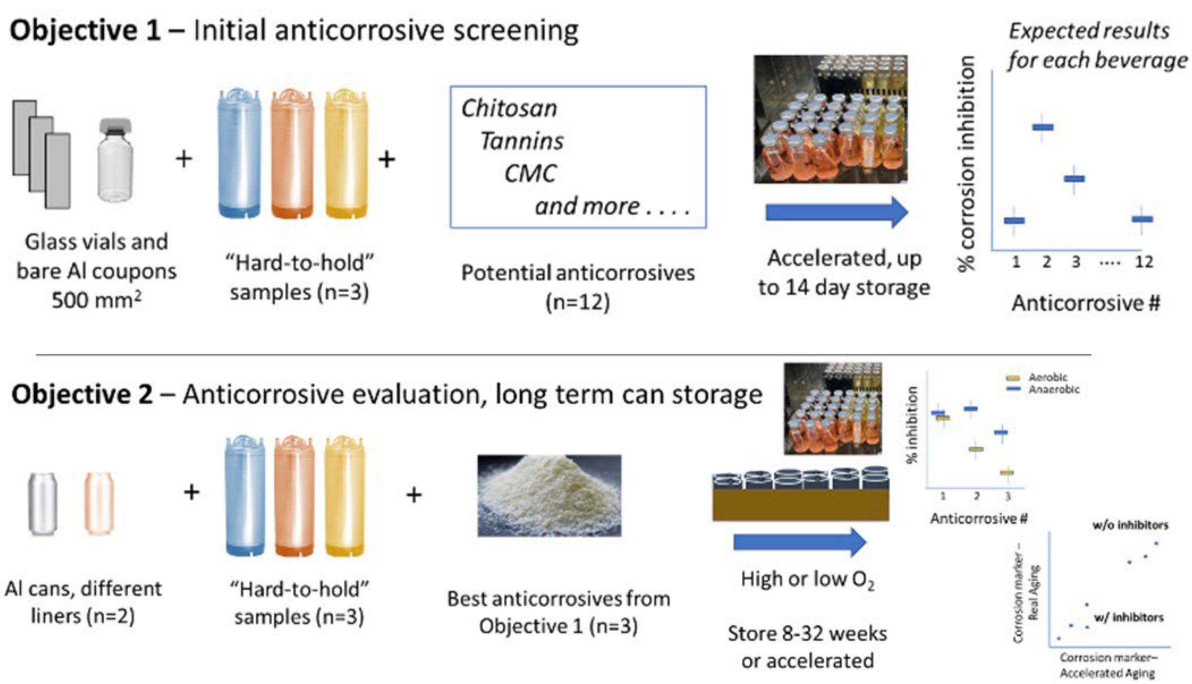

Figure 1 – Experimental design for objectives

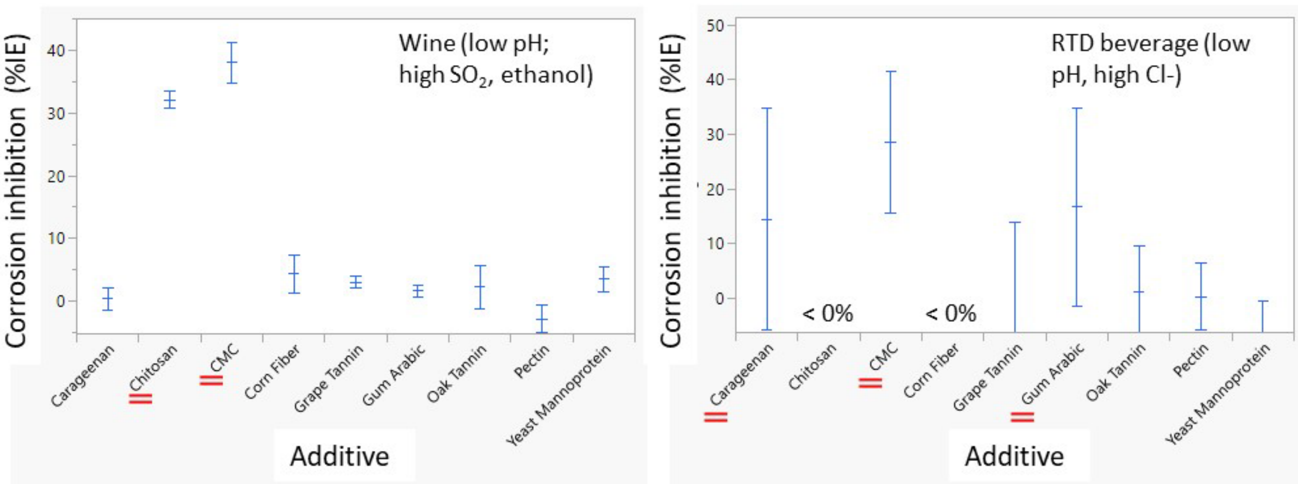

Figure 2 *– Experiment 1 results: Corrosion inhibition of different ingredients following accelerated storage of wine (left) or an RTD beverage (right) in the presence of an unlined aluminum coupon. Higher values of corrosion inhibition indicate a more effective inhibitor, e.g. 40% corrosion inhibition is equivalent to a H_2S (left) or dissolved Al (right) as compared to a control.*

