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Biodegradable Multifunctional Oil Production Chemicals: Thermal Polyaspartates

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BIODEGRADABLE MULTIFUNCTIONAL OIL PRODUCTION CHEMICALS: THERMAL POLYASPARTATES.

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ABSTRACT

Control of both mineral scale and corrosion with a single, environmentally acceptable material is an ambitious goal. Polyaspartate polymers represent a significant milestone in the attainment of this goal. Thermal polyaspartates (TPA) are polycarboxylate polymers derived via thermal condensation of the naturally occurring amino acid aspartic acid. These protein-like polymers are highly biodegradable and non-toxic, and are produced by an environmentally benign manufacturing process. TPA's exhibit excellent mineral scale inhibition activity and CO_2 corrosion control. Laboratory data on scale inhibition and corrosion control in North Sea oil field production applications is presented.

INTRODUCTION

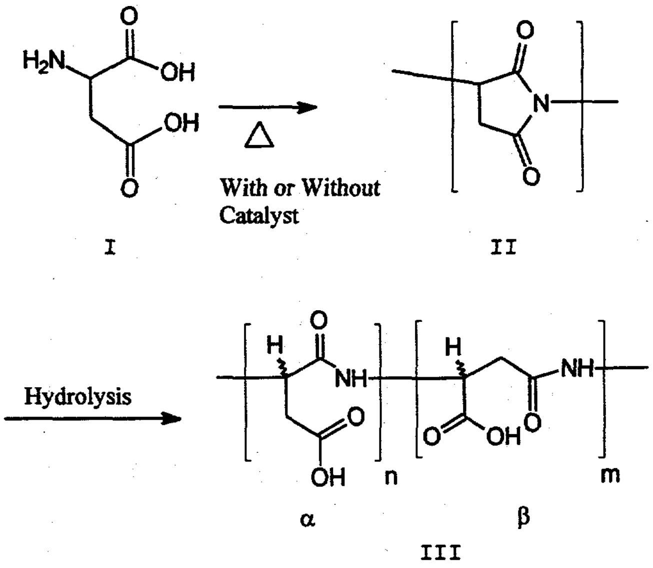
The impact of chemicals on the environment is an issue of increasing global importance. In sensitive areas, such as the North Sea, the need for "green" oil production and drilling chemicals is particularly acute. The effort to establishment of an international system of environmental controls under the Paris Commission (PARCOM) is a clear indication of the importance of environmental issues to the oil industry. In order to meet the challenges of increasingly stringent regulations, the chemical industry has begun to develop production chemicals of lower environmental impact.

Thermal polyaspartates (TPA), as exemplified by the parent polymer, polyaspartic acid, offer an attractive alternative to conventional oil production chemicals. In addition to their activity as scale inhibitors and dispersants[1], polyaspartates have also been shown to have corrosion inhibition activity[2,3], particularly for CO_2-corrosion environments frequently found in oil field applications.

Toxicity, biodegradation and accumulation are key factors in the evaluation of the environmental acceptability of a product in a particular application. Thermal polyaspartates have been demonstrated to be highly biodegradable[4] and low toxicity.[5] This, coupled with the multifunctional character of TPA makes thermal polyaspartate an ideal candidate for use in oil production.

SYNTHESIS

Aspartic acid (I) is one of the few amino acids that will thermally homopolymerize. Heating aspartic acid, either alone or with a catalyst, leads to a linear thermal polycondensation polymer known as polysuccinimide (II). The polymerization is economically accomplished without the use of organic solvents. Hydrolysis of polysuccinimide with aqueous base, such as sodium hydroxide, leads to a random copolymer of α and β aspartate units (III), with the β aspartate comprising about 70%-75% of the repeating units.[6] The polymer is also completely racemic (a 1:1 D/L mixture), in contrast to natural proteins, which generally contain only L amino acids.



