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NEW GENERATION OF WATER-TREATMENT PRODUCTS FORMULATED FROM BIODEGRADABLE AND RENEWABLE RAW MATERIALS

Boris A. Miksic
Alla Y. Furman
Margarita A. Kharshan
Cortec Corporation
4119 White Bear Parkway
St. Paul, MN 55110

ABSTRACT

Corrosion protection was always the important part of industrial development. Effective corrosion inhibitors prolong the life of equipment and machinery and in this way minimize the use of natural resources including ore, oil, petroleum, water, etc.

On the other hand, growing world manufacturing constantly increases the volume of utilized natural resources. A number of regulations were implemented recently for the protection of the environment. The most known among them are North Sea (UK, Norway, Denmark, The Netherlands) and US Gulf Coast lists of the chemicals environmentally acceptable in these regions, limiting the number of chemicals allowed for use in accordance with their level of biodegradability, bioaccumulation and toxicity.

This paper presents several products that are very effective in providing corrosion/scale inhibition and also formulated from biodegradable environmentally friendly raw materials, manufactured from renewable resources. Quality of these products is confirmed by laboratory testing according to ASTM and/or other standards and field results.

INTRODUCTION

Green chemistry is not an absolute goal or destination, but a dedication to a process for continual improvement, wherein the environment is considered along with the chemistry. Chemical products should be designed to preserve the efficiency of function, while reducing the impact on the environment.

These products should be designed so that at the end of their application, the product does not persist in the environment, and it should break down into innocuous degradation products. The development of "green" corrosion inhibitors is a process, which requires the knowledge of the pertinent country regulations, the evaluation of the environmental performance for the environment to which the product will be exposed, and the excellent corrosion protection in the applications this inhibitor is designed for.

The following list provides a glimpse of the principal criteria the chemist must follow to determine whether a given corrosion inhibitor is environmentally acceptable in a given region [1].

North Sea (UK, Norway, Denmark, The Netherlands)
Biodegradability: >60% in 28 days
Marine toxicity: Effective Concentration, 50% (EC_{50})/Lethal Concentration, 50% (LC_{50})>10 mg/L to North Sea species
Bioaccumulation: Log Octanol/Water Partition Coefficient (Pow)<3

US Western Gulf Coast Outer Continental Shelf (OCS)
Marine toxicity: No Observed Effect Concentration (NOEC) of effluent to mysid shrimp and silverside minnow must meet or exceed critical dilution factor (CDF) over a specified period of time (48 h or 7 days)

US Eastern Gulf Coast OCS
Marine toxicity: LC_{50} or effluent to mysid shrimp and silverside minnow must meet or exceed CDF

Eastern Canada
Similar to North Sea criteria
Microtox toxicity is also important

Trinidad and Tobago
Marine toxicity: Residual levels of products in effluent must not exceed 0.01 of LC50 test concentration to Metamysidopsis insularis (a crustacean)
Must also provide biodegradability data.

A different approach can be used to obtain a required or improved environmental profile: one of them is to use biodegradable materials obtained from natural resources as corrosion inhibitors.

The goal of the paper is to show that non-toxic, biodegradable inhibitors may inhibit corrosion as well or better than their more toxic traditional counterparts, depending on the system.
This paper is presenting three products which are serving different applications:

VpCI A - Additive for the condensate lines.

Corrosion is one of the major problems in the boiler condensate systems. Traditionally neutralizing and filming amines have been used to reduce corrosion of condensate lines. Today, environmental and safety issues encourage the formulator to use different approaches for this application. Several years ago one of the 'Green' inhibitors for the condensate lines was formulated and patented [3-5]. This product is based on the combination of sorbitan fatty acid ester and polyoxyethylene derivative of sorbitan fatty acid ester – surfactant usually used as food emulsifier. Our goal was to develop a product, which outperforms all existing products in terms of corrosion protection. In formulation work on VpCI A we have also utilized a combination of the surfactants used in different applications, including cosmetics. These ingredients are salts of amino acids, produced from the raw materials based on renewable resources.

