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**NOVEL CORROSION INHIBITORS DERIVED FROM AGRICULTURAL BY-PRODUCTS:
POTENTIAL APPLICATIONS IN WATER TREATMENT**

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ABSTRACT

The corrosion inhibitive properties of biodegradable, and non-hazardous corn-based by-products were evaluated and screened to identify potential applications. The properties evaluated included contact- and vapor-phase corrosion inhibition, as well as the ability to act as a barrier against corrosive environments such as high acid concentration and salt solutions. Rust and scale removing properties were also tested. During these investigations, it was discovered that a solvent extract from dried distilled grains with solubles (DDGS) demonstrated very good corrosion protection properties for steel in acidic environments. A variety of plant extracts have been shown to inhibit corrosion of steel in acidic conditions, but such activity has not previously been demonstrated with corn extracts. Aqueous corn extracts also proved to provide corrosion protection when used as an inhibitor in de-icing compounds. The details of these findings and potential applications are reported herein.

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 Some of the techniques implemented include: material selection, cathodic protection, protective coatings, and corrosion inhibitors.

In a search to find new technologies for the aforementioned techniques, products that are made from renewable, biodegradable, and non-hazardous raw materials have become of particular interest due to a growing consciousness of environmental concerns. As government policy continues to promote green alternatives to petrochemicals, the availability and utility of agricultural by-products will become economically advantageous. The results reported herein demonstrate the use of agricultural by-products as potential corrosion inhibitors.

The materials chosen for this study were corn derived by-products from ethanol production. The by-products evaluated include thin stillage, thick stillage, and dried distilled grains with solubles (DDGS). Thin stillage is the resultant material left behind in still bottoms after the fermentation process is complete and the ethanol has been removed. Further reduction in moisture content results in thick stillage. DDGS are co-products of ethanol production which are nutrient rich solids containing the protein, fiber and oils remaining after starch and sorghum have been removed during the ethanol process. For this reason, DDGS are commonly used as livestock feed. One third of the grain that goes into ethanol production comes out as DDGS.²

Each of these materials is solid or semi-solid at room temperature and testing was generally done through liquid extraction. The thick pasty texture, tendency to phase separate, and high moisture content of the stillage samples resulted in the need for precautionary measures to prevent spoilage and were therefore more difficult to handle. As a result, the DDGS were used for most of the experiments. Furthermore, the DDGS are an attractive raw material as they contain all the basic components found in stillage, with the addition of other insoluble materials, representing the broadest composition, but also the most complex.

The corrosion inhibitive properties of the corn-based by-products were evaluated and screened to identify potential applications. The properties evaluated included contact- and vapor-phase corrosion inhibition, as well as the ability to act as a barrier against corrosive environments such as high acid concentration and salt solutions. Rust and scale removing properties were also tested. During these investigations, it was discovered that a solvent extract from DDGS demonstrated very good corrosion protection properties for steel in acidic environments. A variety of plant extracts have been shown to inhibit corrosion of steel in acidic conditions, but such activity has not previously been demonstrated with corn extracts.³⁻⁹ Aqueous corn extracts also proved to provide corrosion protection when used as an inhibitor in de-icing compounds. The details of these findings and potential applications are reported herein.

EXPERIMENTAL PROCEDURES

DDGS are of solid, grain-like consistencies that were found to be insoluble in most conventional solvents. Therefore, liquid extractions were carried out in order to obtain a convenient material to work with. Both solvent extraction and aqueous extractions were found useful in isolating corrosion inhibitive compounds with unique properties. Due to the

insolubility of the starting material a Soxhlet extraction was carried out in an effort to extract as much soluble content as possible. To these ends, a highly polar solvent, ethyl acetate, was chosen as the extracting medium. Approximately 40 grams of DDGS were placed inside the thimble and extracted overnight into 250 mL of ethyl acetate. Removal of the solvent under reduced pressure gave yield to an amber colored viscous oil in low yield (20%). The oil was subjected to acidic solutions and the corrosion preventative properties evaluated according to a modified ASTM G31^{(1),10} immersion corrosion testing. 200 mL of 10% hydrochloric acid, sulfuric acid, phosphoric acid and 20% citric acid were added to individual 8 ounce glass jars. To the acid solution, 2 grams (2%) of the amber oil were added. Carbon steel coupons (SAE 1010) were cleaned and their initial mass recorded. The cleaned coupons were immersed within the acidic solutions and maintained at room temperature. After 24 hours, the coupons were removed from the solution, immediately rinsed with water, cleaned and dried. The mass of the cleaned coupons was recorded and the mass lost calculated.

