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**Question 59: What is your experience with hot preheat train and heater fouling attributed to waxy crudes? What methods can be used to identify fouling that is specific to wax in crudes?**

**WEBER** [Marathon Petroleum Corporation (MPC)]

MPC has seen an increase in hot train fouling when processing light tight oils, which tend to be more paraffinic than conventional crudes. The leading theory is that, combined with conventional or heavy bitumen crudes, the crude mix experiences asphaltene destabilization. The asphaltenes then precipitate on heat exchanger surfaces, decreasing effective heat transfer and increasing pressure drop. We have done a few trials with an asphaltene stabilizer combined with an antifoulant; however, the results of that trial were inconclusive.

In another case, we were actually getting ready to start a chemical trial when the fouling leveled off, so we did not move forward with it. The point is that the fouling has been very unpredictable. We have not been able to correlate it to a specific crude or a specific combination of crudes, but the theory of asphaltene destabilization is well-documented within industry.

A second theory has to do with the deposition of heavy waxes; and then, the subsequent thermal cracking causing fouling in the preheat train. If that mechanism was suspected, we would analyze the foulant for the hydrogen-to-carbon (H/C) ratio. Obviously, a higher hydrogen (lower H/C) ratio will indicate a more paraffinic foulant. We have seen waxy fouling in the cold train, but we have not confirmed that as a fouling mechanism in the hot train.

**BRADEN** (NALCO Champion)

Paraffin wax is, of course, a long-chain-saturated hydrocarbon. The hydrogen-to-carbon ratio is typically 7:1 by chemical element analysis, which is one of the techniques Nalco Champion uses to identify the origin of the deposit. The reason is that it is on the hot side, not on the cold side. We expect waxier crude foulant in the cold-side preheat rather than in the hot-side preheat. So, Nalco Champion would want to make sure that it is waxy crude on the hot side and that the refinery obtains a sample of the deposit from the heat exchanger cleanout. Sometimes, if the refinery lets the heat exchangers cool down, the waxes will come out. Some of the waxes can have a melting point up to 90°C (194°F).

So first, identify the waxy crudes by doing a SARA analysis, which measures the concentration of saturates, aromatic, resins, and asphaltene fractions in the deposit sample. The carbon distribution is measured by gas chromatography. These studies will provide information about the crude and the percentage of the crude chain lengths and will provide information on the types of deposits are formed in the heat exchangers when using these types of crudes. I know the Bakken crude can have about 2% (and greater) of C35 as we measured it. So you do have some long-chain waxy crudes in the light tight oils. It is just a matter of identification.

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**MIKE ADKINS** (KP Engineering, LP)

You mentioned a lot about the light tight oils. I am wondering if anyone has any experience with the yellow, black crudes out of Utah.

**BRADEN** (NALCO Champion)

As was mentioned in yesterday's Keynote Address, the light tight oils, particularly Bakken, can be anywhere from clear to cloudy to black, depending on where they are produced. We find that in shipments, the wax comes out, particularly in railcars. There is a research project that is trying to solve that issue.

In the refinery, my personal experience is that you have wax deposits in the cold preheat going to the desalter. Trying to develop a program for wax deposits in the pre-heat exchangers (pre-desalter) is difficult; because normally for upstream applications, the crude is heated past its melting point. A paraffin-stabilizing agent or paraffin inhibitor is added; however, in order for the inhibitor to be effective, it must be above the melting point. So, you are trying to develop chemical programs to disperse the wax crystals and prevent the wax crystals from depositing on the walls of the pipeline. So it is an issue that we do see in the cold preheat, and we are working on it.

**SAMUEL LORDO** (NALCO Champion)

For the black and yellow wax, really the biggest issues we have seen are actually from what looks like upstream additives – bromides, in particular – that are coming out in the hydroprocessing area as bromic chloride salts. So that is a little different. Typically, we worry about ammonium chloride. Those two crudes tend to have bromine-type contamination, so you do see some issues with them.

On the heater fouling, what we now see, particularly in the crude heater – which is unusual in the refining world – is that run-lengths are going from three to four years down to three months and that they have to pig the furnace tubes repetitively.

