VAPOR CORROSION AND SCALE INHIBITORS FORMULATED FROM BIODEGRADABLE AND RENEWABLE RAW MATERIALS

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ABSTRACT

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

On the other side 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

<u>Eastern Canada</u>
Similar to North Sea criteria
Microtox toxicity is also important

<u>Trinidad and Tobago</u>
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 approaches can be used to obtain a required or improved environmental profile:
1. replacement of solvent- or oil-based carriers in formulations with water-based technology, while these technologies provide an environmentally conscious method of corrosion protection [2], they can be cost and time prohibitive for certain operations. In these cases, the manufacturer was left with no choice but to use hazardous for environment petroleum-based products, or simply do nothing.
2. replacement of petroleum-based carriers with the solvents, manufactured from renewable resources. This has been accomplished by combining VpCI's with soy-derived oils to formulate anticorrosion products for many different applications.
3. use of biodegradable materials obtained from natural resources as a corrosion inhibitors.

The focus of paper will be limited with the last two approaches. The goal of this paper is to show that non-toxic inhibitors may inhibit corrosion as well or better than their more toxic traditional counterparts, depending on the system.

EXPERIMENTAL

This paper is presenting two products which are serving different applications:
-   crude oil additive
-   antiscalant/corrosion inhibitor

In developing of these products, a battery of testing were undertaken to ensure that the desired properties were achieved. These included the choice of materials, evaluation of corrosion inhibiting and antiscaling properties, and environmental aspect.

The choice of materials

1. Soybean oil methyl ester was chosen as a carrier based on:
    a. Excellent environmental and safety profile:
        -   Non-toxic: The acute oral LD_{50} is greater than 17.5 g/kg body weight. By comparison, table salt is nearly 10 times more toxic.
        -   Biodegradable
        -   Very mild irritant
    b. Chemistry of this product: being a triglyceride of the blend of saturated and unsaturated fatty acids (methyl esters), this product provides some additional corrosion protection to the metallic substrates
    c. Solvency of soybean oil methyl ester which is similar or better to petroleum-derived products
2. Natural polymers as an antisclants
    Majority of nowadays 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 break throw in this are made by products based on the

Polyaspartates [3]. These antiscalants do not attack the colored metals, they are more environmentally acceptable than polymers/polyphosphonates, but they cannot be considered as 'green' because the source of raw material for their manufacture is petroleum.

In this work three polymers were studied: soy polymer, milk polymer – casein and polysaccharide. Soy polymer was the derivative of the protein portion of the soy beans. It is consisted from 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 interface, exposing the reactive site of their aminoacid site chains. Soy protein tends to orient and fixes their positively charged (cationic) sites to negative sites on the opposing surface. The anionic side of the chain orients themselves to face the water phase.

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

Polysaccharide utilized in this work is mainly extracted from the sea weeds and utilized in 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,

carrageenans, and alginates. These extracts are used in numerous foods, pharmaceutical, cosmetic, and industrial applications.

It was also shown [4] that some of the natural polymeric materials are able to scavenge the metal ions from surrounding water.

All of the above allow to suggest that mentioned above natural polymers might act as a scale inhibitors in the water.

Corrosion Testing

The most important factor in product development is the capability of product to prevent the corrosion process from occurring. An assortment of standard tests were used to compare the new "green" VpCI products with products that are commercially available.

The following corrosion tests were performed for the soybean oil-based crude oil additive.

- Wheel Test Method (NACE 1D 182) [5]
  This test is a dynamic test performed by placing fluids (kerosene, brine, and inhibitor) in a bottle with a metal test specimen at 150°F for 24 hours. Brine contained 0.62% sodium chloride, 0.305% calcium chloride, 0.186% magnesium chloride hexahydrate and 89.89% distilled water and was saturated with carbon dioxide (CO_2). Hydrogen sulfide (H_2S) has been generated "in situ" by adding 1700 mg/L of Acetic Acid and 3530 mg/L of fresh, reagent grade sodium sulfide (Na_2Sx9H_2O) to the brine.

  Two types of the test were performed: Continuous Treatment and Film persistency tests. During Continuous treatment test brine contained inhibitor during whole testing period. For Film Persistency testing metal specimens were inserted into the brine containing the corrosion inhibitor for 1 hour, followed by 1 hour rinsing with the same brine without inhibitor. Than test was

continued in the fresh portion of the same brine for the next 22 hours.

After the test the weight loss of metal specimens were evaluated and corrosion rate/percent protection was calculated.

- Dynamic circuit test
  This test simulates conditions in pipelines and was described in [6]. The conditions of the test were:
  > Temperature – Ambient
  > Brine Velocity – 6-8 m/min
  > Pressure – 2-3 psi
  > Material – Carbon Steel
  > Brine – 5%NaCl + 0.5% Acetic Acid saturated with H_2S
  > Test Duration – 24 hours
  > Inhibitor Dose – 50 ppm

  Corrosion rate of carbon steel was measured using corrosion rate monitor Corrater 9030, manufactured by Rohback Cosasco System Inc.