I

II

III

In the absence of any additives, the dry thermal polymerization of aspartic acid to polysuccinimide leads to a polymer of ca. 5000-6000 weight average molecular weight (Mw). The process appears to be self limiting and highly reproducible. Conversions of monomer to polymer of greater than 95% are easily accomplished.[7] The addition of catalysts that result in the formation of a melt phase during the polymerization provides a means of tailoring the molecular weight of the polymer. Depending upon the catalyst and conditions used, molecular weights of from Mw 2000 to Mw 30000 are readily obtained.

BIODEGRADABILITY

One question of importance is what effect do the structural differences (high β content, D,L mixture) of thermal polyaspartates from natural polypeptides have on the biodegradability of the polymer. The Inherent Biodegradability of sodium polyaspartate derived from the dry thermal polymerization of aspartic acid has been evaluated by an independent testing laboratory using the Zahn-Wellens Test (OECD Guideline 302B). Sodium polyaspartate at a concentration of 200 mg carbon/L and mineral nutrients in an aqueous medium was exposed to activated sludge for a period of 28 days. Biodegradation was determined by following the dissolved organic carbon (DOC) level over the duration of the test. The percentage of the total DOC removed by the microorganisms in the sludge is equal to the degree of biodegradation. The results are presented in Table 1 and Figure 1 below in comparison to diethylene glycol reference compound. The % DOC removal for TPA after 28 days averaged 85% for two test runs. Test substances with results of greater than 20% DOC removal are considered to be inherently biodegradable. Results of greater than 70% DOC removal are considered to be evidence of Ultimate Biodegradability.

The Ultimate Biodegradability of TPA was further tested by the same laboratory in a Closed Bottle Test (OECD 301D Method) using pre-adapted inoculum from the Zahn-Wellens Test (ZW Test). In this method, the test substance (at 5 and 10 mg/L concentrations) and mineral nutrients were exposed to pre-adapted inoculum from the ZW Test. The ratio of the biological oxygen demand of the sample to the chemical oxygen demand (BOD/COD) is an indication of the degree of biodegradation. Thermal polyaspartate showed a 70% degree of biodegradation in this 28 day test.

Table 1. Zahn-Wellens Test for Inherent Biodegradability (OECD 302B) for TPA.

Test Substance	**% DOC Removal**	**After Days:**		
200 mgC/L	**7**	**14**	**21**	**28**
TPA	24	60	82	83
TPA	24	61	84	87
diethylene glycol	98	98	100	100

