

# A SUSTAINABLE APPROACH TO IMPROVEMENT OF CORROSION PROTECTION COATINGS FOR STEEL STRUCTURES

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## ABSTRACT

Corrosion is a primary factor compromising the safety and service life of steel structures. Corrosion protection coatings are generally employed for protection of the steel structures that are exposed to different aggressive environments. This research evaluated the use of biobased ion exchangers as a sustainable means of improving corrosion protection coatings.

Two base polymer coatings (vinyl and coal-tar epoxy) were considered. The following types and dosages of biobased ion exchangers were evaluated in these coatings: (i) strong-base ion exchange cellulose in OH, PO<sub>4</sub>, SiO<sub>3</sub>, BO<sub>3</sub>, NO<sub>2</sub>, SO<sub>4</sub> and NO<sub>3</sub> forms at 1% by weight of resin; (ii) weak-acid starch citrate ion exchanger in H form at 1 wt.%; and (iii) strong-base ion exchange cellulose in OH form at 2 wt.%. In addition, a strong-base ion exchange resin in OH form was considered at 1 and 2 wt.% as control. Different coating formulations were evaluated based on the outcomes of salt-fog corrosion, moisture resistance, pull-off strength, and abrasion resistance tests. The introduction of certain biobased ion exchangers in protective coatings was found to be an effective means of achieving improved levels of corrosion resistance, adhesion capacity, moisture stability and abrasion resistance.

## KEYWORDS

Biobased ion exchanger, Protective coatings, Corrosion resistance, Sustainability, Moisture stability, Adhesion capacity, Abrasion resistance

## INTRODUCTION

### Preface

The cost burden associated with corrosion of metals is ~3.4% of the global GDP.<sup>1</sup> Use of protective coatings is a common approach to mitigating corrosion of steel structures. The global markets for protective coatings are approaching \$50 billion.<sup>2</sup> There are, however, limits on the extent of protection against corrosion provided by coatings. Their effectiveness can diminish over time due to a host of factors, including deterioration of coatings under environmental, erosive and other

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<sup>1</sup> <http://impact.nace.org/economic-impact.aspx>

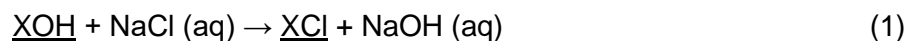
<sup>2</sup> <https://www.grandviewresearch.com/press-release/global-protective-coatings-market>

damaging effects. The work presented here seeks to develop an economical and sustainable approach to improvement of corrosion protection coatings. This approach employs biobased ion exchangers derived from different sources, emphasizing agricultural residues which are abundantly available (320 million tons/yr in the United States) and are generally of limited monetary value. Applications in protective coatings can consume close to 300,000 tons/yr of biobased ion exchangers [1-3]. The corrosion inhibitors currently used in protective coatings could pose environmental hazards; they are costly (few thousand dollars per ton) and are made using exhaustible raw materials.

Many byproducts of agricultural crop processing have native ion-exchange attributes provided by their constituent polymers (especially cellulose). Cost-effective strategies involving chemical modification and crosslinking have been developed to enhance the ion-exchange capacity and physical stability of ion exchangers derived from crop residues [1]. These biobased ion exchangers provide a desired balance of performance, cost and sustainability attributes. They could be used in polymer-based protective coatings to remove aggressive ions from corrosive solutions as they diffuse through coatings towards metallic surfaces.

Corrosion, as an electrochemical reaction, requires the presence of an electrolyte. Pure water, unlike solutions (which incorporate ions), is a poor electrolyte. Certain ions (e.g.,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) not only form electrolytes but also stimulate corrosion reactions [4]. This investigation used biobased ion exchangers in protective coatings with the objective of removing such aggressive ions as well as their counter-ions from the solutions diffusing through the coating towards steel surfaces, thereby abating both the electrolyte and the corrosion stimulants.

Ion exchangers are insoluble solid materials which carry exchangeable cations or anions [5,6]. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution. Ion exchangers comprise a framework with electric surplus charge together with mobile counter-ions. Carriers of exchangeable cations and anions are called cation exchangers and anion exchangers, respectively. A typical anion exchange is:



The resulting  $\text{NaOH}$  can be removed from the solution through a typical cation exchange:



where, X is a structural unit of the anion and cation exchangers ( $\underline{\text{XOH}}$  and  $\underline{\text{XH}}$ , respectively), (aq) indicates that the electrolyte is in aqueous solution, and solid phases are underlined.

Insoluble cation and anion exchangers of particular forms are used commonly to substantially deionize salt solutions. Ion exchangers of petrochemical, mineral and plant origins are used in water purification.

## Basic Principles

Fine anion and cation exchangers ( $\text{XOH}$  and  $\text{XH}$ ) were incorporated into protective coatings in order to remove soluble corrosive salts (anions and cations) from the diffusing solutions (Fig. 1). The ion-exchange process was used in this approach to diminish the electrolyte, and to render the corrosive solutions innocuous as they diffuse into the coating towards the metal surfaces. The example of Fig. 1 depicts the ion-exchange effects which essentially remove  $\text{NaCl}$  from the salt solution as it diffuses through the coating (by converting  $\text{NaCl}$  to  $\text{H}_2\text{O}$ ). Removal of  $\text{Na}^+$  and  $\text{Cl}^-$  ions from the solution diminishes the electrolyte, and mitigates the corrosive effects of chloride ions.