- Static test in an autoclave
  Brine was prepared according to NACE Standard TM-01-77 [7]: 50g NaCl + 5mL Acetic Acid + De-ionized water in 1L volumetric flask. Inhibitor was added at the concentration level of 500 ppm. Metal panels were submersed into the brine and H_2S was pressed into the autoclave at 40 psi. The test temperature was 145°F. Weight loss of carbon steel panels was evaluated after 24 hours of testing.

- Rotating Cylinder Electrode Test [8]
  This test is recommended by ASTM G 170-01 "Standard Guide for Evaluating and Qualifying Oilfield and Refinery Corrosion Inhibitors in the Laboratory". The test was performed in brine containing 95% of synthetic seawater and 5% of diesel fuel under

continuous purging of CO_2 at the temperature of 70°C and the rotating rate of 2000 r/min. Inhibitor was diluted with diesel fuel in the ratio 1:10. Carbon Steel working electrode was immersed in this mixture for 10 minutes and then left for 2 hours at the room conditions for air-drying; the excess of the inhibitor was removed from the bottom surface of electrode with filter paper. Corrosion rate was determined after 6 hours of the testing by analyzing the polarization curves obtained in Linear Polarization technique. Then percent of protection was calculated.

The following tests were performed for antiscalant/corrosion inhibitor.

- Half-immersion Corrosion test [2]
  Panels of different metals (carbon steel, galvanized steel, aluminum, and copper) were immersed in thee 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.

- 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 corrosion rate was determined

  The conditions in 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" [9] were used. These are the static laboratory tests 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$_2$O 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$_2$O + 3.68 g/L MgCl$_2$ x 6H$_2$O + 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 placed 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 remained in the solution was evaluated according to ASTM D-11269 "Standard Test Method for Hardness in Water" [10].

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

Environmental Aspect

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, have a low level of biodegradability, or may bioaccumulate in the living organisms. The Paris Commission (Parcom) developed a protocol consisting of three tests: bioaccumulation, biodegradation, and toxicity.

Bioaccumulation

Bioaccumulation of substances within aquatic organisms can lead to toxic effects over long period of time. The potential of bioaccumulation is determined by measuring the n-octanol/water partition coefficient of a specific chemical compound.

The partition coefficient Pow was determined according to OECD Guideline 317 [11], the log Pow must be lower than 3.

Biodegradation

Based on OECD Guideline, biodegradation is a measure of the length of time over which a substance will remain in the environment. The OECD 306 test guideline [12] is primarily used for biodegradation in marine environments. Chemical compounds are subjected to a 28-day Biochemical Oxygen Demand (BOD-28) test. In order to be rapidly degradable, at least 60% degradation of the substance must be attained within 28 days of the start of the test.

The absence of rapid degradation in the environment can mean that a chemical compound in the water has the potential to exert toxicity over a wide temporal and spatial range.

Another definition of biodegradability is "capable of being readily decomposed by biological means, especially by bacterial action". There

are two methods of measuring decomposition. One is "Biochemical Oxygen Demand" (BOD), which is a measure of the actual oxygen consumed by microorganisms during conversion of the material to carbon dioxide and water. The other is "Chemical Oxygen Demand" (COD), which is a measure of the theoretical amount of oxygen required to convert the material to carbon dioxide and water. (Note: The BOD test utilizes active microorganisms, requires a minimum of 5 days, and is difficult to reproduce. The COD test uses common inorganic chemicals, takes about two hours, and is easily duplicated.)

"Percent Biodegradation" is the ratio of BOD/COD times 100. This value is typically reported for date after 5, 10, 20, and 30 days. Some studies suggest that if 60% or more biodegradation occurs within 28 days, the product may be considered "biodegradable" and would be largely removed from the waste water system. Different methods of determining percent biodegradation may give different results. In order to make meaningful comparisons, the same test methods and calculations must be used.

Aquatic Toxicity [13]

Toxicity testing is run on organisms related to different levels of the food chain. This includes primary producers such as algae (*Skeletonema constatum*), consumers such as fish and crustaceans (*Acartia tonsa*), and sediment reworkers such as seabed worms (*Corophium volutator*).

The toxicity is usually assessed by determining an algae species 72 or 96 hour EC_{50}, a crustacean species 48 hour EC_{50} and a sediment reworker 240 hour LC_{50}.

EC_{50} is the effective concentration of a chemical substance necessary to negatively affect 50% of the aquatic organism population. LC_{50} is the effective concentration of a chemical compound required to kill 50% of the population.

In addition, 96 hours Marine Fish Acute Toxicity test was performed.

RESULTS

VpCI A – Soybean oil methyl ester based inhibitor for the crude oil

Corrosion testing

Wheel test results are shown in the Tables 1, 2, and 3.