To determine the protection afforded by the solvent extract in salt water solutions the following test was conducted. Two jars were filled with synthetic seawater. To one sample of seawater, 0.5% w/w of the solvent extract was added. A second sample of seawater was used as a control. The extract was found to be immiscible with seawater and therefore phase separation occurred forming an oily layer on the top of the solution. Carbon steel coupons (SAE 1010)⁽²⁾ were immersed in the two test solutions. The contents were agitated continuously throughout in order to distribute the extract throughout the solution and expose the surface of the metal to the extract. After being immersed for 48 hours, the coupons were removed from the solution, cleaned and visually inspected for corrosion.

In addition to solvent extractions, DDGS were also subjected to aqueous extraction techniques. Examples in the literature suggest that corn proteins show increased solubility at higher pH levels.¹¹ To this effect, an aqueous extraction was performed with water treated with ammonium hydroxide. A ratio of one part DDGS, four parts water, and one part ammonium hydroxide (30%) was found to function well as the extractant. Alternately, for the extraction of thick stillage, a ratio of 2 parts stillage, 2 parts water and 1 part ammonium hydroxide was implemented as the extractant. The DDGS were soaked in the extractant media and incubated for forty hours at 80° C and the resultant slurry filtered. To increase yield, the filtrate was pressed with mechanical force to extract any remaining solubles. The non-volatile content of the aqueous extract was determined to be 11%.

The aqueous extract was tested to evaluate its potential use as a deicing compound. Evaluation included freezing point determination and analysis of the corrosion inhibiting properties through PNS¹²⁻¹⁵ testing. Sample formulations were first screened to determine the freezing point. A minimum of -35°C was required to be considered as a potential candidate for corrosion testing, or PNS testing. Various formulations containing ethylene glycol, propylene glycol, calcium chloride (CaCl₂), water, and aqueous extract were screened. Freezing point determination was conducted in the following manner. Liquid samples (100 mL) were placed in steel pint cans and placed in a temperature controlled chamber at -40°C. The samples were exposed for 24 hours and then visually examined for signs of freezing. If the sample froze at -40°C the temperature was adjusted and the process repeated until the freezing point was determined. The minimum temperature in which the sample did not freeze was recorded.

⁽¹⁾ American Standard Test Method

⁽²⁾ Society of Automotive Engineers

Sample formulations which exceeded the minimum freezing point requirements were further subjected to PNS testing. Carbon steel (UNS G10100) coupons were cleaned, dimensionally measured and their mass recorded. Test solutions were prepared at 3% in de-ionized water. Two control samples, one 3% sodium chloride solution and one deionized water, were also prepared. Metal coupons were hung from an automatic PNS testing apparatus (Figure 1) and introduced into the test solutions for ten minutes per hour. The total test duration was 72 hours. At the conclusion of the test, the coupons were disassembled, immediately washed with water and placed into an acid-based cleaning solution. After cleansing, the coupons were rinsed with deionized water, dried and their final mass recorded. The mass lost was calculated and the corrosion rate determined.

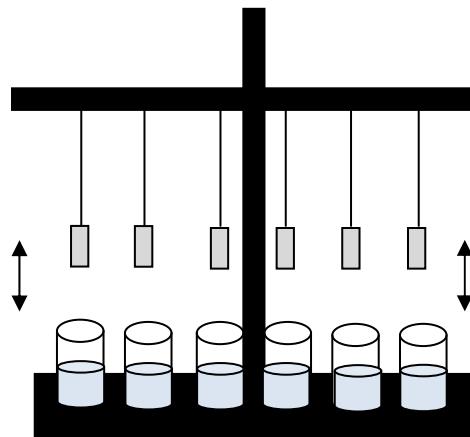


FIGURE 1: Schematic representation of the automatic PNS testing apparatus

To gain insight to the chemical composition, the aqueous and solvent extracts were analyzed using gas chromatography mass spectroscopy (GCMS), liquid chromatography mass spectroscopy (LCMS) and Fourier-Transform infrared spectroscopy (FTIR). The test parameters used for the gas chromatography analysis are detailed in Table 1. The solvent extract was dissolved 1:1 with acetone and subjected to GCMS analysis. Similarly, the aqueous extract was dissolved in dichloromethane and the solvent layer was utilized for analysis. The LCMS sample preparation was conducted in the same manner.