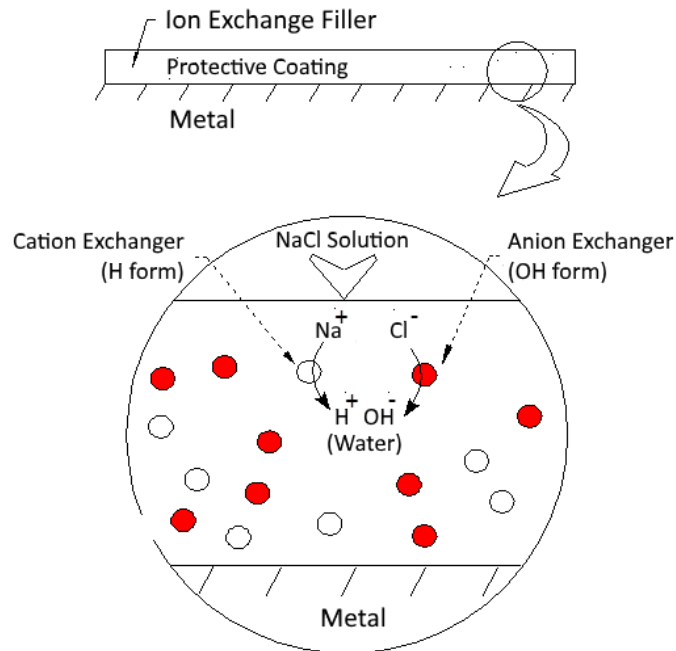


Fig. 1 - Schematic depiction of the approach.

Ion exchange occurs because the ion exchanger prefers one species to the other. The preference for one species may have several reasons. The most important are [5-8]: (i) electrostatic interactions between the charged framework and counter-ions depend on the size and, in particular, the valence of the counter-ion; and (ii) large counter-ions may be sterically excluded from the narrow pores of ion exchanger. These and other factors lead to preferential uptake of certain species by the ion exchanger. The ability of ion exchanger to distinguish between various counter-ion species is called *selectivity*. In the case of a cation exchanger, for example, the selectivity sequence  $K^+ > NH_4^+ > Na^+ > H^+$  implies that the cation exchanger in hydrogen ( $H^+$ ) form can exchange the  $K^+$ ,  $NH_4^+$  and  $Na^+$  cations.

## Different Types of Ion Exchangers

Ion exchangers are available in resin, plant (cellulose, starch, etc.) and mineral forms. The general structural principle (i.e., a framework with electric surplus charge and mobile counter-ions) is common to all ion exchangers. Nevertheless, various types of ion exchanger show marked differences in behavior.

Ion exchange *resins* in the form of crosslinked polyelectrolytes are in common use [5-9]. The matrix of these polymers is hydrophobic; hydrophilic components are introduced by the incorporation of ionic groups such as  $-SO_3^-H^+$ . Ion-exchange resins are made insoluble by introduction of crosslinks which interconnect the various hydrocarbon chains; an ion-exchange resin particle is practically one single macromolecule. The ion-exchange behavior as well as the chemical, thermal and mechanical stability of different ion-exchange resins depend mainly on the structure and the degree of crosslinking of matrix, and also on the nature and number of fixed ionic groups. The most common polymer matrix used today is based on crosslinked polystyrene. Sulfonated copolymers of styrene and divinylbenzene are some commonly used ion exchangers. Cation-exchange resins are subdivided into strong-acid and weak-acid groups; similarly, anion-exchange resins are divided into strong-base and weak-base materials. Different ion-exchange resins generally provide 1-10 meq/g capacity for ion exchange.

Biobased ion exchangers are produced by attaching substitute groups with basic or acidic properties to plant-based (cellulose, starch, etc.) molecules [10]. Their ion-exchange properties are similar to those of ion-exchange resins. Biobased ion exchangers, however, are generally finer with greater specific surface area. Their porous structure provides for a higher rate of exchange, and allows for entrance and attachment of large molecules that are not readily adsorbed in ion-exchange resins [7-9]. The cellulose used for production of biobased ion exchangers is commonly derived from wood and cotton. Biobased ion exchangers can also be produced via chemical modification and crosslinking of agricultural residues such as corn stalk, sugar beet pulp, soybean hull and wheat straw [11,12].

The following considerations provide the rationale for use of biobased ion exchangers in lieu of ion-exchange resin in corrosion protection coatings: (i) many biobased ion exchangers, when compared with ion-exchange resins, offer higher rates of exchange and greater accessibility for diverse categories of ions; (ii) the commonly higher fineness of biobased ion exchangers favors their use as filler in polymer coatings; (iii) application in protective coatings does not involve regeneration; the favorable regeneration qualities of ion-exchange resins are thus irrelevant in this application; (iv) the cost of biobased ion exchangers is an order of magnitude less than that of ion-exchange resins; and (v) agricultural residues, which are available in tremendous quantities and are generally of limited monetary value, can be used as raw materials for production of biobased ion exchangers.

### Ion-Exchange Celluloses

The biobased ion exchangers used in this investigation were: (i) a strong-base anion exchange cellulose (Whatman® from Millipore Sigma) in OH<sup>-</sup>, PO<sub>4</sub><sup>-</sup>, SiO<sub>3</sub><sup>-</sup>, BO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> forms; (ii) a weak-acid cation exchange starch (starch citrate in H<sup>+</sup> form); and (iii) a strong-base anion exchange cellulose (Whatman® from Millipore Sigma). In addition, a strong-base anion exchange resin in OH<sup>-</sup> form (Dowex Marathon MSA from DOW Chemical) was used as control.

The biobased anion exchangers were received in Cl<sup>-</sup> form, and were converted into other ionic forms to provide them with the capability to render corrosion protection effect by exchanging the diffusing Cl<sup>-</sup> ions with innocuous anions. All biobased ion exchangers were dried in an oven at 55°C for 18 hours, and then subjected to size reduction via ball-milling. For this purpose, a ceramic jar was used together with ceramic balls, and the biobased ion exchangers were milled to 6-9 μm



particle size.