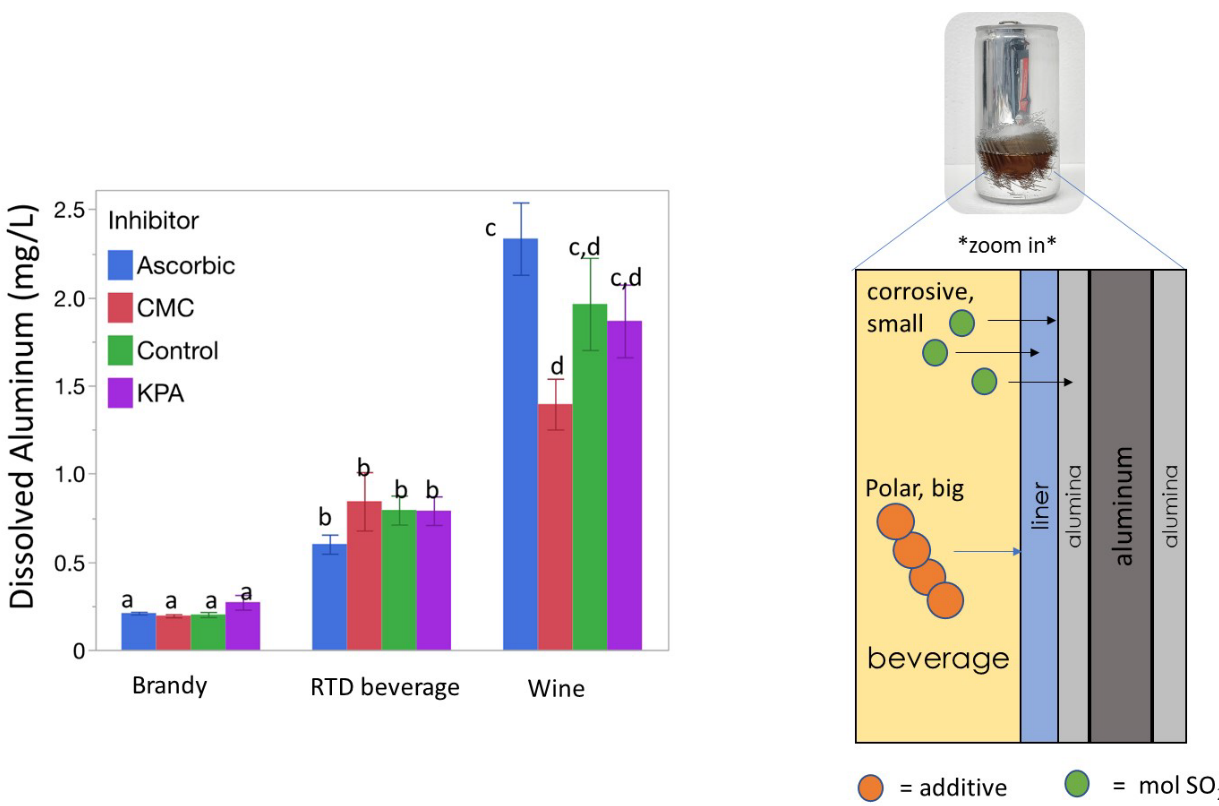

Figure 3 *– Experiment 2 results. (left) Dissolved aluminum after 2 months storage of beverages in lined cans is not affected by the presence of putative anticorrosives. (right) hypothesis for lack of impact of anticorrosives in lined cans as compared to unlined coupons. In lined cans, anticorrosives are unable to reach aluminum surface to provide anticorrosive effect.*

SECTION 3:

Project summary and objectives: Previous work by our group has shown that SO2 in wine may corrode aluminum beverage cans and form hydrogen sulfide (H_2S, “rotten egg” off-aroma), which limits the shelf-life of canned wine products. Several industries rely on anticorrosive additives to limit corrosion of aluminum components, but this concept has not been extended to wine or other beverages. In Objective 1, we screened several approved wine additives with reported or suspected anticorrosive activity. In Objective 2, we repeated these experiments with long-term storage trials in aluminum beverage cans, for which the most promising three additives were evaluated.

Importance of research to the NY wine industry: Although beverage cans continue to represent one of the fastest growing sectors of wine packaging, several producers in New York State and elsewhere have expressed hesitancy about adopting cans due concerns about off-aromas and shelf-life due to reaction of wine components and the can. Identifying approved wine additives with anticorrosive activity will provide a simple approach for winemakers to use cans while minimizing problems during storage.

Project Results/next steps: In Objective 1, a high SO_2 white wine was spiked with different additives prior to storage in the presence of bare aluminum. We observed that certain additives could limit H_2S formation. In Objective 2, we repeated these experiments with long-term storage trials of wine in aluminum beverage cans using three selected additives. No anticorrosive effect was observed under these conditions, likely because the liner prevented the anticorrosive additive from reaching the metal surface. However, these preliminary results from the work were included in a proposal that resulted in successful multi-year USDA-AFRI award. This newly funded work will allow our team to explore strategies to transport anticorrosive ingredients to the metal surface.