VpCI A, Concentration, ppm	Percent protection, %
5	92.3
25	95.5
100	98.7

Table 1. Continuous Treatment

VpCI A, Concentration, ppm	Percent protection, %
100	89.9
250	93.7

Table 2. Film Persistency

Test method	Inhibitor based on soybean, % protection (VpCI A)	Conventional inhibitor, based on mineral spirit, % protection
Dynamic Circuit Test	78.6	69.4
Static Test in Autoclave	91.7	89.1
Rotating Cylinder Electrode	96.1	-

Table 3. Comprising of the performance of corrosion inhibitor based on soybean oil (VpCI A) vs. Conventional inhibitor, based on mineral spirit

Toxicity Testing

5 days	10 days	25 days
39.3%	52.4%	>60%

Table 4. Biodegradability (%)

Test		Result	Exposure time, hours
Skeletonema constatum	EC_{50}	100 ppm	72
Acartia tonsa	LC_{50}	135 ppm	48
Corophium volutator	LC_{50}	10017 ppm	240
Scophthalmus maximus (fish test)	LC_{50}	347 ppm	96

Table 5. Aquatic toxicity (testing performed in accordance with Oslo-Paris commission protocol)

Bioaccumulation

The measured value of the logarithm of the partition coefficient, log Pow, is reported in Table 6.

Test method	Limit	Result
OECD 117 log Pow	<3	1.75

Table 6. Partition Coefficient

VpCI B – 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 7, Fig. 1)

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 polymer	3550	54.2	4150	87.2
Polysaccharide based	3100	16.7	4200	89.7
(VpCI B)Soy-based polymer	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 brain; Cc – concentration of Ca in control sample.

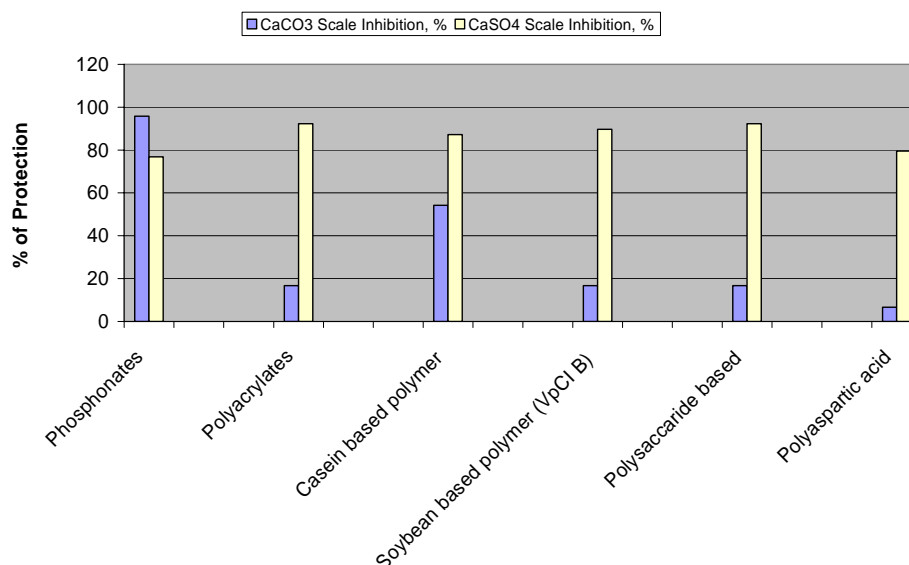**Table 7. Scale Inhibition, titration data according to ASTM D-1126**

Figure 1. 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

In Table 8 shown results of the immersion corrosion test.

Material	Carbon Steel	Galvanized steel	Aluminum	Copper
Organohosphonate	Corrosion	Corrosion	Corrosion	Corrosion
Polyacrylate	Corrosion	Corrosion	Severe Corrosion	Severe Corrosion
Casein-based polymer	Very slight Corrosion	Very slight Corrosion	No visible Corrosion	No visible Corrosion
Soy-based polymer (VpCI B)	No visible Corrosion	No visible Corrosion	No visible Corrosion	No visible Corrosion
Polysaccharide 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

Table 8. Corrosion data. 1000 ppm of scale inhibitor in tap water; 72 hours at room temperature

Data presented in Table 8 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 anotic and cathodic reactions.

Material	Presence of Scales	Corrosion Rate, mmpy		
	On steel coupon	Carbon Steel	Galvanized Steel	Copper
Organophophonate / Polyacrylates/ Molybdate/ Triasol – 25 ppm	No visible	1.8	1.1	0.056
VpCI B 25ppm	No visible	0.8	1.1	0.026
Control	No visible	-----	------	------

Table 9. Results of testing in the pilot cooling tower

The results from the Table 9 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.

CONCLUSION

The new "green" VpCIs offer the advantage of meeting the legislative requirements of the country or region where they are used. In many areas of the world inhibitors with the quantified environmental profile are required. These "green" inhibitors give the users more flexibility in terms of chemical use and inventory. Beyond the legal requirements, using "green" products also shows environmental awareness and concern.

As shown in this work, less-toxic products (VpCI A) inhibiting corrosion as well or better than their more toxic traditional counterparts used in petrochemical industry.

VpCI B, being a "green" natural polymer-based antiscalant/corrosion inhibitor provides the same or better level of scale inhibition as traditional organophosphonates, polyacrylates and polyaspartic acid-based material. In addition to antiscaling properties, VpCI B is a very good multimetal corrosion inhibitor, and that's why VpCI B is a very effective fully biodegradable multifunctional additive for water-treatment applications.

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