Fig. 2 shows an example biobased ion exchanger used in protective coatings.



*Fig. 2 - An example biobased ion exchanger (anion-exchange cellulose in  $\text{SO}_3^-$  form) after ball milling.*

### Formulation of Protective Coatings

Two different coating formulations based on vinyl and coal-tar epoxy were used in this investigation. Strong-base and weak-acid biobased ion exchangers of different ionic forms were incorporated into these polymer matrices as corrosion inhibitors.

Vinyl resins are used to formulate high-efficiency anti-corrosion coatings due to their good physicochemical characteristics (chemical resistance, and desired barrier qualities against water and oxygen). Vinyl resins modified with maleic acid can be applied directly on steel surfaces because acid groups improve adhesion. Tricresyl phosphate was employed as a plasticizer at a resin: plasticizer weight ratio of 4:1. The long-chain copolymer of vinyl consolidates into a film which is resistant to water, weathering, immersion, acids, alkalis, and many other chemicals. The vinyl-based resin used in this investigation (Trade Name: UCAR-Solution Vinyl Resin supplied by Union Carbide) can be applied without a primer. Tricresyl Phosphate (Trade Name: Tritolyl Phosphate, Tec 90% mixture of isomers - Sigma Aldrich) was used as plasticizer at 25% by weight of resin to make the vinyl resin flexible.

Coal-tar epoxies, with coal tar used as filler, rely upon barrier qualities against moisture movement for protection of steel against corrosion. They provide desired adhesion capacity, and can be applied directly on roughened (e.g., sandblasted) steel surfaces. The coal tar filler provides for improved moisture resistance without undermining the toughness, adhesion capacity, UV resistance and thermal stability of epoxy. The desired alkali resistance of epoxies benefits their performance under seawater exposure. Cathodic protection is another favorable attribute of epoxy resin; the high dielectric strength of these coatings contributes insulating qualities which prevent the electrochemical flow that drives the corrosion process.

The biobased ion exchangers and the control ion-exchange resin introduced earlier were used as corrosion inhibitors. Ferric (Iron III) oxide (<5 micron particle size, 99+% supplied by Sigma Aldrich) and barium sulfate (98% supplied by Sigma Aldrich) were also used in the coating composition. Isobutylketone (4-methyl-2-pentanone, 99+%), xylene (xylene isomers plus ethylbenzene), and butyl acetate (99.5+% A.C.S. reagent), supplied by Sigma Aldrich, were used as solvent at 10:20:70 weight ratios.

The composition of the vinyl-based corrosion protection coatings considered in this investigation are presented in Tab. 1. The compositions of the coal-tar epoxy Parts A and B are presented in

Tab. 2. The protective coating formulations with (or without) ion exchangers considered in the experimental program are introduced in Tab. 3.

Tab. 1 - Compositions of vinyl-based corrosion protection coatings.

Constituent	Weight%
Ferric Oxide	19
Barium Sulfate	19
Vinyl Resin	50
Tricresyl phosphate	12

Tab. 2 - Composition of the corrosion protection coating based on coal-tar epoxy.

(a) Part A

Material	Trade Name	Manufacturer/Supplier	Weight%
Coal-tar	Coal-tar.	Alpha Aesar	35.5
Versamid	VERSAMID 100PMX60	Palmer Holland,	24.4
Nyral 300	Nyral 300 Industrial Talc	R.T. Vandorbilt Company, Inc,	24.8
CAB-O Lite M-5	CAB-O SIL M-5	Cabot Corporation	5.90
Aluminum Stearate	Aluminum Stearate, Technical Grade	Alpha Aesar	0.80
Xylol	o-xylene, HPLC Grade, 96%	Alpha Aesar	8.60

(b) Part B

Material	Trade Name	Manufacturer/Supplier	Weight%
Epoxy Araldite 471x75	Araldite GZ 471X-75, Xylene Solution	Vantico, Inc	46.3
Butanol	1-Butanol, A.C.S., 99.4+%	Alpha Aesar	11.5
Cellosolve Acetate	2-Ethoxyethyl acetate, 98%	Sigma Aldrich	7.70
Xylol	o-xylene, HPLC Grade, 96%	Alpha Aesar	34.5

Tab. 3 - The protective coating formulations considered in the experimental program.

Polymer	Ion Exchanger	Specimen #	Ion Exchanger Weight% (Form)
Vinyl	None	VR-0	0
	Starch citrate cation exchanger (H <sup>+</sup> form)	VRCAH-1	1 (H <sup>+</sup> )
	Strong-base anion exchange cellulose	VRCBOH-1	1 (OH <sup>-</sup> )
		VRCBOH-2	2 (OH <sup>-</sup> )
		VRCBSIO3-1	1 (SiO <sub>3</sub> <sup>-</sup> )
		VRCBPO4-1	1 (PO <sub>4</sub> <sup>-</sup> )
		VRCBBO3-1	1 (BO <sub>3</sub> <sup>-</sup> )
		VRCBSO4-1	1 (SO <sub>4</sub> <sup>-</sup> )
		VRCBNO2-1	1 (in NO <sub>2</sub> <sup>-</sup> )
		VRCBNO3-1	1 (in NO <sub>3</sub> <sup>-</sup> )
	Strong-base anion exchange resin	VRRBOH-1	1 (OH <sup>-</sup> )
VRRBOH-2		2 (OH <sup>-</sup> )	
Coal-tar Epoxy	None	CT-0	0
	Starch citrate cation exchanger (H <sup>+</sup> form)	CTCAH-1	1 (H <sup>+</sup> )
	Strong-base anion exchange cellulose	CTCBOH-1	1 (OH <sup>-</sup> )
		CTCBOH-2	2 (OH <sup>-</sup> )
		CTCBSIO3-1	1 (SiO <sub>3</sub> <sup>-</sup> )
CTCBPO4-1		1 (PO <sub>4</sub> <sup>-</sup> )	

