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# NOVEL VAPOR CORROSION INHIBITORS DERIVED FROM AGRI-PRODUCTS

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## ABSTRACT

The annual cost of corrosion in the United States alone is estimated to be greater than $300 billion. To combat this issue, approximately $121 billion per year are spent on methods to prevent and control corrosion. Of this total, $0.4 billion are spent on vapor corrosion inhibitors (VCI). New technologies and raw materials derived from renewable, biodegradable, and non-hazardous raw materials are of particular interest for use as VCI chemicals. As government policy continues to promote green alternatives to petrochemicals, the availability and utility of agricultural products and by-products will become economically advantageous.

The corrosion inhibitive properties of several agri-products were evaluated and screened for their corrosion inhibiting performance and to identify potential applications. The properties evaluated included contact- and vapor- corrosion inhibition, as well as the ability to provide protection against corrosive environments such as high acid concentration and salt solutions. Rust and scale removing properties were also explored. During these investigations, it was discovered that sugar beet molasses and raffinate demonstrated very good vapor corrosion inhibiting properties. The details of these findings and potential applications are reported herein.

Key Words: Molasses, Raffinate, Vapor Corrosion Inhibitor (VCI), Renewable, Biodegradable

## INTRODUCTION

The annual cost of corrosion in the United States alone is estimated to be greater than $300 billion. To combat this issue, approximately $121 billion per year are spent on methods to prevent and control corrosion.[1] Of this total, $0.4 billion are spent on vapor corrosion inhibitors (VCI). New technologies and raw materials derived from renewable, biodegradable, and non-hazardous raw materials are of particular interest for use as VCI chemicals. As government policy continues to promote green alternatives to petrochemicals, the availability and utility of agricultural products and by-products will become economically advantageous.

In an effort to prepare corrosion inhibitors using renewable and non-hazardous materials that are also biodegradable, a number of agriculture by-products have been evaluated for corrosion inhibitive properties. One particularly interesting by-product is found to be molasses and raffinate from sugar productions.

Molasses is the liquid residue after sucrose crystals have been harvested in sugar production from sugar beets or sugar cane[2]. When molasses is further processed to remove more sugar, it becomes raffinate. For the purpose of discussing vapor corrosion inhibition, the term molasses and raffinate are used interchangeably.

It has been reported that molasses and raffinate (de-sugared molasses) act as multimetal corrosion inhibitors when added to water based electrolytes.[3] This paper presents the results of investigation on whether molasses, raffinate and their fractions are able to provide corrosion inhibition in the vapor. The possibility of enhancing their vapor corrosion inhibition was also evaluated through distillation, cation exchange, ultra-filtration and reacting with common volatile nitrogen containing components such as ammonia or amines.

## EXPERIMENTAL PROCEDURES

### Materials

Sugar beet molasses and raffinate were of feedstock grade, obtained from American Crystal Sugar[(1)]. Samples of two food grade sugar cane molasses were also tested. They are 'Black Strap'[(2)](referred to as "Sample 1 food grade molasses" in the following text) and 'Full Flavor'[(3)](as: Sample 2 food grade molasses) from Brer Rabbit [(4)] brand.

ACS grade chemicals including: ammonium hydroxide solution (~30% in water), monoethanolamine, ethanol, and methanol were used in this study.

Vapor corrosion inhibition was evaluated on metal plugs made from steel SAE 1010[(5)].

(1) Trade name.
(2) Trade name.
(3) Trade name.
(4) Trade name.
(5) Society of Automotive Engineers.

## Distillation

Distillation was carried out on sugar beet raffinate to evaluate the possibility of concentrating corrosion inhibiting components through differences in volatility. Typically, the distillate collected had an apparent boiling point of 100°C. Up to 30% of the starting material was collected via distillation. The temperature of the pot residue was approximately 127°C when distillation was terminated. About 70% of starting material remained as pot residue.

## Cation Exchange

Cation exchange was performed with Dowex®[6] HCR-W2 H cation exchange resin from J.T. Baker. Before the test, the resin was washed with de-ionized water. The wet resin was added to a solution of 50% diluted raffinate. After decanting the resin, the pH of the solutions was adjusted to 9.8 with aqueous ammonia.

## Ultrafiltration

Ultrafiltration size fractionation was performed with a Stirred Ultrafiltration Cell Model 8400 (Millipore)[7]. Diluted raffinate (raffinate:water ratio 1:1) was subjected to sequential size fractionation using cellulose membranes with cutoffs in NMW of 30,000, 10,000, 3000, and 1000.

## Alcohol Precipitation

An alcohol mixture (ethanol:methanol 85:15 w/w) was added to a solution of 50% diluted raffinate. The weight ratio of alcohol:raffinate was 2.8:1. Precipitates were formed, separated from the supernatant by centrifugation, and later re-dissolved in de-ionized water.

