NOVEL HIGH PERFORMANCE ADDITIVES FOR ASPHALTENE CONTROL IN OIL PRODUCTION OPERATIONS

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ABSTRACT

This paper describes a unique asphaltene inhibitor development project in which the basic chemistry and product formulations are specifically designed for oil production operations. Key stages of the development project, including the description of a matrix of development products, performance evaluations in crude oils, physical property characterisation, environmental assessments and manufacturing trials, are reviewed. A new range of high performance asphaltene inhibitors, characterised by broad spectrum efficacy, ideal physical properties for deepwater deployment and low environmental impact for offshore operations, has been identified.

1. INTRODUCTION

Oilfield operators have deployed chemicals to prevent and remediate field problems associated with asphaltene precipitation and deposition over many decades. Historically, it has been most common to remove asphaltene deposits in producer wells and topsides facilities using aromatic solvents, such as xylene and toluene. However, it is ultimately more cost effective to implement a preventative strategy for asphaltene deposition, particularly in production wells where intervention and deferred oil costs significantly outweigh chemical treatment costs. Industry experts predict that an increasing number of oilfield developments, notably for deepwater operations, will look to advanced additive technology to control asphaltene related flow assurance problems.

The worldwide market for asphaltene deposition inhibitors is small in oilfield terms and very small by mainstream chemical industry standards. As such this market sector has attracted few major R&D programmes and, commonly, oilfield asphaltene inhibitors have been formulated using additive technology developed for other downstream oil industry markets. In recent years there has been a renewed interest in additives for asphaltene control with various technical papers presenting laboratory evaluation and field trials of new asphaltene inhibitors. [1 – 3]

The DART (Downhole Asphaltene Remediation Technology) JIP was established in 1996 by BP and nine major oil companies to develop an inhibitor/dispersant package to prevent asphaltene deposition in wells and reservoirs. In 2001 JD Horizons acquired a licence from BP to develop, manufacture and market asphaltene inhibitors and dispersants. The subsequent development project reviewed in this paper concentrates on one generic polymer type identified in the DART programme.

In advance of the laboratory development phase and following detailed technical discussions with DART member companies and other industry experts, a list of critical project objectives was established – see Table 1.

Table 1 Product Development Objectives

Objective
High performance asphaltene inhibition
Broad spectrum efficacy
Easy handling
Low environmental impact
Existing chemical registration
Manufacturing assets in place
Cost effective

Specifying and quantifying technical performance proved to be a difficult exercise. However, key markets, such as the Gulf of Mexico and other deepwater regions, were clearly identified as critical targets for new asphaltene inhibition technologies. In contrast many industry contacts provided very specific deliverables for oilfield deployment and environmental impact. In particular, for subsea umbilical deployment for deepwater field developments, additives must exhibit low viscosity, low pour point, high flash point and long-term hot and cold temperature stability with no evidence of insolubles in fine filtration tests. From an environmental perspective the North Sea/OSPARCOM regulatory system represents the most comprehensive assessment of chemicals utilised in the offshore oil industry, in terms of toxicity, biodegradation and bioaccumulation. High flash point aromatic solvents were selected for product formulation in preference to good technical but hazardous solvents, such as xylene and toluene.

Other product development targets reflect the need to avoid or minimise capital investment and product registration costs which could not be commercially justified for low volume, niche product markets. For this project JD Horizons has entered into a product development and manufacturing agreement with Pentagon Chemical Specialties based in Workington (UK), a specialist contract manufacturer of performance chemicals for the oil industry.

2. TECHNICAL PROGRAMME & RESULTS

The programme was conceived and implemented as a fast track development project underpinned by technical data generated in the DART JIP. The majority of the technical studies were conducted in a twelve month period from September 2001. Manufacturing trials extended from August 2002 to April 2003. Regular contacts with and development product evaluations by industry experts represented an atypical but essential feature of the product development process, designed to deliver an additive technology meeting state-of-the-art and future industry needs. The overall programme was carried out in three stages –

