

Changing perspective

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Refiners are changing their perspective on the best way to take advantage of low cost high acid crudes. Some who have relied solely on metallurgy to protect against naphthenic acid corrosion are now starting up chemical programs. Others are reevaluating existing chemical programs to improve safety and reduce risk. Those planning to wait on using high acid crudes until installation of improved metallurgy are reevaluating this strategy. Profits lost by waiting can be hundreds of millions of dollars; most of that potential profit can be realised using chemical programs. Refiner confidence in new technology is driving the change.

Capital vs operating costs

Due to their inherent corrosivity, high total acid number (TAN) crudes (crudes containing high levels of naphthenic acids) are priced at a significant discount to benchmark crudes. It is estimated that worldwide production of high TAN crudes will increase from 1.2 million bpd in 2000 to 4.5 million bpd in 2020.¹ High TAN crudes represent a profit improvement opportunity of billions of dollars per year, globally.

Three common ways to benefit financially from high TAN opportunities are:

- Carefully evaluate the TAN limits of existing metallurgy and operate more consistently at the safe limit without equipment modifications or use of corrosion inhibitors.
- Same as Option 1 and invest in improved metallurgy to further increase TAN and operate without corrosion inhibitors.
- Same as Option 1 and operate with corrosion inhibitors and further increase TAN with existing metallurgy; incrementally invest in metallurgy when cost justified on reducing chemical and monitoring costs.

The incremental investment in metallurgy involves long lead times and significant capital. The opportunity cost of waiting for the shutdown to install the metallurgy can be hundreds of millions of dollars for a medium sized refinery. Competition for capital for other projects is significant and the long term financial return is uncertain because of unpredictability in the amount of the future discount for high acid crudes.

Chemical costs vary due to many factors, but a rule of thumb is they will typically range between 2 - 6% of the crude discount. When considered in light of the larger variation in crude discount, corrosion inhibitor costs are not driving the decision. Chemicals can be implemented quickly and without

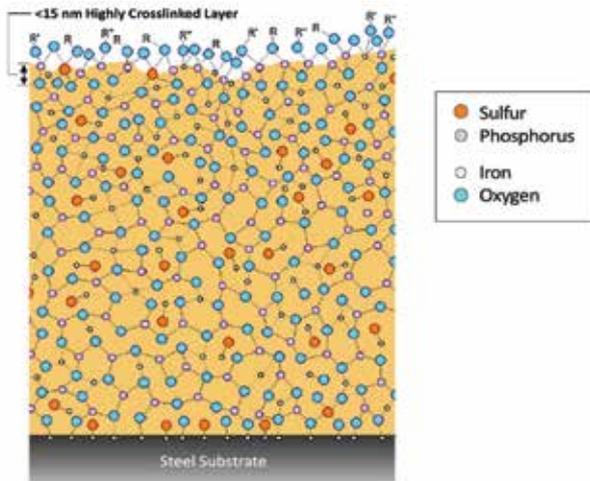


Figure 1. Protective layer formed by corrosion inhibitor.

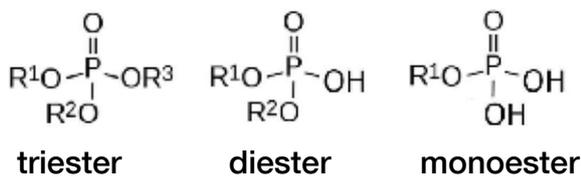


Figure 2. All phosphate esters are not equal. Mono and diesters are acidic. Triesters are neutral.