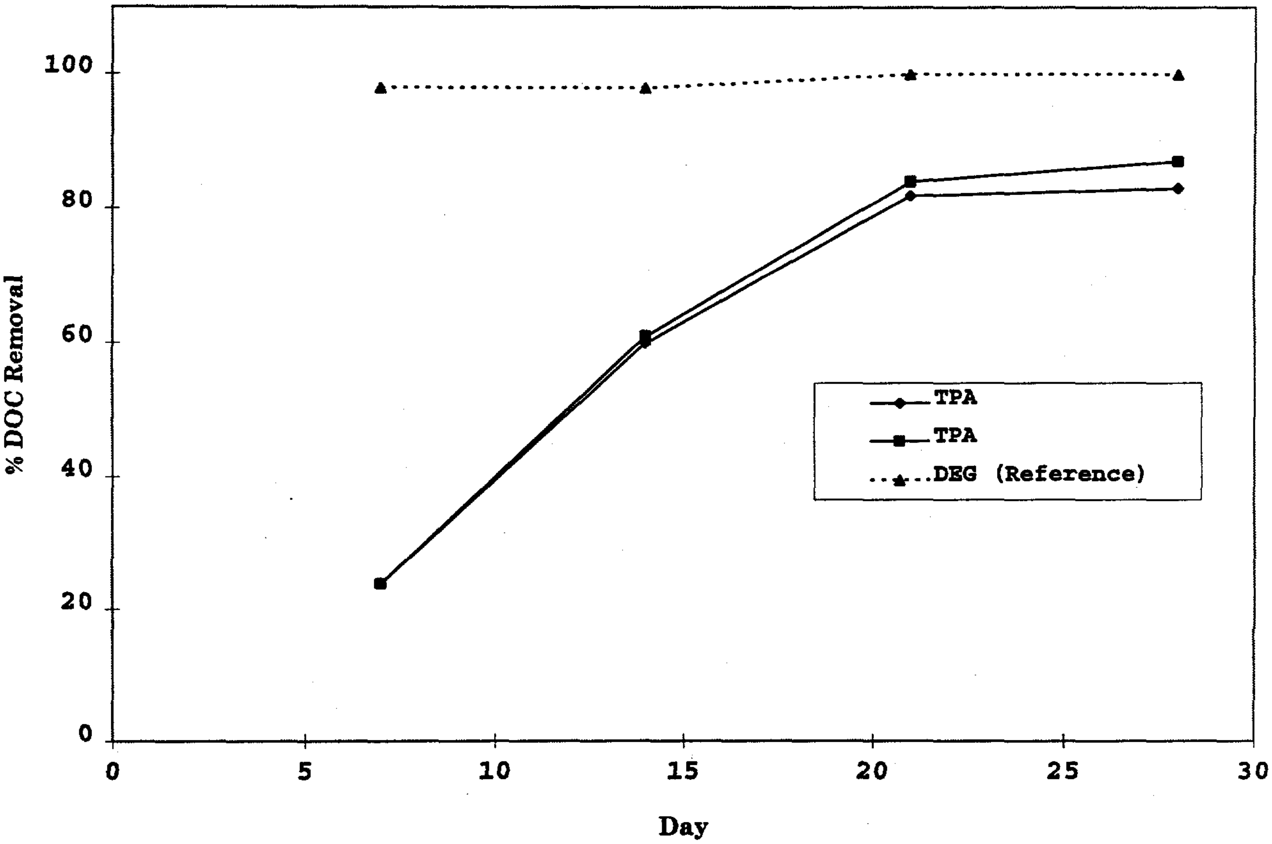


Figure 1. Zahn-Wellens Test for Inherent Biodegradability of Thermal Polyaspartate (TPA).

TOXICITY STUDIES

The toxicity of oil production chemicals is of concern for both environmental impact in use and for worker safety in handling. Toxicity studies of commercially produced TPA were performed using EPA/TSCA guidelines on mammalian test models. Our test results indicate that TPA is non-toxic and poses not hazards from exposure during use and handling. Toxicity tests using model organisms *Daphnia pulex* (Water Fleas), *Pimephales promelas* (Fathead Minnows), *Selenastrum capriornutum* (Algae), and *Photobacteria* (Microtox) were performed to assess environmental toxicity. All tests were performed by independent laboratories.

Environmental Toxicity.

A forty-eight hour toxicity bioassay was performed on *Daphnia pulex* (Water Fleas) less than 24 hours. old. Dosages of TPA varied between 625 mg/L to 10,000 mg/L and the mortality rates were measured at 24 and 48 hours. The lethal concentrations killing 50% of the organism (48 hour LC_{50}) was computed to be 1792 mg/L at 95% confidence level.

A forty-eight hour acute toxicity bioassay was performed on *Pimephales promelas* (Fathead Minnows) less than 24 hr. old. Dosages of TPA varied between 625 mg/L to 10,000 mg/L and 10,000 mg/L and the mortality rates were measured at 24 and 48 hours. The lethal concentration killing 50% of the organism (48 hour LC_{50}) was computed to be 2117 mg/L at 95% confidence level.

A ninety-six hour algae chronic toxicity test was performed on *Selenastrum capricornutum* at a stock culture of 7 days with an initial cell density of 10,000±10%. Dosages of TPA were varied between 62 mg/L and 1000 mg/L. The no-observed effect concentration was 62 mg/L, the lowest observed effect concentration was 125 mg/L and the chronic value was 88 mg/L.

Toxicity assays on *Photobacteria* were also performed. Concentrations of TPA varied between 45,000 mg/L and 90,000 mg/L. The product concentrations that induced a specific response in the microorganism were at 79,000 mg/L in at 5 minute and 54,000 mg/L product at 15 minutes.