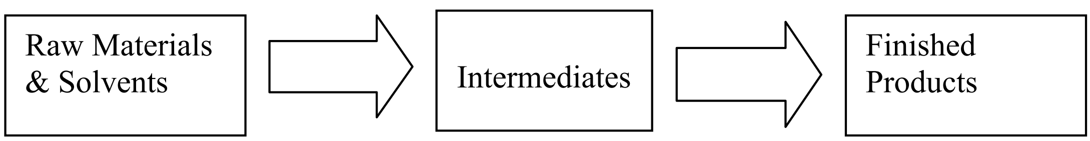
Phase I	Product synthesis and performance testing
Phase II	Pre-commercialisation study
Phase III	Manufacturing trials & product launch

Selected product candidates from a development product matrix were carried forward to Phase II based on in-house and external performance evaluations. The second phase included extended performance testing, physical property characterisation and environmental testing on high performance products shortlisted for commercialisation. Thereafter, three products were selected for manufacturing trials in support of the commercial product line launched in December 2002.

2.1 Polymer Synthesis

As indicated above the current development project relates to one generic polymer type. Confidentiality clauses within the licensing agreement provide against any disclosure of the detailed chemistry. However, the general preparation for this complex polymer chemistry may be described as a three stage synthesis scheme. Production of the base polymer raw material is outsourced. The essential technology for asphaltene control is centred on the synthesis of proprietary intermediates and derivative polymers – see Figure 1. All development products comprised 50 wt% polymer in a high flash point aromatic solvent, such as Solvesso 150 or equivalents.

Figure 1 Polymer Synthesis Scheme



Variables
- Monomers
- Solvents
- Mole ratios
- Reaction conditions
- Physical properties eg viscosity
- Manufacturing process
- By products
- Economics

A designed matrix of development products was prepared for an initial phase of performance testing to examine the relationship between polymer structure and effects against a number of key variables in the second and third stage reaction schemes. The development product matrix, outlined in Table 2, included three intermediate types with a maximum of five different derivatisation schemes. Previous experience had suggested that the final reaction stage would have the greatest impact on product performance. However, early performance testing showed that the intermediate was also an important contributor to desired asphaltene inhibition and dispersancy effects.

Table 2 Development Product Matrix

Intermediate / 2nd Stage Reaction Scheme	***Intermediates***		
	INT 1	***INT 2***	***INT 3***
Scheme A	DP 0110/1	DP 0110/4	DP 0110/8
Scheme B	DP 0110/2	DP 0110/5	DP 0110/9
Scheme C	DP 0110/3	DP 0110/6	DP 0110/10
Scheme D	DP 0110/11	DP 0110/7	
Scheme E		DP 0110/12	

In Phase I the general chemistry and properties of this generic polymer chemistry were reviewed against the overall product development objectives. Some of the key features are summarised in Table 3. In addition to excellent technical performance, this polymer type in solution is notably characterised by excellent cold flow properties, an essential requirement for offshore subsea deployment. Furthermore, the simple elemental make up (comprising only carbon, hydrogen and oxygen) and high molecular weight indicated a likely low environmental impact.

Table 3 General Chemistry and Properties

Chemistry	***Properties***
Dispersant/surfactant polymers	Non ionic
50 wt% in high flash point aromatic solvent	Oil soluble, water insoluble
Contains carbon, hydrogen & oxygen	High temperature stable
No Cl, P, N, S, or heavy metals	Low viscosity
Mw 10,000 – 20,000	Low pour point & high flash point

Regarding the downstream oil industry, the absence of selected trace elements, highlighted in Table 3, is a positive factor vis-a-vis refinery operations and makes no contribution in relation to automotive fuels and lubricants environmental regulations.

2.2 PERFORMANCE EVALUATIONS

Performance testing is a critical aspect of the entire programme from initial development product screening, through extended testing of selected candidates and quality control checks on commercial products. In recent years there have been numerous technical publications on new advanced methods for asphaltene precipitation and deposition testing for both laboratory and field application. [4 – 5] Traditional dispersancy tests using n-alkanes to destabilise crude oils and cause flocculation/deposition of asphaltenes are still widely used for additive selection although more sophisticated techniques utilising live oils in PVT cells are increasingly employed for crude oil asphaltene deposition tendency characterisation and inhibitor testing.[6]

In this project the majority of in-house performance testing has been carried out using a modified version of an asphaltene dispersancy test (ADT) employed in the DART JIP. External expert development product testing has been conducted in company proprietary methods and, in selected cases, including live oil PVT cell tests – data from external testing is not presented in this paper.