	Strong-base anion exchange resin	CTCBBO3-1	1 (in $\text{BO}_3^-$ )
		CTCBSO4-1	1 ( $\text{SO}_4^-$ )
		CTCBNO2-1	1 (in $\text{NO}_2^-$ )
		CTCBNO3-1	1 (in $\text{NO}_3^-$ )
		CTRBOH-1	1 ( $\text{OH}^-$ )
		CTRBOH-2	2 ( $\text{OH}^-$ )

### Preparation of Protective Coatings

The vinyl-based coating was prepared in a laboratory-scale porcelain jar ball mill with 3 liters volume, operated at 60 revolutions per minute with a ceramic ball-to-material weight ratio of 10: 1. These conditions were selected to produce a homogenous end product. The vinyl resin (150 g) was added to the ball mill, and milled for 2 hours. The remaining constituents of the formulation, except for tricresyl phosphate, were then added to the ball mill, and milled for 24 hours. The product was transferred to a laboratory-scale planetary mixer, the tricresyl phosphate constituent was added, and mixed for 10 minutes. Solvents were then added as needed (150 ml initially, and more added if required) to produce the required viscosity, and mixed for 20 minutes. The end product was left for 24 hours to ensure homogeneity, and then applied.

Coatings based on coal-tar epoxy were mixed for 20 minutes in a planetary mixer with polyamide and the remaining constituents of Part A of the formulation. Part B of the formulation was then added, and mixing was continued for 20 more minutes.

### Selection, Preparation and Coating of Steel Substrates

ASTM A 1008–CS Type B steel (Cold Rolled) was obtained from Heidtman Steel Products, Inc. This is a low-carbon matte finish steel that is suitable for application of paints and enamels. Its yield and tensile strengths are 38,000, and 52,000 psi, respectively. The steel was cut into 76.2mm x 127mm (3in x 5 in) pieces. Edges were rounded, and corners were made smooth. The steel surfaces were vigorously rubbed using clean lint-less cloth wet with mineral spirits until all soluble and loosely adhering particles removed. The surfaces were then flushed with clean solvent, and dried at 52 to 93°C (125 to 200°F) before use or storage (ASTM D 609 Procedure D). Fig. 3a shows examples of the resulting substrate that are ready for application of protective coatings.

Protective coatings were applied following ASTM C823 Procedure B, using a dip coater that withdraws test specimens from a container of the coating material at a constant rate. The coating thickness after withdrawal was measured per ASTM D1005 (Fig. 3b). The withdrawal rate was adjusted to yield the targeted coating thickness (measured at three different locations).



(a) A substrate prepare for coating (b) Withdrawal of substrate from the coating mix

Fig. 3 - Example substrate and the coating process.

## Test Methods

The pull-off strength of protective coatings was measured following the ASTM D4541 and ASTM B117 procedures using the test setup shown in Fig. 4a. Abrasion resistance was evaluated using the ASTM D968 procedures (Fig. 4b). Salt fog corrosion tests (Fig. 4c) were performed on scribed (Fig. 4c) or non-scribed tests per ASTM D1654 (Fig. 4d). The exposure period was 1944 hours. Loss of adhesion at the scribe mark for scribed specimens, and blistering associated with corrosion for non-scribed specimens (as well as other failure conditions) were evaluated per ASTM D1654 and ASTM D714, respectively. In the case of the scribed specimens, corrosion rating was based on the extension of paint loss from the scribe mark, with ratings of 10 and 0 assigned to cases with 0 mm (0 in) and 13 mm (5/8 in) scribe extension, respectively. The non-scribed specimens were dried with paper towel, and their surfaces were evaluated for detection of corrosion spots, blisters and any other types of failure. When the character of failure permitted, photographic blister standards (ASTM D714) were used to describe the results with respect to the size of blisters or corroded areas. Moisture resistance tests were performed for evaluating the stability of protective coatings when immersed in water (Fig. 4e). Specimens were immersed in water at 27°C, and were evaluated for any indication of degradation, including color change, blistering and loss of adhesion.

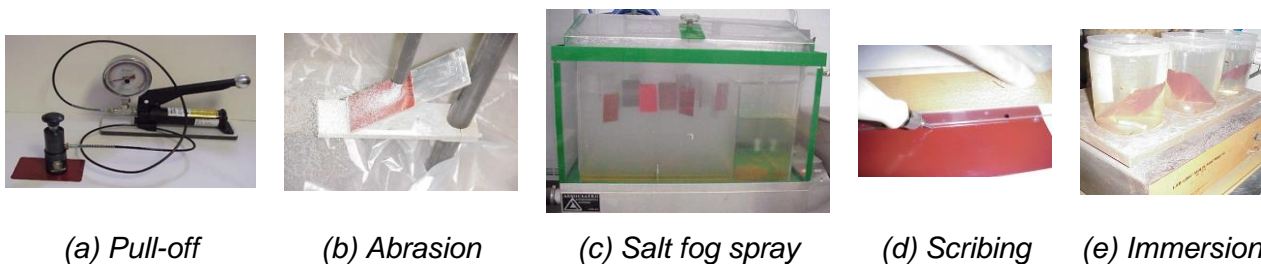


Fig. 4 - Test setups.