VpCI B - The corrosion inhibitor for fresh water.

The basic ingredient in formulation of VpCI B is very similar to one which is used in the filming inhibitor for the condensate lines (VpCI A). In addition, VpCI B contains vapor phase corrosion inhibitor which provides protection to the areas unreachable for contact corrosion inhibitor.

VpCI C - Antisclant corrosion inhibitor.

The majority of antiscalants by their chemical nature belong to phosphonates and acrylic polymers. These chemicals have been effective antiscalants, at the same time they are not free from the limitations in their use; for example, their corrosiveness to copper and galvanized steel. Also phosphates are becoming increasingly restricted in terms of release to the environment. The recent breakthrough in this field is made by products based on the Polyaspartates [6]. These antiscalants do not attack colored metals, they are more environmentally acceptable than polymers/organophosphonates, but they cannot be considered as 'green' because the source of the basic raw material for their manufacture is petroleum.

In this work three polymers were studied: soy polymer, milk polymer – casein and alginic acid. Soy polymer is the derivative of the protein portion of the soy beans. It is consisted of individual amino acids (protein's building blocks). Amino acids contain both a basic amino group (NH_2) and the acidic carboxyl group (COOH). Soy protein in water does not exist as a true solution, but as a colloidal solution called sol. Sols consist of aggregates of several protein molecules, or micelles. These protein micelles are tightly wrapped in an envelope of water and carry an electric charge. Proteins in sols tend to concentrate in interfaces and can be considered as natural wetting agents, surface tension reducers and/or protective colloids. Despite their relatively large size, proteins spread into extremely thin films at an interface, exposing the reactive site of their amino acid site chains. Soy protein tends to orient and fixes its positively charged (cationic) sites to negative sites on the opposing surface. The anionic side of the chain orients itself to face the water phase.

Water-soluble casein-based proteins are also amphoteric, allowing for both cationic and anionic binding. They are successfully used in the construction industry as admixtures to concrete.

Alginic acid is mainly extracted from the sea weeds and utilized in the pharmaceutical industry and for the water waste treatment. Marine algae, as primary producers, are ecologically important, and economically have been used as food and medicines for centuries. Today, various species of marine algae provide not only food but also produce extracts such as agar, carrageen, and alginates. These extracts are used in numerous foods, pharmaceutical, cosmetic, and industrial applications.

It was also shown [7] that some of the natural polymeric materials are able to scavenge the metal ions from surrounding water.

All of the above suggests that the above mentioned natural polymers might act as scale inhibitors in the water.

EXPERIMENTAL

Environmental Testing

Biobased Content. To confirm that the raw materials used in formulations are made from renewable resources the content of Carbon 14 was determined. Carbon 14 dating is an accurate method for determining the age of things that have biological origin such as natural fibers, animal bones, etc.. All plants and animals are made up of chemicals that contain three types of carbon isotopes. The most common is carbon 12. It generally accounts for roughly 99% of all the carbon atoms found in a plant or animal. Another isotope is carbon 13 that comprises 1% of the total. The third isotope is carbon 14. It is found in living plants or animals in the ratio of one carbon14 atom for every trillion carbon 12 atoms and it is the same ratio as in the atmosphere from which it is digested. The ratio begins to change when plant or animal dies and it is no longer taking carbon from nature. Carbon 14, unlike carbon 12 and carbon 13 is radioactive. This means that over time the carbon 14 atoms will decay. When the isotope carbon 14 decays it gives off a beta particle and in doing so becomes nitrogen 14. The amount of carbon 12 and carbon 13 remains constant. Thus, if we are able to measure the percentage of carbon 14 that remains in a sample we can determine its age. Radiometric test for Carbon 14 determination was applied [2]. The data confirming that all materials described in this paper are manufactured from renewable resources, presented in table 1.