TABLE 1. GCMS Conditions

GCMS	HP5890 GC with HP5970 MSD
Column	DB5MS 30m x 0.25mm x 0.25 µm
Carrier gas	Helium
Injection mode	Split
Injection temperature	290 °C
Interface temperature	310 °C
GC temperature ramp	10°C/3min; 10°C/min to 200°C/0 min; 40°C/min to 280°C/5min
Mass range	29-550 amu

TABLE 2. LCMS Conditions

Column	Prodigy C8 5u, 150mm x 3.2mm x5μm
Solvent A	H ₂ O
Solvent B	Acetonitrile
Flow	0.5 mL/min
Column temperature	Ambient
Injection amount	10 μL
Gradient	10% B to 90% B in 30 minutes, hold 90% for 2 minutes
LCMS modes	Electrospray (ES) + and – Atmospheric pressure chemical ionization (APCI) + and -
Drying gas, N ₂	8 L/min
Drying gas temperature	300°C
Nebulizer pressure	40 psig
Capillary voltage	4000 V (ES) 3000 V (APCI)
Vaporizor	350°C (APCI)
Corona	4 μA (APCI)
Fragmentor	100
Gain	3
Scan range	100-1350 amu
LCMS method	Scout.m (APCI) Scoutes.m (ES)

FTIR spectroscopy was conducted on both the solvent and aqueous extracts in liquid phase using a Perkin Elmer Paragon 1000 FTIR spectrometer. The solvent extract was analyzed neat on a KBr disc. The aqueous extract was dissolved in dichloromethane and the solvent layer was cast onto a KBr disc.

RESULTS

Acid Immersion Test

The corrosion protection afforded by the solvent extract in the presence of acidic solutions was determined based on the mass loss of the metal coupons and the corresponding corrosion rates. The corrosion rate in mils per year (MPY) was calculated according to Equation 1; where W equals the mass lost reported to the nearest 0.001 g, A corresponds to the area of the metal coupon to the nearest 0.1 cm², T is the exposure time recorded to the nearest 0.1 hour, and D represents the metal density (7.85 g/cc for steel). The percent corrosion protection afforded was determined according to Equation 2; where C_c represents the corrosion rate without inhibitor and C_i the corrosion rate with inhibitor. The results are reported in Table 3 below.

$$\text{Corrosion Rate (MPY)} = \frac{3.45 \times 10^6 * W}{A * T * D} \quad (\text{Equation 1})$$

$$Z = \frac{(C_c - C_i)}{C_c} \times 100$$

(Equation 2)

TABLE 3. Protection of steel from acid corrosion by DDGS solvent extract

Acid	Acid concentration	Z (% Corrosion protection)
Hydrochloric	10%	97%
Sulfuric	10%	95%
Phosphoric	10%	90.9%
Citric	20%	87.7%

Salt Water Immersion Test

The protection afforded by the solvent extract in salt water solution is demonstrated in Figures 2 and 3. Figure 2 shows the coupons immediately after removal from the test solution. The coupon on the left displays the film forming properties of the solvent extract. This viscous yellow film acts as an air, moisture and salt barrier protecting the coupon from salt water attack and corrosion. This film, however, was easily removed using conventional detergent. Figure 3 illustrates the results after the coupon has been cleaned showing no corrosion on the surface. As displayed in Figure 2, the Control sample was found to have a lot of corrosion on the surface.