The simple ADT test protocol is outlined as follows –

- Inject 100 ul of dilute inhibitor solution into 100 ml graduated test tube
- Add known volume, eg 0.5 to 5 ml, of crude oil to test tube and mix
- Add hexane (pentane or heptane) to 100 ml assay and mix
- Incubate for minimum 3 hours at 30^{o}C
- Record volume of basal deposits
- Calculate inhibitor effect (%) vs treat rate (ppm) vs blank
- Blank test – 5 replicates; inhibitor test – 3 replicates

Stabilised crude oil samples were provided by DART JIP members for development product testing using the ADT protocol. Crude oils were sourced from producing or development fields with a history or prediction of asphaltene deposition and, in some cases, existing inhibitor treatment programmes. A total of six crude oils, from the North Sea, West Africa, Gulf of Mexico and South America regions, were utilised for screening and advanced performance testing throughout the development project. The specific field identity, detailed crude oil analyses and field operation information was not provided to JD Horizons. The crude oils were simply characterised by regional origin and an arbitrary asphaltene content - low < 1 wt%, medium 1 – 5 wt% and high > 5 wt%. Commercial asphaltene inhibitors/dispersants and a development product identified in the DART JIP were used for performance benchmarking purposes.

A large amount of performance data was generated in the initial product screening phase and subsequent testing for selected products in Phase II. Some examples of this work are presented in Figures 2, 3 & 4. The data in Figure 2 is generated in a low asphaltene content crude from a North Sea field with a history of topsides asphaltene deposition. In this case the most effective inhibitors, DP 0110/2 & DP 0110/3, provide complete removal of asphaltene flocculation with treat rates under 10 ppm, a significantly superior performance to the DART development product and a commercial product. In a medium asphaltene GOM crude oil, see Figure 3, complete removal of aspahltene flocculation is still not achieved at 1400 ppm but the best development products eg DP 0110/11, are rated superior to benchmark products. The results in Figure 4 are based on another medium asphaltene content GOM crude oil, known to be relatively insensitive to additive effects on asphaltene deposition in laboratory tests. In this study development products exhibited significantly superior performance to commercial products but, at best, only achieved 40 % inhibition of asphaltene flocculation. However, in this test there is a clear performance trend between polymer structure and effect in the 1000 ppm treat rate case.

A complete review of the test data generated in-house and by external experts in Phase I showed a remarkable and unambiguous pattern of development product performance. While all the development products demonstrated an asphaltene inhibitor/dispersant performance, the sub group based on intermediate type I and derivative schemes 2, 3 & 4 provided superior performance in virtually all crude oils and test methods employed. Indeed, development products, DP 0110/11 and DP 0110/12, were synthesised on the basis of initial test data to test this structure/effect relationship. This product sub-group has been reported as highly effective in reducing asphaltene deposition in live oil PVT cell tests.

Three products – DP 0110/2, DP 0110/3 and DP 0110/11 – were selected for the pre-commercialisation study in Phase II. Subsequent performance testing has continued to confirm the superior performance and broad spectrum activity of this product family, although no one product is superior against all asphaltenic crude oil types.

2.3 PHYSICAL PROPERTY CHARACTERISATION

As described in the introduction, ease of handling was established as a key product development objective for this programme. In particular, cold flow properties have been identified as a key physical property for offshore/deepwater deployment. Ultra-low viscosity is an absolute requirement for liquid products being deployed by continuous injection via a small internal diameter subsea umbilical over long distances at seabed temperatures.

Typical physical properties have been measured by independent laboratories using industry standard techniques and protocols. A summary of physical properties for three development products is shown in Table 4. In addition, a data set is also shown for DP 0206/5 – a 50/50 dilution of DP 0110/3 in aromatic solvent, highlighting viscosity characteristics for a typical field formulation.