Toxicity Test. Once the chemicals are disposed of in the sea or river, there are concerns that some of them will persist and will have a detrimental effect on the environment. These compounds may be toxic to marine life. A 48-hr static acute M. bania test (EPA/600/4-90/027F) was performed and No Observable Effect Concentration (NOEC) and the Lowest Observable Effect Concentration (LOEC) were determined. It was found that water containing 1200 ppm of VpCI A can be discharged into the sea if critical dilution for this water is 24%. (Usually critical dilutions from 9% to 24% are specified for the discharge). [6]

Corrosion Testing

1. Screening immersion and half immersion corrosion tests were performed [8].
   Panels of different metals (carbon steel, galvanized steel, aluminum, and copper) were immersed in three test solutions, using tap water as a control. The testing conditions: 72 hours at room temperature. After the testing, the panels were removed from the solution and visually inspected for the presence of corrosion.

2. An immersion test was carried out with 300 ppm of VpCI A added to de-ionized (DI) water at 95°-100°C for 10 days in static conditions and at 75°-85°C for 48 hours in dynamic conditions (200 rpm).

3. Electrochemical tests [9] were carried out using Potentiostate/Galvanostate 'Versastate' manufactured by EG&G Instruments Princeton Applied Research Corp. with Model SoftCorr 11 352/252 Corrosion Measurements & Analysis Software. Working electrode was made from carbon steel SAE 1018, reference and a calomel saturated and high-density graphite was the counter electrode. Tafel plots for the VpCI A study were obtained at room temperature under dynamic conditions (200 rpm), Corrosion potential for VpCI B study was monitored at 80°C for 4 hours in the following solutions:
   a) 5% Diammonium EDTA in de-ionized water;

b) 5% Diammonium EDTA with Ammonia and Hydrogen Peroxide added to provide the passivation of carbon steel and pH 9.3 (according to the cleaning/ passivating procedure currently applied in boiler cleaning operation);

c) 5% Diammonium EDTA with Ammonia, Hydrogen Peroxide and VpCI B.

4. Pilot Cooling Tower Test. The real life test was performed in the pilot cooling tower. Coupons made from carbon steel SAE 1010, copper CDA 12, and hot-dipped galvanized steel HD Galvanized were placed inside the piping system of cooling tower for 3 months and then evaluated for the presence of corrosion.

   The conditions of the cooling tower were:

   Cooling Range: 5-8°C
   Drift and Evaporation: 12 L/hour
   Blowdown: ~15% of the make-up water
   Cycles of Concentration: ~3.7

Evaluation of antiscaling properties

For this evaluation the test methods described in the NACE Standard TM-0374-2001 'Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium sulfate and Calcium Carbonate from Solution' [10] was used. This is the static laboratory test designed to give a measure of the ability of scale inhibitor to prevent the precipitation of calcium carbonate and calcium sulfate from solution at 71°C.

For the test, synthetic brines were prepared:

- Calcium Sulfate precipitation test: Calcium brine – 7.5g/L NaCl + 11.0 g/L $CaClx2H_2O$ and Sulfate containing solution – 7.5 g/L NaCl + 10.66 g/L $NaSO_4$
- Calcium Carbonate precipitation tests – Calcium containing brine 12.15g/L $CaCl_2$ x $2H_2O$ + 3.68 g/L $MgCl_2$ x $6H_2O$ + 33.0 g/L NaCl and Bicarbonate containing brine 7.36 g/L $NaHCO_3$ + 33.0 g/L NaCl, saturated with CO_2.

Solutions for each test were connected in the test cell and scale inhibitor was added to them at concentration level of 10 ppm.

Testing cells were placed in the oven set at 71°C for 24 hours. After that the concentration level of calcium ions renamed in the solution was evaluated according to ASTM D-11269 Standard Test Method for Hardness in Water [11].