**SALVATORE TORRISI, JR.** (Criterion Catalysts & Technologies)

Yes, it is a real technical term, "pig".

**SAMUEL LORDO** (NALCO Champion)

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We have identified the foulant as a formation of polycyclic aromatic material. This is directly related to the LTOs, so it is a little different theory than the theory of paraffin cracking and reforming. It is more of a molecular rearrangement, which makes more sense since nature likes to keep it simple. There are some effective mitigating techniques for this fouling mechanism. We observe fouling starting when the refiners start to process light tight oils at greater than 80%.

**DENNIS HAYNES** (NALCO Champion)

There has been some wax-like material that has fouled preheats. It is not common, yet it has occurred and seems to be more frequent than in the past. If the suspect whole crude is available, it may be tested for insoluble material, then thermally stressed in an autoclave and then re-tested to determine if the non-asphaltene material became insoluble due to thermal stresses and indicative of potential fouling tendency. If a sample of the foulant material is available from the process, it can be analyzed H/C ratio, solubility testing, etc. to determine if it is an asphaltenic material or more wax-like.

**GARY HAWKINS** (Emerson Process Management)

Light tight oils are an example of crudes with a high paraffinic content and high filterable solids [200 to 300 ppb (parts per billion)] that are recognized as having a high propensity for fouling in the cooler section of the preheat train and also for introducing instability of the asphaltene phase which results in increased fouling in the hotter sections of the preheat train. Refiners are investing in more pressure and temperature measurements around the heat exchangers to gain better visibility to the fouling as it happens, and the advent of wireless field devices has lowered the capital cost hurdles of adding instrumentation.

**RALPH WAGNER** (Dorf Ketal)

The SARA analysis of the deposit, the H/C ratio of each component, and elemental analysis will help characterize the extent to which paraffinic waxes are a component of the deposit. Testing the solubility of the deposit in a paraffinic solvent will further quantify the extent to which wax in the crudes is a root cause of the fouling. Chemical and blending strategies are available to mitigate the problem.

**JOHN WEBER** [Marathon Petroleum Corporation (MPC)]

MPC has observed higher fouling rates of heat exchangers in the hot train correlated with an increase in processing light tight oils. These crude oils tend to have a higher wax content and lower asphaltene content than conventional crudes. Within the industry, two proposed theories for this elevated fouling are asphaltene destabilization and heavy wax deposition.

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Asphaltene destabilization has been well documented within industry and is thought to be caused by crude incompatibility between the LTOs and conventional oils and/or heavy bitumen crude types.

Another theory involves the deposition of heavy/high melting point waxes in the hot train. The waxes are thought to thermally crack, then polymerize, and subsequently foul exchangers and heaters. Higher H/C ratios in the foulant would be expected from this fouling mechanism versus asphaltene fouling. While paraffin wax fouling in cold train has been well documented, this fouling mechanism has not been confirmed in the hot train within MPC's experience.

### **MICHAEL BRADEN** (NALCO Champion)

Paraffin wax produced from crude oil consists primarily of long-chain, saturated hydrocarbons (linear alkanes/n-paraffins) with carbon chain lengths of C18 to C75+, having individual melting points from 40 to 70°C (104 to 158°F); and in some cases, up to 90°C (194°F).

High melting waxy crudes can cause deposits in the cold heat exchangers (prior to the desalter unit) and have been found in the desalter rag layer when the desalter temperature is not high enough to melt the wax.

Waxy crudes are identified by having an H/C ratio of 7 or less as determined by mass spectrometry. (As an aside, gums can have an H/C ratio of 7 to 12; resins have an H/C ratio of 8 to 9; asphaltenes have an H/C ratio of 9 to 12; an H/C ratio of 12 to 17 is oxidized and/or dehydrogenated organics; and coke has an H/C ratio of >17.)

Identification of waxy crudes begins with a current crude assay, SARA analysis and carbon number distribution by gas chromatography (GC). This will provide information about the crude and the percentage of carbon chain lengths of the crude.

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