## RESULTS

### Pull-Off Strength

Failure in pull-off tests generally occurred at the coating-substrate interface for vinyl coatings (Fig. 5a), and through the coating thickness for coal-tar epoxy coatings (Fig. 5b). Four replicated pull-off tests were performed with each coating formulation. The pull-off strength test results are presented in Fig. 6. The pull-off strengths of coatings based on coal-tar epoxy are observed to be smaller than those based on vinyl. Given the differences in failure modes of these two coating systems (Fig. 5), however, the lower pull-off strength of coatings based on coal-tar epoxy does not necessarily point at their lower adhesion capacity. The pull-off strength test results for vinyl coatings indicate that different biobased ion exchangers can either decrease or increase the pull-off strength; the effects are moderate to small. The highest pull-off strength of vinyl-based coatings was obtained with the addition of 1 wt.% strong-base anion exchange cellulose in OH<sup>-</sup> form. The addition of strong-base anion exchange resin at 2 wt.%, on the other hand, produced the lowest pull-off strength for vinyl-based coatings. The effects of biobased ion exchangers on the pull-off strength of the coal-tar epoxy coating were moderate to small. Addition of strong-base anion exchange cellulose in NO<sub>3</sub><sup>-</sup> form at 1 wt.% produced a slight rise in the pull-off strength of coal-tar epoxy. The lowest pull-off strength for coatings based on coal-tar epoxy was obtained with the addition of strong-base anion exchange resin in OH<sup>-</sup> form at 1 wt.%. This drop was the only statistically significant change (at 5% level of significance) in pull-off strength of the coal-tar epoxy coatings resulting from the addition of ion exchangers.



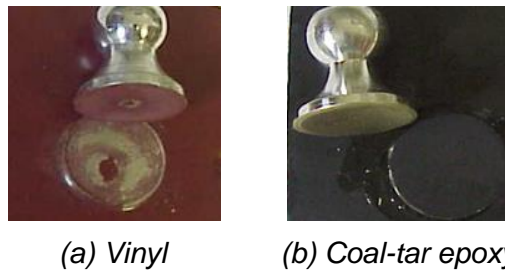


Fig. 5 - Typical failure modes in pull-off tests.

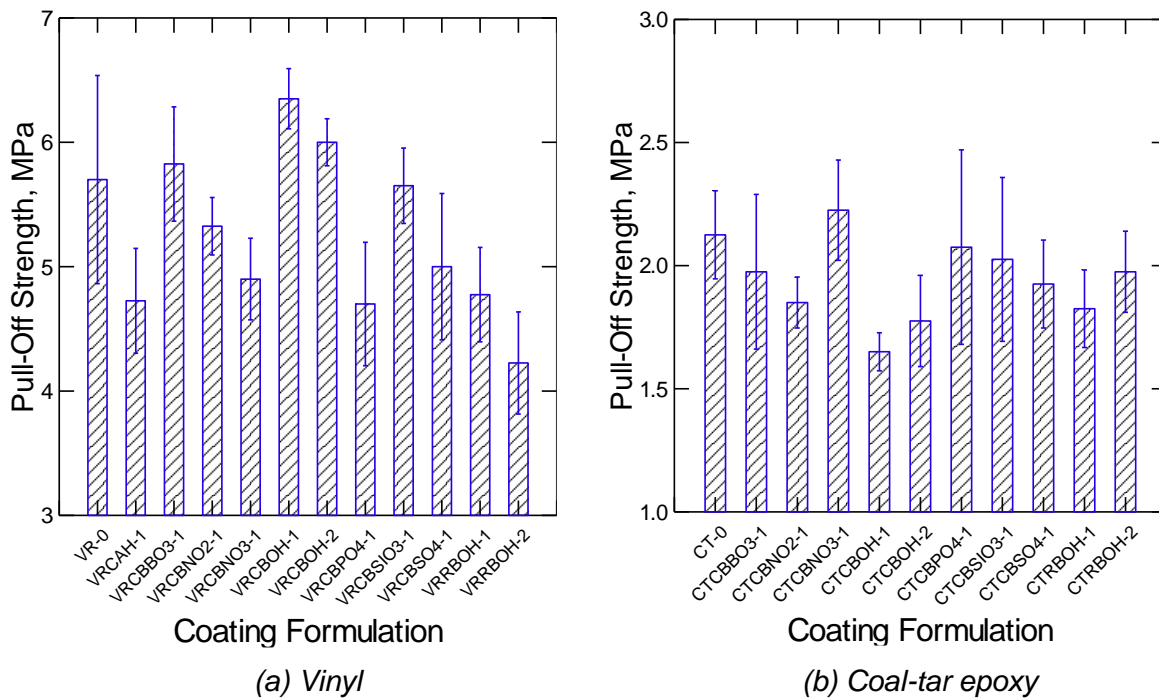


Fig. 6 - Pull-off strength test results (means & standard errors).

## Abrasion Resistance

Four replicated abrasion tests performed for each coating; the test results are presented in Fig. 7. Vinyl-based coatings are observed to provide relatively high levels of abrasion resistance when compared with the coatings based on coal-tar epoxy. There was a statistically significant improvement (at 5% level of significance) of the abrasion resistance of vinyl-based coatings with the addition of 1 wt.% strong-base ion-exchange cellulose in  $\text{NO}_3^-$  form. The effects of most bio-based ion exchangers on the abrasion resistance of the vinyl-based coating were not statistically significant. Only the anion exchange resin (at 1 and 2 wt.%) and the cation exchange starch citrate (at 1 wt.%) had statistically significant adverse effects (at 5% level of significance) on the abrasion resistance of the vinyl-based coating. In the case of coatings based on coal-tar epoxy, addition of 1 wt.% strong-base ion-exchange cellulose in  $\text{NO}_3^-$  form or 1 wt.% anion exchange resin in  $\text{OH}^-$  form produced statistically significant (at 5% level of significance) improvements in abrasion resistance.