Using these data percent of scale inhibition was calculated:
% Inhibition = 100 x (Ca – Cb):(Cc – Cb), where:
Ca – Ca^{2+} concentration in the treated sample after precipitation
Cb – Ca^{2+} concentration in the blank after precipitation
Cc – Ca^{2+} concentration in the blank before precipitation

RESULTS

The results of biobased content evaluated by independent laboratory are presented at the Table1. This data shows that the formulations of VpCIs A, B and C contain mostly the ingredients manufactured from the renewable resources.

TABLE 1
BIOBASED CONTENT

Sample	C14 content, % modern carbon, pMC	Biobased content, %
Additive to Condensate (VpCI A)	88.5+-0.6	84.3
Corrosion Inhibitor for fresh water (VpCI B)	72.5+-0.5	69.1
Antiscalant/ Corrosion Inhibitor (VpCI C)	95.6+-0.3	91.5

Study of VpCI A – additive to the condensate lines

The data of study of VpCI A - corrosion inhibitor for the protection of condensate lines are presented in the **Table 2** and **Figure 1.**

According to the results of the immersion corrosion test, performed at 90°C in dynamic conditions and electrochemical test at the room temperature, VpCI A provides effective corrosion protection in fresh water.

TABLE 2
PROTECTIVE PROPERTIES OF VPCI A (ADDITIVE FOR CONDENSATE LINES)

	Dynamic Conditions, 90oC		**Tafel Plots, dynamic conditions**	
Material	**Mass Loss, g/**	**Protective Power, Z%***	**Corrosion Rate, (mmpy)**	**Protective Power, Z%**
VpCI A, 300 ppm	0.0970 (No visible corrosion)	91.49	0.233	87.01
Control*	0.1269 (Corrosion after 0.5 Hr.)	-	1.794	-

$$Z = \frac{CR_c - CR_i}{CR_c} \times 100\%, \text{ where}$$

*DI water

CR_c = Corrosion rate in DI water

CR_i = Corrosion rate in presence of inhibitor

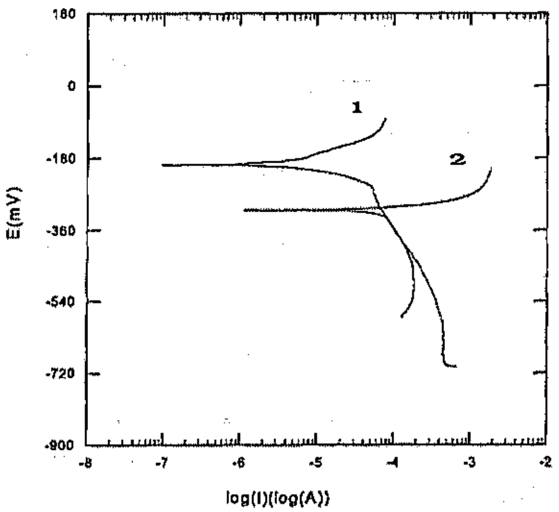


FIGURE 1 - Tafel plots. 1 - 300ppm VpCI A in de-ionized water; 2 – De-ionized water. Ambient temperature, 200 rpm.

Study of VpCI B – corrosion inhibitor for fresh water

The half immersion corrosion test on different metals was performed in static conditions at the room temperature. VpCI B - was added to the tap water at the range of concentrations 250 – 1000 ppm. The results are presented in Table 3.

TABLE 3
PROTECTIVE PROPERTIES OF VPCI B – CORROSION INHIBITOR FOR FRESH WATER

Material	**Carbon Steel**	**Aluminum**	**Copper**
250 ppm	Corrosion	Slight Corrosion	No visible Corrosion
500 ppm	Very slight Corrosion	No visible Corrosion	No visible Corrosion
750 ppm	No visible Corrosion	No visible Corrosion	No visible Corrosion
1000 ppm	No visible Corrosion	No visible Corrosion	No visible Corrosion
Control	Corrosion	Corrosion	Corrosion

The results presented in Table 3 show that VpCI B provides corrosion protection in liquid and vapor phases and also is very effective in low concentration on the different metals.