From the toxicity studies using both mammalian and environmental test models, it can be concluded [illegible] TPA can be considered non-toxic (Category D in the UK Offshore Chemical Notification scheme).

PERFORMANCE TESTING

1. Scale Inhibition.

The performance of TPA has been evaluated against commercially available phophonate chemistry in synthetic formation/sea water mixtures using both Static Scale Precipitation Tests mand Dynamic (Tube Blocking) tests. Full details of these protocols have been described else where.[8]

Static Scale Precipitation Tests.

Barium sulfate assays were performed on Forties water chemistries and calcium carbonate performance was evaluated against Miller formation water. All water chemistries used are given in **Table 2.**

Table 2. Water Chemistries.

ION	FORTIES (ppm)	MILLER (ppm)	NORTH SEA (ppm)
Sodium	252	28100	11010
Potassium	372	1630	460
Magnesium	504	113	1368
Calcium	2809	615	428
Strontium	574	65	8
Chloride	52360	46050	19700
Bicarbonate	496	1655	124
Sulfate	0	0	2960

The test pH was 6.0 and the temperature was 95 °C. For the barium sulfate assay, formation water:sea water ratios of 90:10 and 50:50 were used. These ratios represent the worst case barium sulfate scaling as identified in laboratory mixing tests and computer scale simulations. The results of the barium sulfate tests at a 90:10 ration of formation water:sea water are given in **Table 3**. The % efficiency of inhibition was 100% for both TPA and commercial phosphonate from 5 ppm to 25 ppm inhibitor concentrations. The results for a 50:50 ratio of formation water:sea water are given in **Table 4**.

Table 3. Forties Barium Sulfate Scaling Test (90:10, Formation water:Sea water)

	% Efficiency		
Chemical	**5 ppm**	**10 ppm**	**25 ppm**
Commercial Phosphonate	100	100	100
TPA	100	100	100

Table 4. Forties Barium Sulfate Scaling Test (50:50, Formation water:Sea water)

	% Efficiency		
Chemical	**5 ppm**	**10 ppm**	**25 ppm**
Commercial Phosphonate	6	15	30
TPA	9	13	20

Similarly, the results for the calcium carbonate assay (Miller formation water) at 25 and 50 ppm inhibitor concentration are reproduced in **Table 5**.

Table 5. Miller Calcium Carbonate Scaling Tests.

Chemical	% Efficiency 25 ppm	50 ppm
Commercial Phosphonate	45	54
TPA	33	42

Dynamic (Tube Blocking) Tests.

Dynamic tests are used in conjunction with the static tests as a chemical evaluation tool to fine tune inhibitor concentrations required prior to field trials. The two incompatible brines (formation water and sea water) are pumped separately at pressure into a test oven. The fluids, once at temperature, mix in a T-piece and are pumped together through a 1 m long, coiled section of capillary tubing. The time taken for the tube to block (determined by the pressure differential across the coil) is recorded in the presence and absence of scale inhibitors. All results are given **in Table 6**. Under Forties conditions, without inhibitor, the tube blocks up in 30 minutes. The currently used Forties scale inhibitor at 20 ppm concentration keeps the tube open for 24 hours. TPA was able to keep the tube clear down to 6.25 ppm, where the pressure was just beginning to rise at 245 hours. At 12.5 ppm, TPA kept the tube open with no pressure increase for the 24 hour test period.

Table 6. Tube Blocking Results (Forties conditions, Barite Scale, 95 C, 250 bar, pH 6.

Chemical	Concentration	Time to Block
None		30 minutes
Forties Inhibitor	20 ppm	24 hours
TPA	12.5 ppm	24 hours
TPA	6.25 ppm	24 hours*

* Increases in Pressure indicated just failing at 24 hours.

2. Corrosion Test Data.

The performance of TPA in Forties water chemistry has been evaluated in a standard CO_2 bubble test.[3] The results of TPA vs. the best commercially available product are shown in **Figure 2**. The behavior of the polymeric thermal polyaspartate as a corrosion inhibitor is surprisingly similar to the commercial monomeric corrosion inhibitor (rapid drop in corrosion rate immediately after addition of the chemical). The level of inhibition achieved is between 80 and 85 %.