## Chemical Treatment with Ammonia or Aminoalcohol.

Combination of molasses or raffinate with 20%, 10%, and 5% of ammonium hydroxide solution or 5% monoethanolamine were obtained.

## Vapor Inhibition Ability (VIA) Test

Molasses, raffinate and all obtained fractions and final products of the above described processes were evaluated for their vapor corrosion inhibiting ability. VIA tests were performed as follows. A sample of vapor inhibitor was placed for 20 hrs in proximity to a freshly polished and cleaned carbon steel plug in a capped jar at ambient temperature. Then a relative humidity of nearly 100% was created in the jar (via addition of 3% glycerol-deionized water solution to the bottom of the jar) for 2 hrs at ambient temperature. The whole assembly (Figure 1) was then brought to 40°C for another 2 hrs. After being exposed to near 100%RH at 40°C for 2 hrs, the surface of the steel plug was visually inspected relative to a 'control' steel plug which was from the jar without inhibitor sample. The test surface of the plug was graded from 0 to 3 depending on the amount of corrosion on the plug; 0 indicating the same amount of corrosion as on the 'Control' plug and 3 indicating no visible corrosion on the plug (Figure 2). Tests were run in triplicate. Grades 2 and 3 are considered passing.

(6) Trade name.
(7) Trade name.

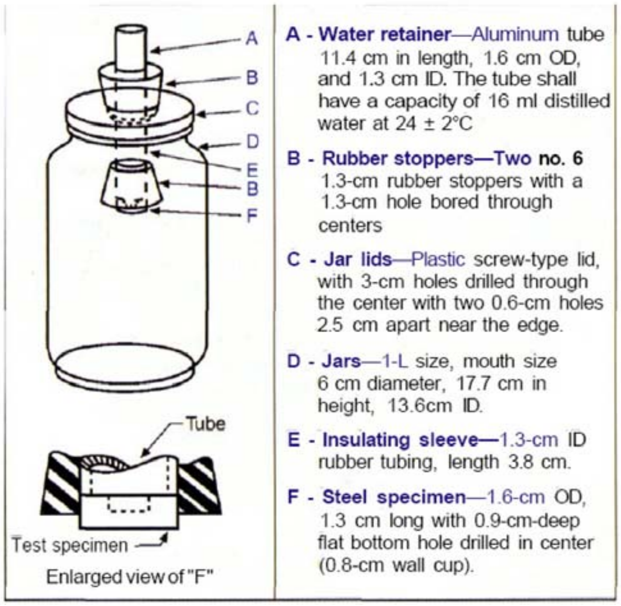


**FIGURE 1: VIA Test Assembly**

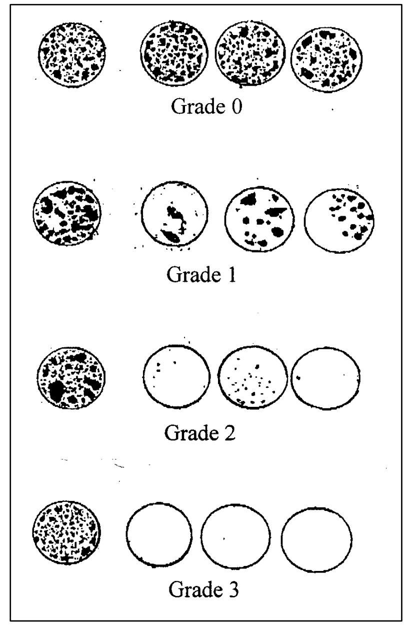


**FIGURE 2: VIA Plug Grading**

**Chemical Identification**

Identification of vapor corrosion inhibitors, the headspace of the jar containing molasses, was analyzed by SPME GC/MS. The analysis was done by piercing a hole in the jar cover and inserting a SPME fiber (PDMS/DVB) into the hole and exposing it for 30 min at ambient temperature. The resulting SPME fiber was then placed into the injection port of a GC column (GCMS: Hewlett Packard(3) 6890 GC with 5975 MSD; Column DB5MS 30m x 0.25mm x 1.0µm).The test was performed under the following conditions outlined in Table 1 below.

**TABLE 1**
**GCMS Test Parameters**

| | |
|---|---|
| Carrier Gas | Helium |
| Injection Temperature | 250 °C |
| Interface Temperature | 290 °C |
| GC Temperature Ramp | 10°C/3min; 10°C/min to 200°C/0 min; 40°C/min to 280°C/5 min |
| Mass Range Analyzer | 29-350 amu |

## RESULTS

Molasses and raffinate from sugar beet and from sugar cane were evaluated for vapor corrosion inhibition properties in as-received forms. All showed significant VCI ability (VIA grades 2-3) in as-received forms, Table 2. When sample size was reduced from 5 g to 2.5 g, there was a slight reduction in protection to the steel plug.