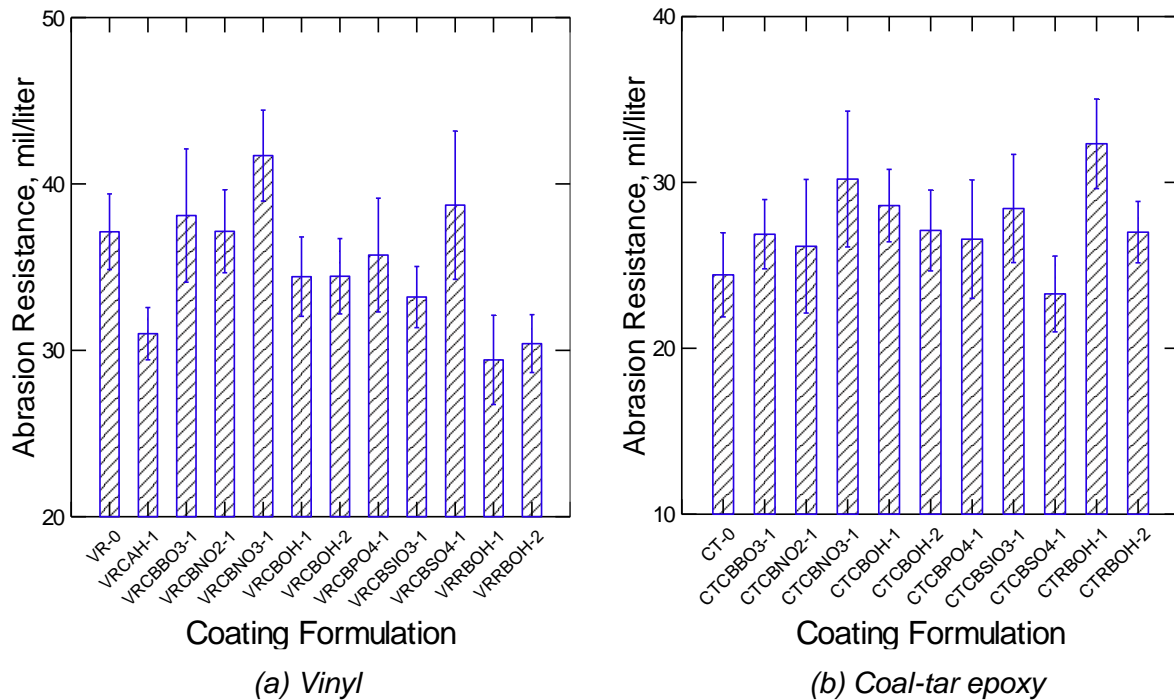


Fig. 7 - Abrasion resistance test results (means & standard errors)

## Salt Fog Corrosion Resistance

### Scribed Specimens

Examples of scribed specimens with modified coatings based on vinyl and coal tar epoxy after exposure to salt fog are presented in Fig. 8. Results of three replicated salt fog corrosion tests performed on scribed specimens with each coating formulation are presented in Fig. 9. In the case of formulations based on vinyl, most ion-exchange celluloses at the dosages considered (1 or 2 wt.%) did not produce notable (statistically significant at 5% level of significance) changes in the salt fog corrosion resistance rating. Introduction of the ion-exchange resin considered here (in  $\text{OH}^-$  form at 1 and 2 wt.%) as well as Starch citrate cation exchanger in  $\text{H}^+$  form at 1 wt.%, on the other hand, compromised the salt fog corrosion resistance rating of the vinyl-based coating. In the case of coating formulations based on coal-tar epoxy, introduction of anion-exchange cellulose in  $\text{NO}_3^-$  form at 1 wt.% and anion-exchange resin in  $\text{OH}^-$  form at 2 wt.% produced notable (statistically significant at 5% level of significance) improvements in the salt fog corrosion resistance rating.



(a) Vinyl coating with 1 wt.% anion exchange cellulose in  $\text{PO}_4^-$  form



(b) Vinyl coating with 1 wt.% anion exchange cellulose in  $\text{NO}_3^-$  form



(c) Coal tar epoxy coating with 1 wt.% anion exchange cellulose in  $SO_4^-$  form

(d) Coal tar epoxy coating with 1 wt.% anion exchange cellulose in  $NO_3^-$  form

Fig. 8 - Examples of scribed specimens after salt fog exposure.