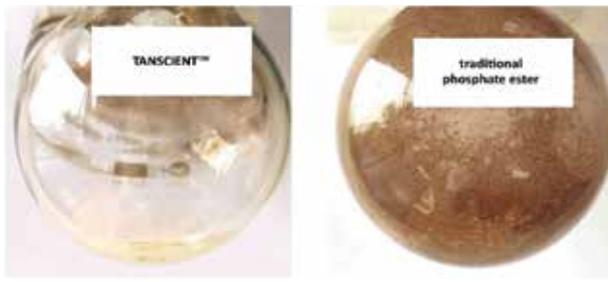


Figure 3. Clear differences. Flasks compare traditional phosphate ester versus new chemistry after 2 hr heat soak test.

a shutdown, adjusted with changing TAN or turned off if the high acid crude is temporarily unavailable or if discounts unexpectedly drop.

Despite these advantages, use of chemicals to increase TAN limits of existing metallurgy is resisted in many cases. Although chemistry is clearly a cost effective option, corrosion control programs are often perceived as having risks that outweigh financial benefits. If control of corrosion is lost, equipment can be damaged and potentially fail. Products of corrosion can foul catalysts. Traditional phosphate ester chemical programs use high levels of phosphorus and increase the risk of fouling downstream hydroprocessing operations.

Case study

New chemistry based on technical insights can address important weaknesses in current product offerings. Dorf Ketal's TANSCIENT™ product offering is an example of this insight.

Protective layer with corrosion inhibitors

Control of naphthenic acid corrosion requires the formation of a protective layer comprised of phosphorus, sulfur, iron and oxygen with a thin highly cross linked organic layer at the surface² (Figure 1).

The 'delivery system' for the phosphorus and oxygen is with the corrosion control chemical, sulfur is either in the crude oil or part of the corrosion inhibitor chemistry. The chemistry of corrosion inhibitors currently in use are predominantly of a class of compounds that are called phosphate esters.

Phosphate esters are phosphorus (P) compounds with groups attached as shown in Figure 2 ('O' for oxygen, 'R' for hydrocarbon.)

Phosphate esters currently in use are a mixture of mono and diesters. Mono and diesters have high acidity, TAN > 100, while triesters are effectively neutral. In addition, current formulations are thermally unstable due to the inherent acidity of the P-OH. Under temperature conditions in use, they rapidly break down into insoluble particulates that are not effective in building the passivation layer. That is, only a fraction of the traditional phosphate ester product remains soluble in the oil to chemically react in the passivation layer. Precipitated phosphorus degradation product introduces potential for harm in downstream equipment from catalyst poisoning and/or fouling. The byproducts of both the thermal degradation product and the intact phosphate ester introduce high acidity into the system with potential for harm. This is especially important during the passivation step when the acidity from high product dosages can dislodge existing surface scale components.

New chemical technology eliminates these concerns. The TANSCIENT product is a triester eliminating the concern from acidity.

Thermal stability and oil solubility

The design of the 'R' groups shown in Figures 1 and 2 enhances thermal stability and oil solubility of the phosphate ester. TANSCIENT™ uses a unique synthesised hydrocarbon (R group). This extra manufacturing step raises the thermal stability and oil solubility beyond current performance levels. The properties developed from combining a triester with a synthesised hydrocarbon increases phosphorous efficiency and allows lowering treatment rates of phosphorus by up to 80%, dramatically reducing concerns about corrosion control and downstream fouling. These improvements are changing the refinery perspective on use of high acid crudes.

Figure 3 shows the results of TANSCIENT product containing 1.2% P versus a traditional phosphate ester containing 7.5% P at equal starting dosages in oil (1% by weight) exposed to a heat soaking test at 290°C (554°F). At the end of the 2 hr test, the oil was removed and soluble phosphorous levels were compared to starting levels. The traditional phosphate ester is not thermally stable; 97.3% of the initially added phosphorous was no longer soluble, blackish deposits adhered to the flask. The comparative cleanliness of the flask with TANSCIENT is apparent, only 4.2% of the initial P was no longer soluble after two hours.

