Institution: University of Hull

Unit of Assessment: B8: Chemistry

Title of case study: A break-through corrosion inhibitor technology for heavily fouled systems

1. Summary of the impact (indicative maximum 100 words)

In partnership with the US company Nalco, the University's Surfactant & Colloid Group developed a new multifunctional technology (Clean n Cor) for the oil industry that both removes accumulated deposits at a metal surface (enabling "break-through" of corrosion inhibitor to the metal surface) and inhibits corrosion. Clean n Cor technology not only protects assets such as oil pipelines against corrosion but also maximises oil production through enhancing water injectivity (water flow per unit pressure drop). Since its launch in 2007, it is currently one of Nalco's fastest growing new technologies and is used at over 100 production locations worldwide.

2. Underpinning research (indicative maximum 500 words)

Organic corrosion inhibitors with surfactant properties are widely used to inhibit the corrosion of oilfield equipment. Injected into piped liquids, they work by adsorbing at the aqueous solution-corroding metal surface where they commonly reduce the corrosion rate by >95%, thereby saving cost/environmental impact. However, their performance over time deteriorates due to the accumulation of oily deposits mixed with clays, corrosion products and biomass (so-called "schmoo") at the metal surface. The accumulation of schmoo on internal pipe surfaces not only prevents the corrosion inhibitor reaching the metal surface but also adversely affects water injectivity (e.g. by reducing the effective internal diameter of a pipe) and thereby causes problems with many oilfield operations.

The key research from Hull underpinning Clean n Cor development was in several stages. The first stage was to realise that the behaviour of surfactant-like corrosion inhibitor-schmoo-water systems follows the patterns of microemulsion phase behaviour of conventional surfactant-oil-water systems enabled the exploitation of Hull's leading work in this area. Early work (published pre-1993 and so not included here) at Hull had significantly advanced the understanding of how oil solubilisation can be maximised and how the oil-water tension can be made ultra-low by "tuning" the tendency of the adsorbed surfactant monolayer to curve – both factors are of critical importance in maximising schmoo removal from corroding metal surfaces.

Secondly, the post-1993 research that underpinned the development of Clean n Cor[1-4] investigated the inter-relationships between the solid-oil, solid-water and oil-water interfacial tensions to understand the surface chemistry relating to the removal of oil from capillaries and the adhesion of different materials to solid surfaces. It identified the key factors responsible for the adhesion of the schmoo to the metal surface and how they could be manipulated, using the understanding of microemulsion behaviour, to ensure good removal. The research described in Ref. 5 then developed a laboratory-based schmoo removal test cell which (i) enabled validation of the fundamental concepts described above and (ii) showed excellent correlation with in-field performance of the multifunctional inhibitor systems. It was used to provide a rapid screening of different complex formulations and thereby enable the product launch of the optimised Clean n Cor system.

Thirdly, although very successful in most oilfield application sites, it emerged that Clean n Cor was not sufficiently effective against the schmoos formed in some particular oilfields and Nalco commissioned further research at Hull in 2012-13 to investigate. The Hull team successfully showed that schmoo from the problem sites contained additional solid components which caused the main removal mechanism to switch from "roll-up" and emulsification (as seen in [5]) to one of solubilisation. Additional principles governing the design of Clean n Cor formulations for such problem sites were established and experiments demonstrated the enhanced performance of new formulation. This recent work is fully described in a commercially sensitive and confidential report.

The underpinning research was undertaken at the University of Hull from 1993 to 2013 by Paul Fletcher (Professor, since 1984), Robert Aveyard (Professor, 1965 to 2001), Bernard Binks (Reader 1988 to 2002, Professor 2002 to present) and John Clint (Reader 1993 to 2006).

3. References to the research (indicative maximum of six references)

(1) Displacement of oil by aqueous surfactant solutions from capillaries sealed at one end. R. Aveyard, B.P. Binks, S. Clark and P.D.I. Fletcher, Colloids & Surfaces A, 1996, **113**, 295.

(2) Adhesion under water: surface energy considerations. J.H. Clint and A.C. Wicks, Int. J. Adhesion & Adhesives, 2001, **21**, 267.

(3) Adhesion and components of solid surface energies. J.H. Clint, Curr. Opinion Colloid & Interface Sci., J.H. Clint, 2001, **6**, 28. (Although a review article, this reference is included here as it contains original analyses by Clint of data published by other authors.)