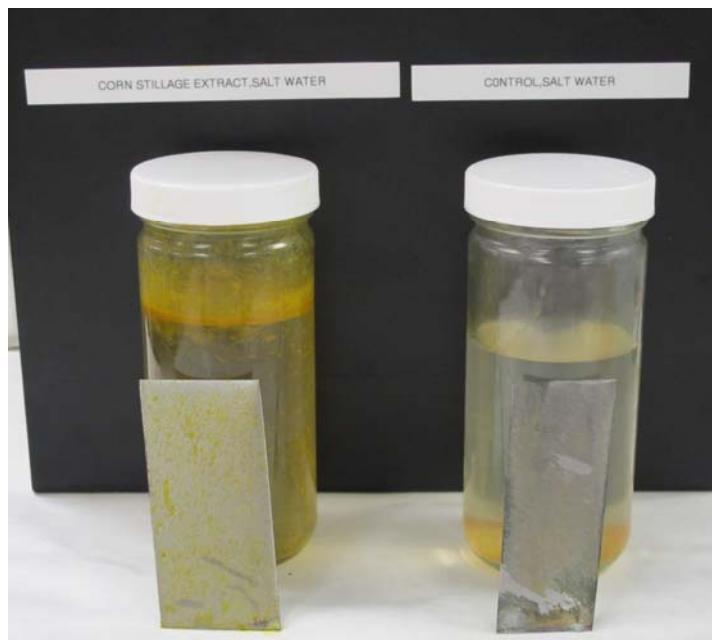


FIGURE 2. Test coupons after removal from salt water immersion test.



FIGURE 3. Solvent extract coupon after cleaning.

DEICER TESTING

The results of the deicer and PNS testing are outlined in Table 4 below. The corrosion rate in mils per year, MPY, was calculated according to Equation 3 where Δm equals the mass lost, A represents the area of the metal coupon, t is exposure time, and the density of the metal represented by ρ . The density used for carbon steel was 7.85 g/cc. A standard correction accounting for the corrosion rate of deionized water (0.42 MPY) was taken into effect. In order for a product to be acceptable the product must be at least 70% less corrosive than standard sodium chloride solution. The effectiveness of the test solutions were compared to sodium chloride and reported as % NaCl corrosion rate.

$$\text{MPY} = \frac{\Delta m * 534}{A * t * \rho} \quad (\text{Equation 3})$$

TABLE 4. Deicer Test Results

Sample #	Composition	Pass/Fail (PNS test)	Corrosion Rate MPY (PNS test)	% NaCl Corrosion Rate	Freezing point (°C)
1	50% Propylene Glycol + 25% Aqueous Extract + 25% Water	Pass	1.73	3.3	-35
2	50% Propylene glycol + 25% Extract from Thick Stillage + 25% Water	Pass	0.07	0.13	-35
3	24% CaCl ₂ + 20% Aqueous Extract + 56% Water	Pass	18.56	29.6	-35
4	NaCl		62.61		
5	Deionized water		0.42		

GAS AND LIQUID CHROMATOGRAPHY

Gas and liquid chromatography results showed that the chemical make up of both the solvent and aqueous extracts are very similar. Due to the complexity in the GCMS and LCMS data, the specific molecular basis of corrosion inhibition could not be established. Some of the major components detected include: long chain fatty acids, C-16 and C-18 specifically, ethyl esters, butanediol, tocopherol, ergost-5-en-ol, sigmast-5-en-3-ol, methoxy propanol, and ethoxy ethanol, amongst a large number of minor peaks.

FTIR SPECTROSCOPY

The FTIR spectra are shown in Figure 4. The spectra are dominated by peaks characteristic of corn oil. However, the peak at 1711 cm⁻¹ is indicative of a carboxylic acid, possibly fatty acid. The broad peak at 3359 cm⁻¹ is indicative of a small amount of hydrogen bonded water or possibly polyols (e.g. glycerol or budantediol).