Special study on Carbon Steel was performed for the evaluation of the possibility of using VpCI B in combination with Hydrogen Peroxide for passivating boilers after cleaning.

After the cleaning with Diammonium EDTA customer protects carbon steel vessels from flash rust by passivating with Hydrogen Peroxide. It was suggested to add 500 ppm of VpCI B for improving of the passivating layer formed by Hydrogen Peroxide treatment; corrosion potential and corrosion rates were measured for the evaluation of the effectiveness of this treatment.
Data of Corrosion potential vs. Time is presented at Figure 2 (see conditions in the experimental) Corrosion potential data presented at Figure 2 confirms that carbon steel actively corrodes in 5% Diammonium EDTA and passivates when Hydrogen Peroxide is added to the solution. Addition of 500 ppmVpCI B makes the corrosion potential further positive and consequently makes the passivation more effective.

The electrodes were extracted from the solution and left at the ambient condition over night. Next morning they were examined for the presence of corrosion. By visual inspection, severe corrosion was found on the not passivated electrode (electrode 1), less corrosion was detected on the electrode passivated with Hydrogen Peroxide (electrode 2), and no visible corrosion appeared on the electrode passivated with both – Hydrogen Peroxide and VpCI B (electrode 3). (Figure 3)

This study confirms that treatment with VpCI B significantly improves the effectiveness of passivation, provided by Hydrogen Peroxide.

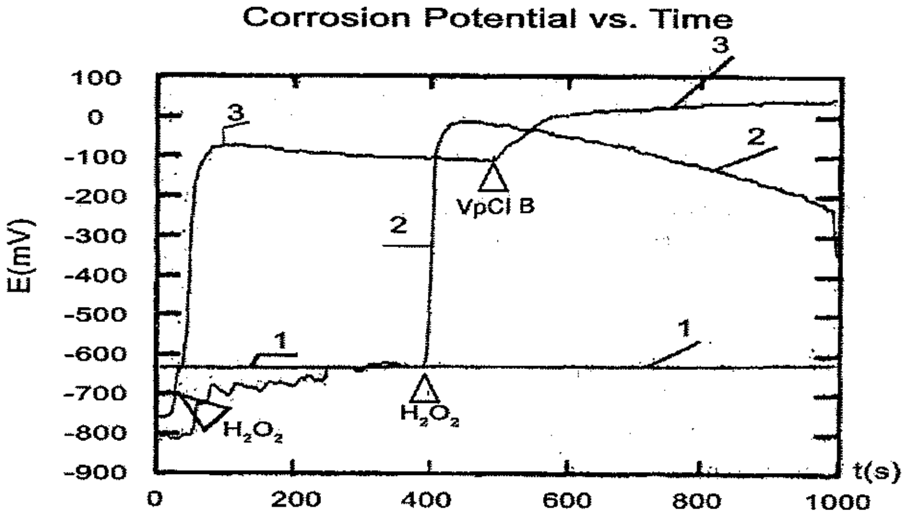
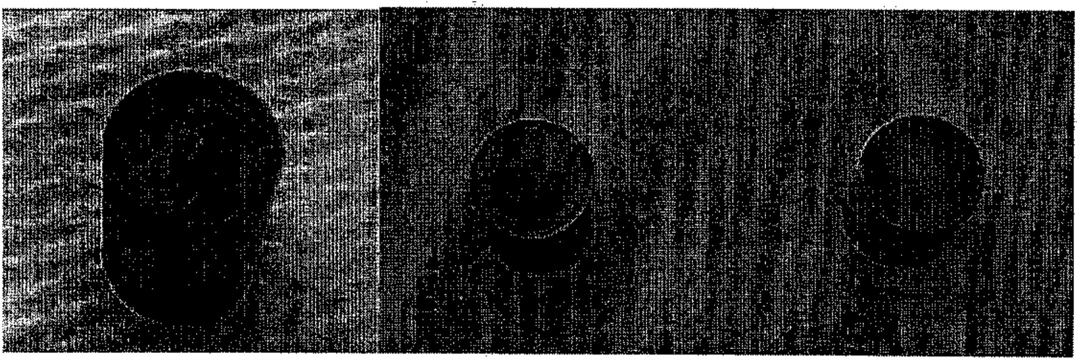