Figure 4 is another stability test to show the speed of thermal degradation. In this test, the starting dosage for each

of the products was equal on a phosphorus basis at 20 ppm, the oil contained TAN of 1.0 of Nap acid. After 5 min, a sample of the material was taken from the flask, quickly cooled to stop the thermal degradation, and then tested for soluble phosphorus. Additional samples were taken over the 2 hr duration of the test. The first sample, at 5 min, shows that more than 50% of the 'P' from the traditional phosphate ester is lost due to precipitation. After about 30 min the thermal degradation leveled off at approximately 80%.

By comparison, TANSICIENT is thermally stable.

Corrosion control

Figure 5 shows laboratory data comparing a TANSICIENT product (1.2% P) with a traditional phosphate ester (7.5% P) tested under severe conditions: 11.3 TAN at 290°C (554°F) in a 4 hr static test with a baseline corrosion rate of 436 mpy. The x axis shows various levels of phosphorus tested with the y axis showing the percentage reduction in the baseline corrosion rate. Dosages here are much higher than required in field conditions; the test is design to illustrate that relative difference in phosphorus efficiency. Comparing TANSICIENT at 3.6 ppm with the traditional phosphate ester at 13.9 ppm, the TANSICIENT has better protection with 75% less phosphorus.

Figure 6 is a short duration dynamic test designed to show the speed and efficacy of passivation dosages under stress conditions. The passivation is done for 4 hr and the passivated coupon is exposed to 5 TAN at 345°C (653°F) with a product dosage of 50 ppm, also for 4 hr. The only variable was passivation dosage. The table converts product dosages to ppm P. In all tests, the dosages of TANSICIENT based on phosphorus are 1/6 the dosages of phosphorus for the traditional phosphate ester. In all cases, the corrosion rates on TANSICIENT are lower; passivation is stronger at 1/6 the phosphorus level.

Risk of fouling

A small fraction of the phosphorus added with traditional phosphate esters is effective for corrosion control, where is the unaccounted material? Traditional phosphate esters are noted for fouling potential in the crude column resulting in increased tower pressure drop with potential for limiting throughput. The Canadian Association of Petroleum Producers has established a specification of 0.5 wppm volatile P in response to a phosphorous fouling study conducted by Canadian Crude Quality Technical Association.

Fouling is not only limited to the crude tower but also in the associated pump around circuit exchangers. Due to the poor stability of iron phosphate scale formed by traditional phosphate based chemistry, scale tends to get dislodged from metal surfaces subjected to velocities and wall shear stress. This dislodged scale fouls the heat exchangers thereby reducing heat transfer rates. Phosphorus and iron can accelerate coking in areas with higher temperature, for example vacuum tower beds.

Many refiners have incorporated hydrotreaters in order to meet the fuel specifications due to the stringent environmental regulations. High phosphorus content in the traditional phosphate ester may impair the downstream unit catalyst increasing fresh catalyst addition and may potentially foul the hydrotreater, decreasing the run length of the unit. If

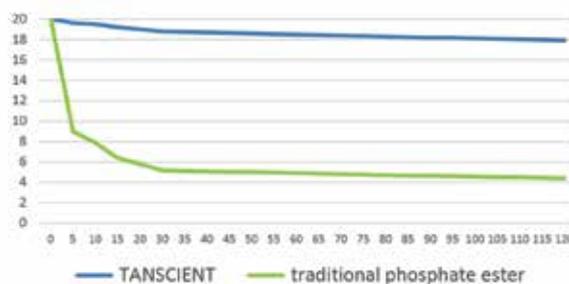


Figure 4. Thermal stability comparison. P (ppm) versus time (min).

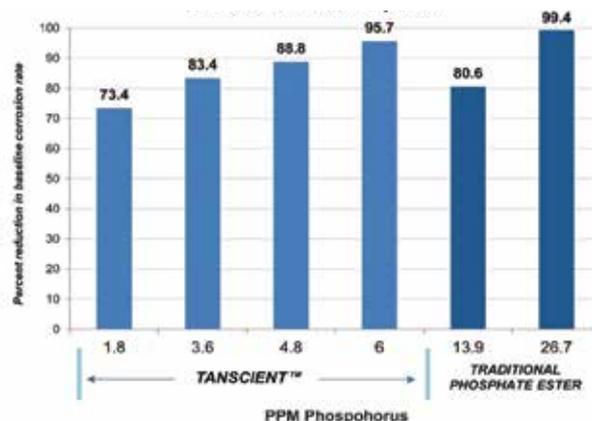


Figure 5. Corrosion control comparison.