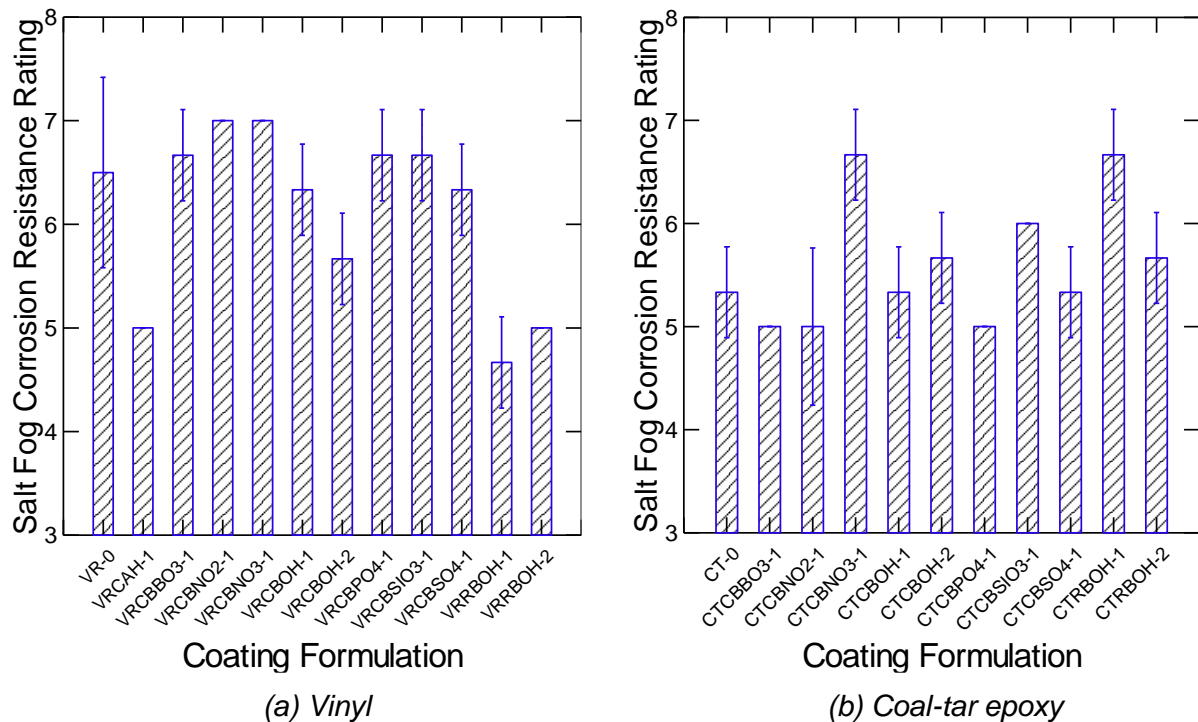


Fig. 9 - Salt fog corrosion test results for scribed specimens (means and standard errors).

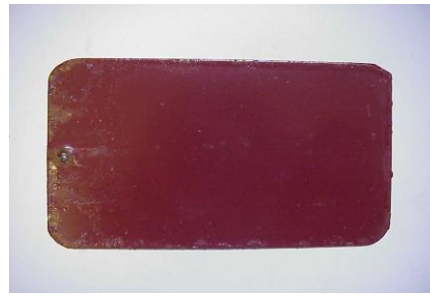
### Non-Scribed Specimens

Examples of non-scribed specimens after completion of the salt fog corrosion exposure period are presented in Fig. 10. In an effort to quantify the test data, the following ratings were assigned to the density of blistering: Few = 1; Medium = 2; Medium Dense = 3; Dense = 4. The blistering level was then defined as the multiplication of the degree and the density of blistering. Fig. 11 presents the blistering level of non-scribed test specimens after completion of the salt fog corrosion period for non-scribed specimens with different coating formulations. As far as the vinyl coatings applied to non-scribed specimens are concerned, the addition of 1 wt.% anion exchange cellulose in  $SiO_3^-$  form and 2% anion exchange cellulose in  $OH^-$  form produced notable and statistically significant reductions in blistering level. The effects of other ion exchange celluloses and resin on the blistering level of non-scribed specimens with vinyl coating were not statistically

significant. In the case of coal tar epoxy-based coatings, addition of 1 wt.% anion exchange cellulose in  $PO_4^-$  form produced notable and statistically significant (at 5% level of significance) reduction in blistering level. The effects of other ion exchange celluloses and ion exchange resin on the blistering level of non-scribed specimens with coal tar epoxy coating were not statistically significant.



(a) Vinyl coating with 1 wt.% anion exchange cellulose in  $PO_4^-$  form



(b) Vinyl coating with 1 wt.% anion exchange cellulose in  $NO_3^-$  form



(c) Coal tar epoxy coating without ion exchanger



(d) Coal tar epoxy coating with anion exchange cellulose in  $NO_3^-$  form

Fig. 10 - Examples of non-scribed specimens after conclusion of the salt fog corrosion exposure period.