Table 4 Physical Property Characterisation

Property	*Method*	*Unit*	*Product*			
			DP 0110/2	*DP 0110/3*	*DP 0110/11*	*DP 0206/5*
Polymer Content	**Weight**	**%**	50	50	50	25
Density	**IP 365**	**g/cm^3**	0.936	0.936	0.936	0.914
Viscosity @20C	**IP 71**	**cSt**	303	255	217	10.2
Viscosity @ 4C	**IP 71**	**cSt**	694	505	449	15.3
Pour Point	**IP 15**	**^oC**	< -50	< -50	< -50	< -50
Flash Point	**PMCC**	**^oC**	> 61	> 61	> 61	> 61

These products, including the 50 wt% concentrate products, are free flowing liquids at temperatures down to 4^{o} C. In addition all have extremely low pour points and high flash points. The flash point is primarily dependant on the solvent selection – in this instance the aromatic solvent selected has a minimum flash point specification of 61^{o}C. All concentrate products can be easily blended/diluted with other solvents such as xylene, toluene or other readily available hydrocarbon solvents for field deployment. It should be noted, however, that critical physical properties, such as viscosity, are dependant on the selection of diluent solvents.

The dilute product DP 0206/5 enjoys an ultra-low viscosity profile even at seabed temperature. Similar viscosity profiles are demonstrated by all 50 wt% polymer concentrate products and the dilute versions. Additional rheological studies (not shown here) confirm that dilute product versions exhibit low viscosity to temperatures as low as minus 25^{o}C and exhibit near Newtonian properties across a wide range of shear rates.

This polymer chemistry is also notable for high temperature stability. A typical thermogravimetric decomposition study in an oxygen free environment is shown in Figure 5. The weight loss curve, and its associated derivative curve indicating rate of weight loss, demonstrates that the polymer begins to degrade about 300^{o}C, with a maximum rate of weight loss around 410^{o}C. With this thermal stability profile these polymers are suitable for downhole application by continuous injection or squeeze deployment techniques.

2.5 ENVIRONMENTAL ASSESSMENTS

A full suite of environmental testing required by OSPARCOM and national regulatory bodies related to the North Sea oil industry market was undertaken at a GLP approved independent laboratory. This environmental assessment includes toxicity testing against four marine species, biodegradation and bioaccumulation tests under prescribed test protocols. A summary of the test data is presented in Table 5. This data set, in addition to other product and component information, also allows a CHARM hazard quotient to be calculated.

Table 5 OSPARCOM Environmental Test Data (DP 0110/3 & Components)

Test Type	*Species/Method*	*Result*
Toxicity	Acartia tonsa	EC_{50} (48 hours) 1,131 mg/l
	Skeletonema costatum	EC_{50} (72 hours) > 1,000 mg/l
	Scophthalmus maximus	LC_{50} (96 hours) > 1,000 mg/l
	Corophium volutator	LC_{50} (10 days) > 10,000 mg/kg
Bioaccumulation	OECD 117 Polymer	Log $P_{o/w}$ 3.6 to 5.1
	OECD 117 Solvent	Log $P_{o/w}$ 3.6 to 5.2
Biodegradation	OECD 306 Polymer	24.6%
	OECD 306 Solvent	52.9%

This product exhibits low toxicity to the four marine species included in this protocol. Indeed, only acartia tonsa recorded an EC_{50} within the normal test concentration range. The partition coefficient data for both polymer and solvent are much as expected for this highly oil soluble, water insoluble product formulation. However, due to the high molecular weight the polymer is not anticipated to be bioaccumulating. OECD 306 data indicate that both the polymer and solvent are inherently biodegradable ie 28 day OECD 306 biodegradation in the range 20 – 60 %.

Subsequently, the data set for this product (and for other members of the asphaltene inhibitor product range) have been submitted within a full HOCNF application to the UK regulatory authorities. All FlowSolve™ Asphaltene Inhibitors have been assigned the lowest hazard Gold category for application in the North Sea and other UK territorial waters. The products carry a taint warning attributable to minor components in the aromatic solvent.

2.6 MANUFACTURING TRIALS

Due to the complex nature of this polymer chemistry and the multi-stage synthesis scheme, the technology transfer from laboratory to commercial plant scale production is an essential and critical part of the additive development project. Past experience has shown that full scale plant production trials are the most effective route to establishing product and manufacturing process data required for routine manufacturing operations. As a result, small scale pilot plant trials were omitted from the scale up process in favour of a direct move to full bulk plant production trials of intermediates and finished products. It is important to note that the manufacturing process is completed by an ultra fine filtration process step.

Manufacturing trials were conducted between September 2002 and April 2003. During this period bulk quantities of key intermediates and three finished products – DP 0110/2, DP 0110/3 and DP 0110/11 - were produced in multi-tonne quantities. In addition to establishing detailed production procedures, quality control methods/specifications and detailed manufacturing costs, intermediates and finished products were subjected to additional performance evaluations and comprehensive physical property testing.