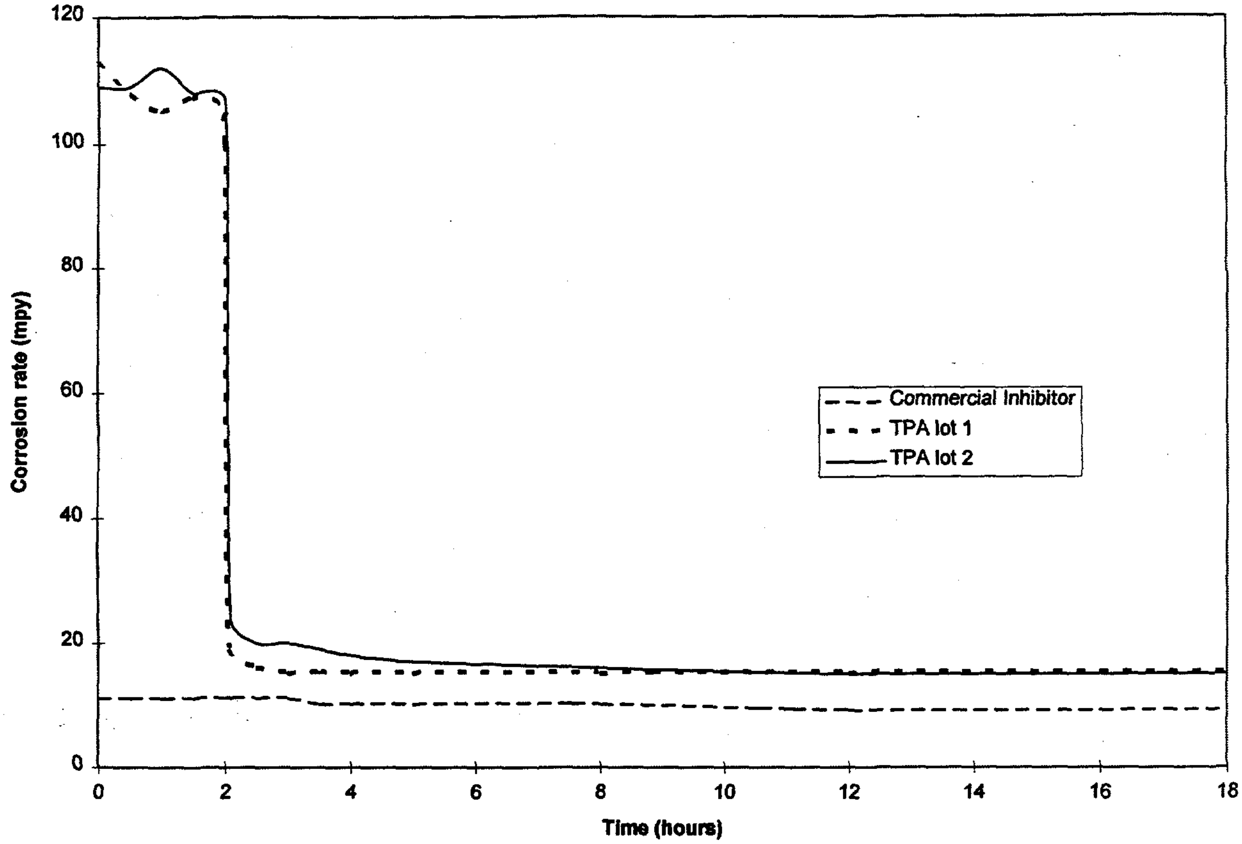


Figure 2. Corrosion Bubble Test Data.

CONCLUSIONS

Thermal polyaspartate (TPA) is a highly biodegradable, non-toxic polycarboxylate polymer having excellent scale inhibition activity, especially for use in water chemistries that are high in barium sulfate content. An added benefit of TPA is its CO_2 corrosion inhibition activity. The combination of environmental friendliness and dual functionality makes TPA an ideal candidate for use in oil production.

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