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Volatile Phosphorus Free Gellants for Hydrocarbon Based Fracturing Systems

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Abstract

In recent years, a number of refineries in Western Canada and the United States have discovered the formation of scale or sludge in their distillation towers. The build up of large amounts of sludge lowers the efficiency of refineries to the point where it must be removed. The process of sludge removal requires that the refinery shut down at a cost of millions of dollars in lost production to the refinery operators. Analysis of the sludge has revealed that it has an extraordinarily high phosphorus content (8 to 12%). Further investigation into the origin of the phosphorus in the sludge raised concerns that chemicals used in hydrocarbon fracturing fluids, specifically volatile phosphorus containing hydrocarbon gellants, are responsible for the refinery fouling. This paper will discuss how the origin of the volatile phosphorus in the hydrocarbon gellants has been determined and how a viable, ultra low volatile phosphorus solution for hydrocarbon gelling has been developed.

Introduction

Hydrocarbon based fracturing fluids are used in water sensitive formations, such as those with high clay content to prevent any loss of permeability due to clay swelling or fines migration. These gels are simple to use from an operational perspective and exhibit consistent viscosity as well as excellent thermal stability. However, problems with hydrocarbon gelling chemicals in the downstream oil and gas industry are putting pressure on the use of this technology. It is, therefore, necessary that the chemisty of gelled hydrocarbon fluids be better understood so solutions to any potential problems with this chemistry be found.

Original hydrocarbon based fracturing fluids relied on the use of viscous crude oils for proppant transport. The main disadvantage of these systems, however, was that they afforded no control over the fracturing fluid viscosity other than the inherent viscosity of the base oil. As a result, there was a need to develop a fluid with a low base viscosity as well as the potential to control rheology using chemical means. To this end, sodium-soap dispersions in a hydrocarbon medium were used to produce micellar solutions with tunable viscosity (Hendrickson 1956). Due to their poor shear stability, these soap dispersions were later displaced with aluminium salts of carboxylic acids, which in turn, were replaced by aluminium phosphate ester salts which increased the temperature range over which hydrocarbon fracturing treatments could be applied (Burnham 1978). The most recent evolution of gelled hydrocarbons has involved the development of ferric iron cross-linked phosphate ester gels which are more robust than previous aluminium phosphate ester gels in terms of both thermal stability and the presence of impurities (Graham 2000).

While phosphate ester type chemicals are now the hydrocarbon gellants of choice, concerns have been raised over their role in causing sludging in refinery distillation towers. Since 1995, refineries in Alberta, British Columbia, Ontario and Pennsylvania have experienced throughput restrictions in their crude distillation towers. Inpsection of the towers revealed the build up of a scale or sludge like material which was impeding tray operation. Further analysis of this sludge material found that it had an extremely high phosphorus content of between 8 and 12% (Kennedy 1999). Work by the Canadian Crude Quality Technical Association (CCQTA) determined that phosphorus compounds were indeed the cause of sludge formation. However, not all phosphorus containing compounds were found to cause problems. Specifically volatile phosphorus compounds contained in hydrocarbon gellants were identified as responsible for the sludge formation. In this case, volatile phosphorus was defined as phosphorus species volatile from initial boiling point (IBP) to 250 °C. In order to prevent refinery fouling, the CCQTA recommended that a specification of 0.5 ± 1.0 ppm volatile phosphorus be implemented at the battery limit. Current industry solutions rely on chemistry that is not yet DSL listed and therefore cannot be applied in