(8) Trade name.

Interestingly, less processed molasses showed better VCI property than the more processed molasses. For instance, feedstock sugar beet molasses showed better VCI than the Sample 1 food grade molasses, Figures 3 and 4, as well as Table 2. Similarly, less processed Sample 1 food grade molasses showed better VCI property than the more processed Sample 2 food grade molasses (picture not shown).

**TABLE 2**
**Plugs from VIA test on raffinate and molasses from sugar beet and sugar cane**

| Sample | Plug #1 | Plug #2 | Plug #3 |
|---|---|---|---|
| 5 g Sugar Beet raffinate | Grade 2 | Grade 3 | Grade 3 |
| 5 g Sugar Beet molasses | Grade 1/0 | Grade 3 | Grade 3 |
| 5 g (Sample 1 food grade molasses) | Grade 1/0 | Grade 2 | Grade2 |
| 5 g (Sample 2 food grade molasses) | Grade 2 | Grade 0 | Grade 0 |
| 2.5 g Sugar Beet raffinate | Grade 2 | Grade 2 | Grade 3 |
| 2.5 g Sugar Beet molasses | Grade 2 | Grade 2 | Grade 3 |
| Control | Grade 0 | - | - |

**FIGURE 3: Plugs after VIA test on sugar beet molasses as-received (5 g sample) vs Control Plug (Right)**

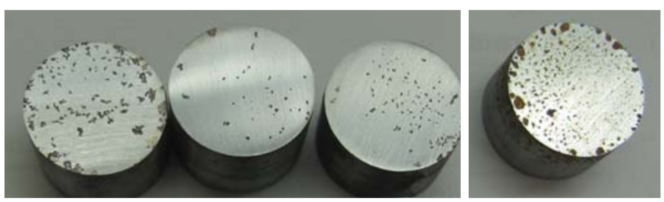

**FIGURE 4: Plugs after VIA test on sugar cane molasses as-received (5 g sample) vs Control Plug (Right)**

**Effect of Distillation of raffinate**

Surprisingly, both distillate and pot residue from the distillation of raffinate showed strong VCI property (Figure 5). 2.5 g of either distillate or pot residue showed better VCI property than 5g of the starting raffinate.

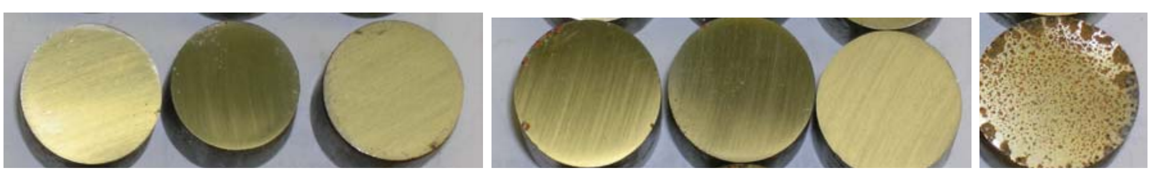

**FIGURE 5: Plugs after VIA test on distillate (left) and pot residue (center) of raffinate compared to control (right)**

**Effect of Ion Exchanging**

Ion exchange using a strong cation exchange resin showed that when potassium ions were removed, and replaced with ammonium, the resulting organic salts demonstrated VCI property (Table 3).

**TABLE 3**
**Plugs from VIA test on raffinate treated with cation exchange resin and neutralized with ammonia (equivalent of 0.3 g raffinate)**

| pH of raffinate treated with cation exchange resin* | Plug 1 | Plug 2 | Plug 3 |
|---|---|---|---|
| 1.94 | Grade 2 | Grade 2 | Grade 2 |

*pH was adjusted to 9.8 with aqueous ammonia prior to conducting VIA test

The cation exchange resin was in the acid form as-received (H+). The affinity of the resin for cations should be Ca ++ > K+ > $NH_4$+ > H+, so the resin should adsorb K+ ions from the raffinate preferentially and release H+ (thus dropping the pH)[4]. The ion-exchange test showed that VCI components in molasses and raffinate most likely existed as potassium salts of a number of organic acids.

**Ultrafiltration**

Ultrafiltration showed that those raffinate fractions of molecular weight (MW) between 1000 to 3000, and of MW above 30,000 demonstrated VCI properties (Table 4).

**TABLE 4**
**Plugs from VIA test on raffinate fractions of different MW (each liquid sample contained 0.5 g solids)**

| MW range of fraction | Plug 1 | Plug 2 | Plug 3 |
|---|---|---|---|
| <1000 | Grade 0 | Grade 0 | Grade 0 |
| 1000-3000 | Grade 3 | Grade 2 | Grade 2 |
| 3000-10000 | Grade 0 | Grade 0 | Grade 0 |
| 10000-30000 | Grade 0 | Grade 0 | Grade 1 |
| >30,000 | Grade 2 | Grade 2 | Grade 2 |
| Control (no raffinate fraction) | Grade 0 | | |

**Alcohol precipitation**

Dried fractions of precipitates and supernatant both demonstrated good VCI property (Table 5).