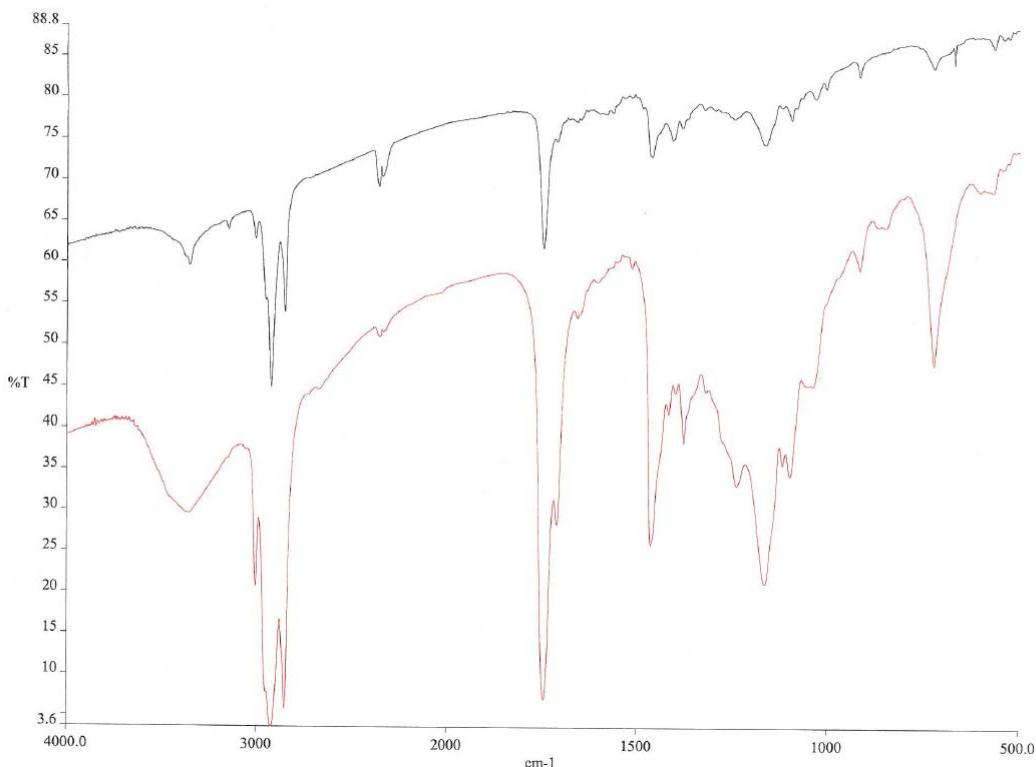


FIGURE 4. FTIR spectrum of solvent extract (red) and aqueous extract (black)

CONCLUSIONS

Potential applications for the use of the isolated extracts include corrosion prevention in acidic and/or salt water solutions such as a component in deicing compounds. The deicing studies revealed several potential formulations which meet the freezing point requirements. Although, the extract doesn't drastically alter the freezing point in comparison to traditional propylene glycol based deicers it does result in increased corrosion protection. Commercially available propylene-glycol based deicing fluids report corrosion rates of 2 to 20 MPY on carbon steel;⁴ meanwhile, the examples displayed offer protection rates as low as 0.07 mils per year.

It was also discovered that the oil extracted from the DDGS forms a tenacious film on metal surfaces which lends itself very well for applications as a float coat. Seawater causes severe corrosion of steel and its alloys. In many cases corrosion protection of metals in seawater is provided by permanent coatings, which can be very costly and labor intensive. A more economical way to prevent corrosion of large metal vessels containing seawater; such as: holding tanks, ballast tanks, off-shore structures, etc, is the use of "float coats." Float coats are typically oil based rust preventatives which demonstrate a high affinity to metal surfaces and are immiscible with water, thereby forming a protective oily film on the metal surface which inhibits corrosion. Any extra rust preventative in the vessel "floats" on the liquid/vapor interface providing additional corrosion protection by replenishment of the film adsorbed on the metal; and to some degree, insulating the water-based electrolyte from air and oxygen.

When used as a float coat, the solvent extract has the following advantages. It does not dry out, harden, or crack after prolonged use. It can be easily removed when necessary using conventional detergents and is very economical to use. The oil extract is bio-based and likely

biodegradable and it doesn't pose a problem for discharge into ground or surface water; however, the maximum concentration for discharge will need to be verified through testing by the EPA laboratory.

Extracts derived from corn-based by-products from ethanol production show promise for use as corrosion inhibitors for the protection of steel in aggressive conditions. As anticipated, the isolated extracts exhibit a complex mix of a large number of organic and inorganic compounds. For this reason, the applied analytical techniques were of limited success in linking specific compounds to the observed corrosion inhibiting properties.

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