Table 6 Performance Testing (ADT) : Laboratory Synthesis vs Plant Production

Product	***Treat Rate (ppm)/Effect (%)***		
	5	***10***	***15***
DP 0110/2 Laboratory	0	68	100
DP 0110/2 Plant	2	45	100
DP 0110/11 Laboratory	8	73	100
DP 0110/11 Plant	2	97	100

Materials from production trials were subjected to standard ADT evaluations compared to laboratory preparations and other product benchmarks. A North Sea crude oil, previously seen to be very sensitive to low treat rates of additive – see Figure 2, was selected for this quality control exercise. Typical results are summarised in Table 6. For all three finished products the treat rate/effect profiles were highly comparable to laboratory synthesised development products.

Additional physical property testing confirmed that products from manufacturing trials were essentially identical to laboratory synthesised development products. Kinematic viscosity measurements have been identified as a critical physical property parameter for manufacturing quality control.

3. CONCLUSIONS

This paper describes a fast track additive development programme, based on a technology licensing agreement with BP on behalf of the DART JIP, to develop asphaltene inhibitors/dispersants for oil production operations. In particular, the product development goals have been established primarily to meet the current and future technology and operational needs for offshore & deepwater oil production.

In general, the project has met or exceeded all of the primary product development goals. While absolute technical efficiency is difficult to quantify, this novel additive technology has been shown to be highly effective in laboratory evaluations, typically demonstrating superior performance to established asphaltene dispersants. A new range of products, characterised by broad spectrum performance in asphaltene control, ideal physical properties for deepwater deployment and low environmental impact for offshore operations, has been identified and commercialised under the FlowSolve™ trademark.

Initial field and plant trials have been undertaken during 2003. It is anticipated that future technical papers will describe detailed evaluations of this new additive technology in both upstream and downstream oil industry applications.

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Figure 2 ADT Results - N. Sea/Low Wt % Asphaltene