FIGURE 2 - Passivation of carbon steel with Hydrogen Peroxide and VpCI B.

1. No passivation
2. Passivation with Hydrogen Peroxide
3. Passivation with Hydrogen Peroxide and VpCI B



1. Not passivated
2. Passivated with Hydrogen Peroxide
3. Passivated with Hydrogen Peroxide and VpCI B

FIGURE 3 - Carbon Steel electrodes after cleaning and passivation.

VpCI C – Antiscalant/corrosion inhibitor

Antiscalant properties. The level of scale inhibition provided by natural polymers was compared with effectiveness of the most popular antiscalants based on polyacrylate, organophosphonates and polyaspartic acid. All scale inhibitors were evaluated at the same concentration level of 10 ppm. (Table 4, Figure 4)

TABLE 4
SCALE INHIBITION, TITRATION DATA ACCORDING TO ASTM D-1126

Materials	$CaCO_3$, ppm	% of inhibition*	$CaSO_4$, ppm	% of inhibition*
Organophosphonate	4050	95.5	3950	76.9
Polyacrylate	3100	16.7	4250	92.3
Casein based	3550	54.2	4150	87.2
Alganic Acid based	3100	16.7	4200	89.7
Soy protein based	3100	16.7	4250	92.3
Polyaspartic acid based	3000	6.6	4000	79.5
Control (w/o scale inhibitor)	2900	-	2450	-
Initial	4100	-	4400	-

* %of scale inhibition= (Ca-Cb)/(Cc-Cb)*100. Where Ca – concentration of Calcium in solution with scale inhibitor; Cc – initial concentration of Ca in brine; Cc – concentration of Ca in control sample.