**TABLE 5**
**Plugs from VIA test on raffinate alcohol precipitation--precipitates and supernatant (0.5 g dried sample)**

| Raffinate fraction | Plug 1 | Plug 2 | Plug 3 |
|---|---|---|---|
| Alcohol precipitates | Grade 2 | Grade 2 | Grade 2 |
| Alcohol supernatant | Grade 2 | Grade 2 | Grade 2 |
| Control | Grade 0 | | |

**Chemical Treatment with Ammonia or Aminoalcohol**

It was found that addition of 5% ammonium hydroxide solution (approx. 1.5% ammonium hydroxide) or 5% of monoethanolamine enhanced the vapor corrosion inhibiting ability of the molasses (Table 6). Increasing the amount of added ammonium hydroxide solution up to 10% or 20% does not further improve the vapor corrosion inhibition of the resulting blend. It was found that ammonium hydroxide by itself showed almost no VCI effect  It was noted that 1g of enhanced molasses (blended with ammonia hydroxide) (Figure 6) showed better VCI protection than 5g of as-received molasses (Figure 3).

The same effect is observed with addition of 5% ammonium hydroxide solution to sugar cane molasses. 1g of enhanced sugar cane molasses (Figure 7) demonstrated better VCI property than 5g of untreated Sample 1 food grade molasses (Figure 4).

**TABLE 6**
**Plugs from VIA test on ammonia/amine-treated molasses**

| Sample | Plug #1 | Plug #2 | Plug #3 |
|---|---|---|---|
| Sugar beet molasses w/ 1.5 % $NH_4OH$ (1g) | 3 | 3 | 3 |
| Sugar beet molasses w/ 5 % Monoethanolamine (1g) | 3 | 3 | 3 |
| (Sample 1 food grade molasses) w/ 1.5 % $NH_4OH$ (1g) | 3 | 3 | 3 |
| Aqueous $NH_4OH$ (0.25g) | 0 | 0 | 0 |
| Control | 0 | 0 | 0 |


**FIGURE 6. Plugs from VIA test of enhanced sugar beet molasses (1g sample) (Top row: sugar beet molasses with 1.5% $NH_4OH$, Middle row: sugar beet molasses with 5% monoethanolamine, Bottom row: $NH_4OH$ only.  The right most plugs are from the control)**

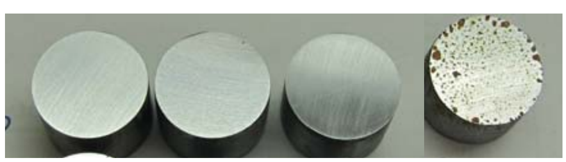

**FIGURE 7. Plugs from VIA test of enhanced sugar cane molasses (1g sample) treated with 1.5% $NH_4OH$**

It is possible that when aqueous ammonia ($NH_4OH$) was added to molasses or raffinate, ammonium salts were formed. Since ammonium salts of weak organic acids generally dissociate less than potassium salts, and are more volatile, the addition of ammonia thus enhances the VCI property of molasses or raffinate. The same reasoning stands for the enhanced VCI ability of molasses or raffinate by addition of simple amines.

## DISCUSSION

Compounds identified by GC/MS analysis included a number of organic acids, ketones, aldehydes, pyrazines, alcohols, alkenes, pyrrolidinones, lactones, and furanones. SPME GC/MS analysis of the volatile portion (which included vapor corrosion inhibitors) of molasses showed generally the same groups of molecules. Some of the identified components match those found in the aroma analysis of molasses,[5] such as furan and its derivative.

It is a known fact that vapor corrosion inhibition is mostly provided by the salts of weak volatile acids and weak volatile bases.[6] Molasses and raffinate appear to be a good source of such materials. The compounds responsible for volatile inhibition were apparent in both low molecular weight range and in high molecular weight range. Chemical reaction, or substitution of cations with amine/ammonia, positively affects vapor corrosion inhibiting ability of molasses and raffinate.

## CONCLUSION

Feedstock sugar beet molasses and raffinate are compelling raw materials for use as vapor corrosion inhibitors (VCI). Furthermore, the addition of ammonium hydroxide or volatile amine can greatly enhance the VCI property of these compounds. The fact that molasses and raffinate possess significant vapor corrosion inhibition enables the possibility of using these non-hazardous, renewable and biodegradable agricultural by-products as major components in a variety of corrosion inhibitor applications.

## ACKNOWLEDGEMENTS
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