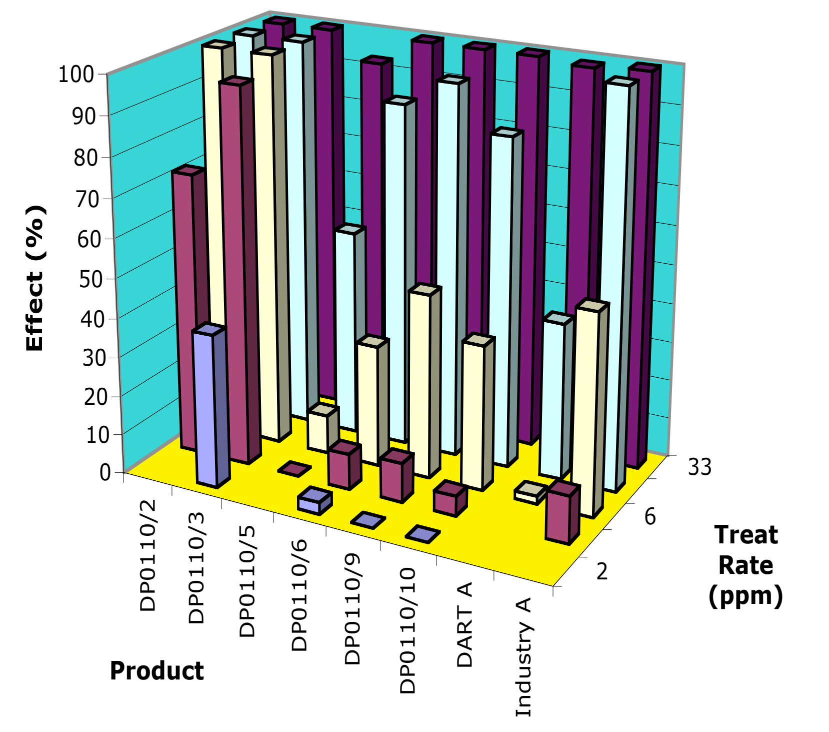

Figure 3 ADT Results - GOM/Medium Wt% Asphaltene

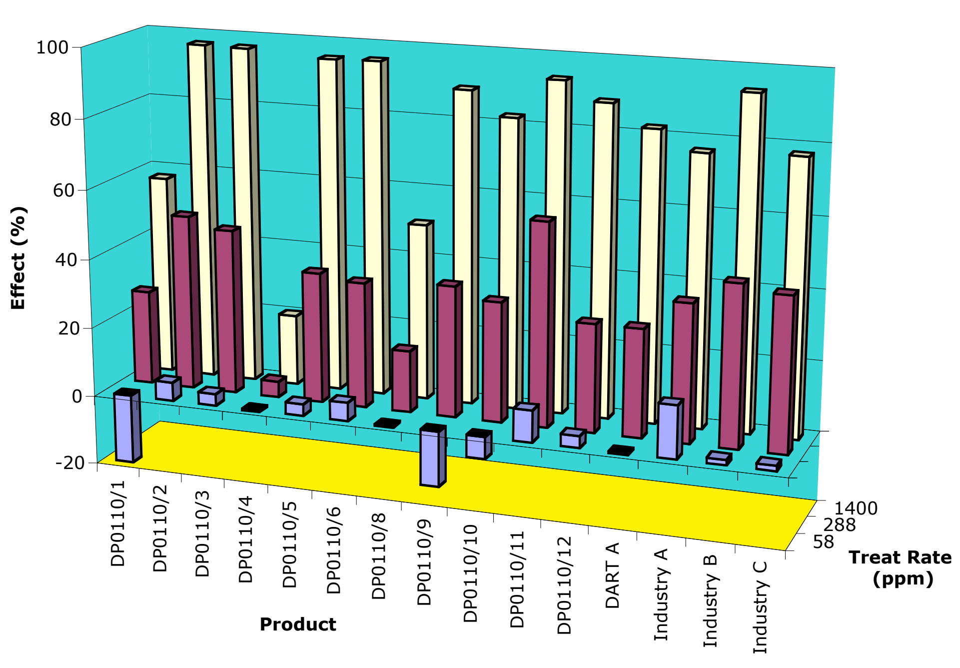

Figure 4 ADT Results - GOM/Medium Wt % Asphaltene

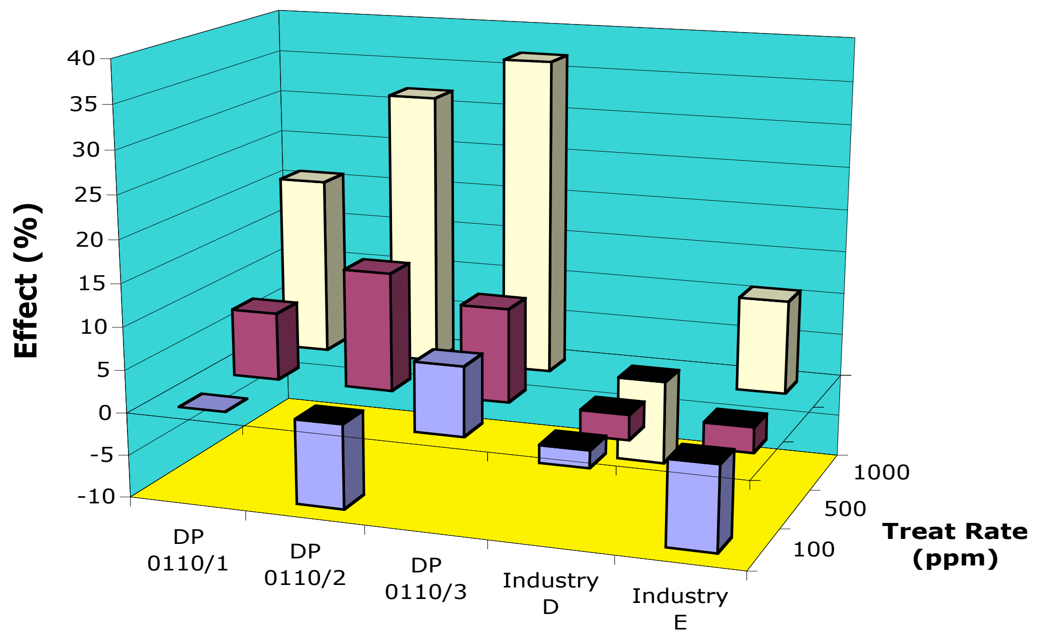

Figure 5 Thermogravimetric Analysis (DP 0110/3)