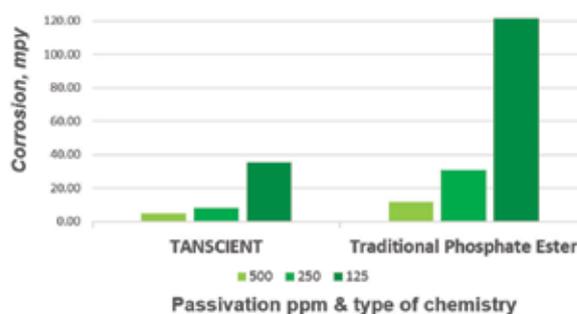


Figure 6. Passivation performance comparison (see Table 1 for details).

Table 1. Dynamic test data at 345°C for 4 hr, TAN = 5 mg KOH/gm, 50 ppm product maintenance dosage

Product passivation dosage	PPM P with TANSICIENT	PPM P with traditional phosphate ester
125 ppm	1.5 ppm	9.4 ppm
250 ppm	3.0 ppm	18.8 ppm
500 ppm	6.0 ppm	37.5 ppm

control of corrosion is lost, equipment can be damaged and harmful products of corrosion such as iron naphthenate can foul hydrotreater or other unit catalysts under prevailing conditions in those units (soluble iron naphthenate quickly reacts to form iron sulfide that deposits in the catalyst bed).

The incremental risks of using unnecessarily high phosphorus levels in traditional phosphate ester programs are not always perceived at the conceptual stage when a corrosion control program is being evaluated. The risk of fouling is difficult to quantify, but has been significant enough to cause expensive problems over time and discourage some refiners from using corrosion inhibitors.

TANSCIENT controls corrosion with up to 80% less phosphorous added, dramatically reducing the need for refiners to expose equipment to fouling risk.

Treat rate comparisons

Current treat rates with traditional phosphate esters are typically in the range of 0.7 - 5 ppm of P.

The amount of P required to obtain equal corrosion protection with TANSCIENT is approximately 0.1 - 0.5 ppm P. For refiners desiring very low corrosion rates or operation at higher TAN, TANSCIENT offers the option to increase treat rates without concern about the impact of high phosphorus levels. This also offers greater flexibility to respond to a sudden spike of TAN or loss of passivation. For refiners using high TAN sporadically, TANSCIENT offers more flexibility to safely build passivation layer with minimum impact on existing surface chemistry.

Conclusion

It is widely accepted that corrosion control reactions to protect against naphthenic acid corrosion requires the development of a robust relatively non-permeable scale. Historically, the most successful inhibitors have been based on soluble phosphorus and sulfur. Up until now, this has been typically achieved by dosing with phosphate ester formulations (mixture of mono and diesters) that deliver the phosphorus to the metal surface in forms that are both thermally unstable and highly acidic. Only a small fraction of the phosphorus added with traditional phosphate esters is effectively reacting with the surface. Most of the phosphorus is unable to stay oil soluble and thermally stable and is a potential foulant.

New options are available to increase the margin of safety without fear of fouling, increasing equipment life and reversing old perceptions about the risk of chemical programs. Greater confidence in chemical programs changes refinery perspective on the need to 'metal up', improving capital efficiency. 

References

1. *Study on oil refining and oil market prepared by Purvin and Gertz Inc. for European Commission.*
2. KIM, B., MOURHATCH, R., ASWATH, P.B., 'Properties of tribofilms formed with ashless dithiophosphate and zinc dialkyl dithiophosphate under extreme pressure conditions', *Tribology International*, 2010.