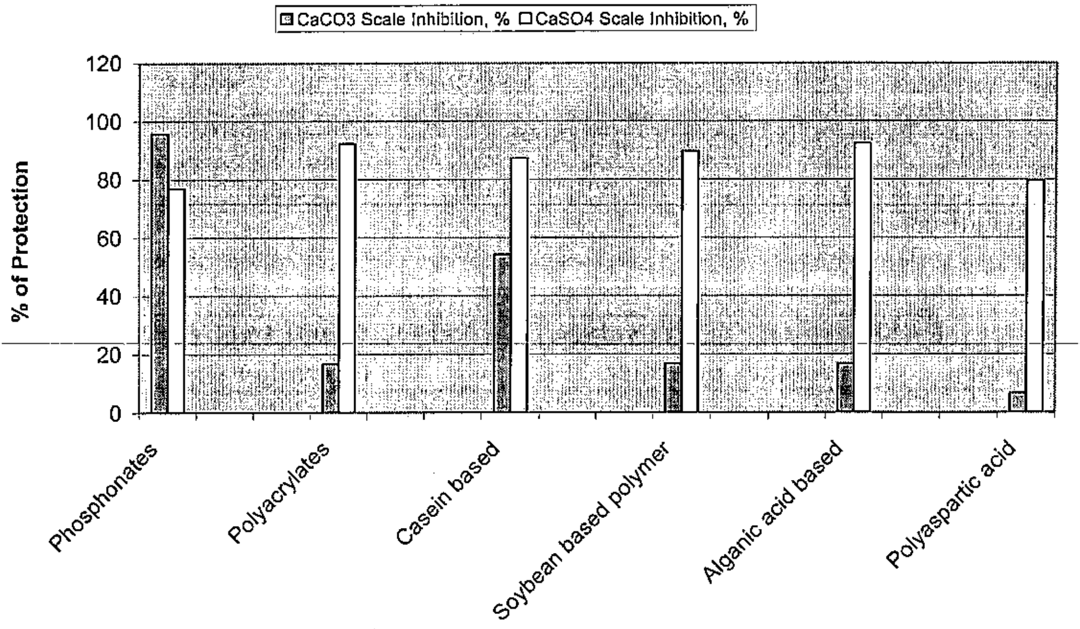


FIGURE 4 - Scale Inhibition (% of Protection)

As one can see, natural polymers provide better protection against calcium sulfate scale formation than phosphonates, and are more effective than polyacrylates and polyasparates in preventing calcium carbonate scaling.

Anticorrosion properties

Data presented in Table 5 show that products based on natural polymers outperformed organophosphonate, polyacrylate and polyasparate based products as corrosion inhibitors. It is very important that natural polymers provide corrosion protection not only for ferrous metals but also for aluminum, galvanized steel and copper. Based on their molecular size and micelle structure it is possible that they belong to the 'precipitation' type of inhibitors, which affect both anodic and cathodic reactions.[12]

TABLE 5
CORROSION DATA
1000 PPM OF SCALE INHIBITOR IN TAP WATER; 72 HOURS AT ROOM TEMPERATURE

Material	Carbon Steel	Galvanized Steel	Aluminum	Copper
Organophosphonate	Corrosion	Corrosion	Corrosion	Corrosion
Polyacrylate	Corrosion	Corrosion	Severe Corrosion	Severe Corrosion
Casein based	Very slight Corrosion	Very slight Corrosion	No visible Corrosion	No visible Corrosion
Soy protein based	No visible Corrosion	No visible Corrosion	No visible Corrosion	No visible Corrosion
Alganic Acid based	Slight Corrosion	Slight Corrosion	Slight Corrosion	No visible Corrosion
Polyaspartic acid based	Corrosion	Severe Corrosion	Slight Corrosion	Slight Corrosion
Control	Corrosion	Corrosion	Corrosion	Corrosion

Results presented at the Table 6 indicate that it is possible to obtain at least the same performance criteria in cooling tower by utilizing natural polymers only as with the composition of the blend of few inhibitors and antiscalants.

TABLE 6
RESULTS OF TESTING IN THE PILOT COOLING TOWER

Material	Presence of Scales	Corrosion Rate, mmpy		
	On steel coupon	Carbon Steel	Galvanized Steel	Copper
Organophosphonate / Polyacrylates/ Molybdate/TTA – 25 ppm+ 10ppm Towerbrom	No visible	1.8	1.1	0.056
VpCI C 25ppm - + DBNPA	No visible	0.8	1.1	0.026
Control 10ppm Towerbrom	No visible	-----	------	------

Conclusion

1. Three environmentally friendly and economical VpCI products for water treatment are formulated.
2. According to the results of immersion corrosion and electrochemical tests VpCI A effectively protects Carbon Steel from corrosion in wide range of temperatures.
3. According to the results of half immersion corrosion test VpCI B protects Carbon steel, Aluminum and Copper from corrosion in all three phases: liquid, vapor and the vapor/liquid interface. VpCI B also improves the effectiveness of passivation of Carbon Steel when applied in combination with Hydrogen Peroxide.
4. VpCI C, being a "green" natural polymer-based antiscalant/corrosion inhibitor provides the same or better scale inhibition than traditionally used polyacrylates or organophoshonates. In addition to antiscaling properties, VpCI C is a very good multimetal corrosion inhibitor. That's why VpCI C is a very effective fully biodegradable multifunctional additive package for water treatment applications.

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