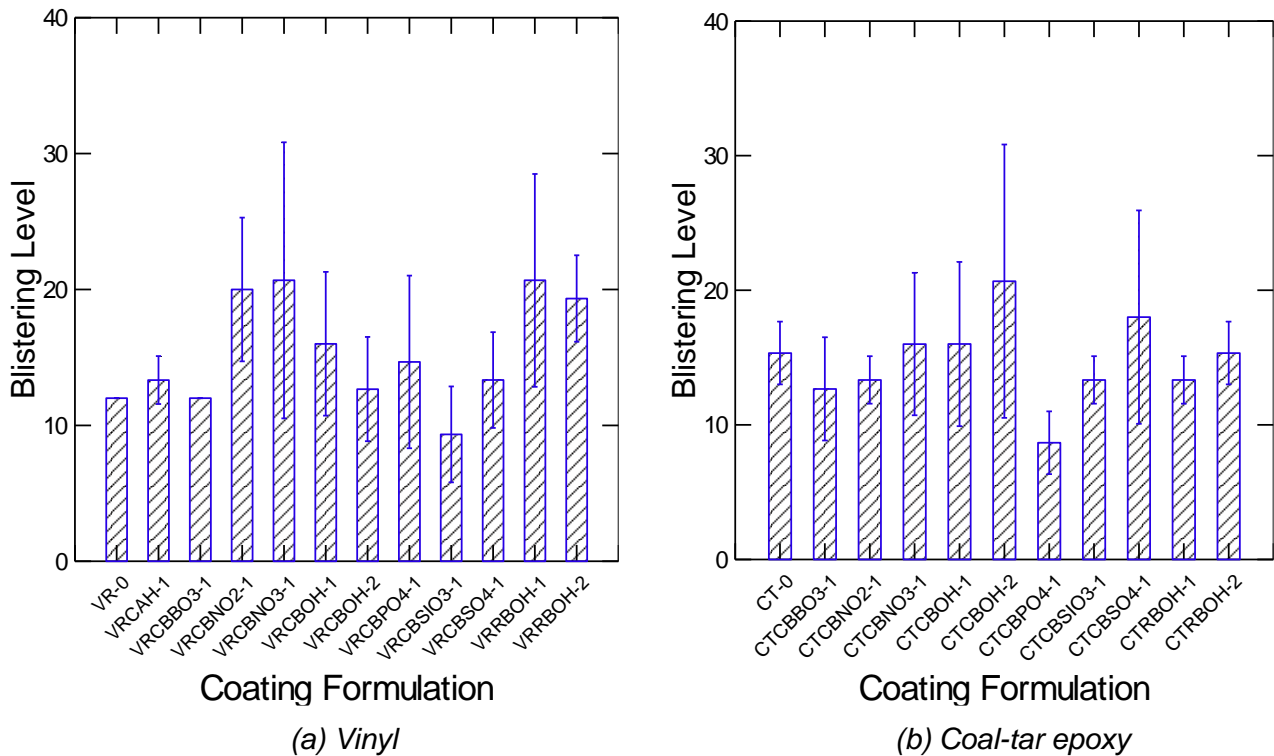
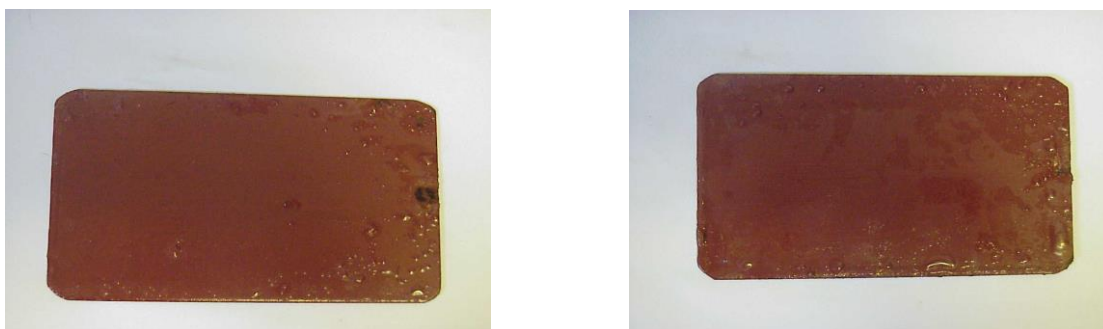


Fig. 11 - Blistering levels (means and standard errors) of non-scribed specimens with different coating formulations after completion of the salt fog corrosion exposure period.

### Moisture Resistance

The extent of damage reflecting on moisture resistance is expressed as the change in color, degree of blistering, or loss of adhesion of the coating. Figure 12 shows examples of vinyl-based coating with different ion exchange celluloses after immersion in water for 81 days. The moisture resistance test results are summarized in

Tab. 4. The moisture resistance of coatings based on vinyl and coal tar epoxy generally benefited from the introduction of biobased ion exchangers. For example, 1 wt.% anion exchange celluloses in  $\text{NO}_3^-$  and  $\text{SiO}_3^-$  forms improved the moisture resistance of vinyl and coal-tar epoxy coatings, respectively.



(a) 1% ion-exchange cellulose in  $\text{SiO}_3$  form (b) 1% ion-exchange cellulose in  $\text{NO}_3$  form

Figure 12. Examples of specimens with vinyl-based coatings incorporating different ion-exchange celluloses after 81 days of immersion.

Tab. 4 - Moisture resistance test results.

Coating Formulation	Color Change	Loss of adhesion	Degree of Blistering
VR-0	No	~25% of surface area lost adhesion	8-Medium Dense
VRCBOH-1	Yes	No	6-Medium Dense
VRCBOH-2	Yes	No	8-Medium
VRCBSIO3-1	Yes	~10% of surface area lost adhesion	8-Medium
VRCBNO3-1	Yes	No	8-Few
VRCBNO2-1	Yes	No	6-Medium
VRRBOH-2	Yes	No	6-Medium Dense
CT-0	Yes	No	4-Dense
CTCBOH-1	Yes	No	6-Medium Dense
CTCBSIO3-1	Yes	No	4-Medium Dense
CTCBNO2-1	Yes	No	8-Few
CTCBNO3-1	Yes	No	6-Medium
CTRBOH-2	Yes	No	4-Dense

The effects of ion exchange celluloses on various aspects of the protective coating performance strongly depends on their type. Statistically significant gains in the abrasion, salt fog corrosion and moisture resistance were realized by the addition of ion exchange cellulose in NO<sub>3</sub><sup>-</sup> form at 1 wt.%. The pull-off strength of the coating was retained in the presence of this ion exchange cellulose. These findings suggest that selective use of ion exchange cellulose in coatings can be a sustainable means of enhancing their protective attributes.

## CONCLUSION

Biobased ion exchangers, including those synthesized using agricultural residues, offer promise as sustainable, environmentally friendly and cost-effective alternatives to the corrosion inhibitors currently used in protective coatings. Biobased ion exchangers, when incorporated into polymer-based protective coatings at 1 to 2 weight%, can remove corrosive ions from the solution diffusing through the coating towards metallic surfaces, thus rendering the originally aggressive solutions innocuous. In addition, biobased ion exchanges either retain or improve the key engineering properties of protective coatings, including their abrasion resistance, pull-off bond strength and moisture resistance. These findings were based on the test data generated using various types of biobased ion exchangers of different ionic forms, which were used in different polymer-based protective coatings. Major distinctions were identified between the effects of different biobased ion exchangers on the performance attributes of specific polymer-based protective coatings. Further investigations are needed in order to explain the differences in the benefits realized by introducing various types of biobased ion exchangers in different protective coatings.

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