(4) "I put it in, but where does it go?" – The fate of corrosion inhibitors in multiphase systems. D.I. Horsup, J.C. Clark, B.P. Binks, P.D.I. Fletcher and J.T. Hicks, NACE Corrosion Conference 2007, paper 06717, 1-32.

(5) A break-through corrosion inhibitor technology for heavily fouled systems. D.I. Horsup, T.S. Dunstan and J.H. Clint, Corrosion, 2009, **65**, 527.

4. Details of the impact (indicative maximum 750 words)

The non-academic beneficiaries in terms of positive economic impacts from the underpinning research are Nalco – which has a successful and effective commercial product line specifically developed with the problem in mind, and its customers who use this product (Clean n Cor). Clean n Cor helps to decrease integrity risks by mitigating the potential for under deposit corrosion in production pipelines which has added benefits for the environment in reducing the instances of corrosion failures in high pressure lines and therefore ensuring a safer working environment for oilfield personnel.

Since 2008, Nalco has sold in excess of 17,000,000 kg of the product to over 300 customers including many of the super-major and major oil companies around the world. In the 5 years since 2008, the Clean n Cor technology has been Nalco's fastest growing new product. The success of the original product has prompted several additional derivative products utilizing the Clean n Cor technology to address more specific niche applications.

Clean n Cor has been used extensively at over 300 oil production locations worldwide, to impart corrosion protection in aging production infrastructure and to maximize water injectivity, with the following economic and other benefits:

- Clean n Cor is injected into fluids at very low concentrations of the active materials (40 – 100 ppm) which ensures the application is extremely cost-effective.
- From a corrosion control perspective, the technology allows operating companies to utilize lower cost steel alloys for the fabrication of injection systems thereby reducing capital costs dramatically.
- Clean n Cor also protects against corrosion from naturally occurring microbes in the system, minimising impact to the environment and protecting personnel in oilfield operations. More specifically Clean n Cor helps to minimize the deposition of solids build up in the production infrastructure and provides the protective film that mitigates corrosion. Minimizing the effects of corrosion results in less failures, and ultimately safer working conditions for employees.
- Oil companies often operate in environmentally sensitive areas and the improvement in corrosion protection will ensure the potential for pipeline failures and the resulting exposure of production fluids into the environment is minimized. This in turn assists oil and gas companies in preserving their licence to operate and protecting their corporate brand.
- Maximizing water injectivity has a dramatic impact on increasing oil and gas production and this is critical today as the global demand for oil and gas approaches the global supply curve. By cleaning the hydrocarbon based deposits that build up in injection systems, the injection differential pressure into the formation is reduced therefore allowing more water to be injected to balance crude oil production and ensure reservoir production pressure is maximized. This has resulted in increases of oil production that ranges between 50 – 100%.
- Clean n Cor also minimizes operational costs that otherwise would be incurred through having to clean out injection wells as they start to plug up over time. This is not only a savings in operational cost, but also a safety advantage. The cleaning process involves the use of heavy

machinery and employees operating on highly pressurized flow lines. Clean n Cor helps to keep the pipes clean chemically as opposed to manually.

To date, there are no other competing technologies to Clean n Cor in the oilfield market place.

Although commercial sensitivity limits the range of specific impact details that can be given here, however the significance of this development and the important role played by Hull researchers was marked by the presentation by Nalco of a plaque to the Department of Chemistry, University of Hull in December 2011. The award is "for collaboration in the area of Surfactant Science that led to the successful development of Clean n Cor".

5. Sources to corroborate the impact (indicative maximum of 10 references)

[A] Vice President, Research and Development, Energy Services at Nalco – corroborating the economic impacts of Clean n Cor for the company since 1st January 2008.

[B] *A break-through technology for maximizing water injectivity and asset integrity* – SPE Production and Operations, #108675, May 2009 – corroborating the benefits of the Clean n Cor technology.

[C] *Integrity control in heavily fouled systems – Phase II – Environmentally sustainable solutions* – D.I. Horsup, R. Meyer, L. Tiwari, T. Dunstan - NACE 2008, Paper #08623 – corroborating the benefits of the Clean n Cor technology.