New coatings to support the oil & gas industry in challenging environments.
By Lee Spoor, Sherwin-Williams Protective & Marine Coatings.

Oil and gas companies are drilling deeper, at higher temperatures and pressures than ever before and need new coatings to perform under these conditions. A new phenolic novolac resin system shows potential as a single-coat, quick-cure coating. Properties such as high acid resistance and toughness mean the coating can support a broad range of cargo, making it even more attractive to customers as a single solution.

As many offshore oil & gas wells/fields move closer to the end of their anticipated lives, new and modern techniques and processes are being employed to extract more hydrocarbon assets from these fields than was first anticipated. Once the initial reserves have been exhausted, the oil & gas companies often have to drill deeper into the seabed to find new or further reserves. Drilling deeper usually means that the oil is hotter and under higher pressure, placing a greater strain on all of the technologies associated with the extraction and processing of the hydrocarbons from the seabed. The higher temperatures and pressures also affect the internal linings, which are used to prevent the corrosion of piping, vessels, tanks and processing equipment.

**ALTERNATIVE TECHNOLOGIES ARE NEEDED TO PRODUCE HIGH-TEMPERATURE HIGH-PRESSURE (HTHP) COATINGS**

Current trends tell us that the temperature and pressure exposures during oil extraction are only increasing. Resistance to hydrocarbon temperatures of 150 °C and above and/or pressures up to 2000 psi are now a common requirement for a coating or lining to be used in these applications. Immersion in crude oil and water produced at these temperatures can be required for some tanks or vessels, and immersion in sea water for external coatings for subsea use have also been discussed. This also brings into play the fact that the coating may need to be compatible with cathodic protection, a feature that is not necessarily a given for coating performance.

Interestingly, in the latest revision of the NORSOK standards (rev 6), the subsea system 7 has been altered to incorporate different scenarios, one of which is a higher temperature system for immersion. System 7C has now been created to cover the immersion of carbon steel at >50 °C, which highlights the need for these types of paint specification in the industry.

These changes mean that the role of protective coatings is under greater scrutiny as they are forced to deal with the higher temperatures and pressures. High temperatures and/or high pressures exert a huge stress on linings and coatings, which then forces paint manufacturers to develop newer technologies to cope with these onerous conditions. Epoxy-based coatings are tried, tested and well understood within the coatings industry. Typically, most ‘standard’ epoxies would not withstand immersion at temperatures greater than 60-80 °C, so alternative technologies need to be considered. Historically, phenolic/novolac epoxies have been used for these types of situations, although the top end immersion performance of some of these can be limited to around 99 °C.

The same applies when considering high-pressure systems. All coatings have some degree of porosity, so higher pressure has a tendency to force more air particles or fluids into the paint film, potentially causing premature breakdown. Creating a more highly cross-linked film, combined with correct pigmentation, can help to produce a much
RESULTS AT A GLANCE

→ A new high temperature, high pressure (HTHP) lining was tested to ensure it would withstand the challenging conditions a lining will face in the oil and gas industry.

→ When cured at ambient temperature the HTHP lining could be returned to service within 24 hours and had strong intercoat adhesion.

→ After being immersed in simulated seawater the only changes to the coating were colour and gloss and there was no impact from immersion in DI water.

→ Testing showed that after curing, the lining can be used with strong acids.

HIGHLY RESISTANT TANK LININGS INCREASE STORAGE FLEXIBILITY

Downstream asset owners, including storage terminals, have expressed the need to have a degree of flexibility over their tanks, and the ability to swap and change cargos from tank to tank is being seen as an increasingly attractive proposition, effectively ‘future-proofing’ the tanks’ internal lining system. By investing in a lining with resistance to all potential commodities and temperatures, storage terminal owners are able to adapt to their clients’ needs and react at short notice to store cargos without needing to re-line the tanks.

Storage flexibility ultimately means being able to cope with some of the more aggressive cargos and so a robust coating needs to be selected in conjunction with the owner’s requirements. The other advantage is that this provides a single solution to keep things simple, which is another message that is being signalled to coating manufacturers.

ONE-COAT APPLICATION AND CURE SPEED ARE CRUCIAL TO INCREASING EFFICIENCY

The other aspect to consider is the lining of such tanks or vessels on site. Often, tanks need to be relined as soon as possible to prevent costly...
downtime and to reduce the project duration, which minimises costs. This is especially true in refurbishment projects. Fast-curing coatings are becoming increasingly popular as these enable tanks to be returned to service within 24 hours of application. The paint film cannot normally be inspected until the film is sufficiently cured and hard enough to resist an inspector walking on the film or carrying out standard inspection tests. These may be as simple as dry film thickness (dft) readings or a potentially damaging adhesion or holiday detection test.

Apart from the curing speed itself, another feature that can help quickly return a lining to service is being able to apply it in a single coat. Good painting practice would suggest that the likelihood of having low areas of dft would be minimised by being applied in two coats – the theory being that should there be a low area after the first coat, it is likely that the second coat will cover this and build up an acceptable thickness. With recent advancements in lining technology, good lining systems with a flexible dft range have been developed to enable the system to be applied in one coat. This helps reduce application time and avoids overcoating issues such as maintaining cleanliness between coats, and applying the second coat too soon or too late. The use of linings with no additional solvents in the formulation helps as this reduces the chances of pinholes or voids and also prevents solvent entrapment. As always, a good inspection regime and attention to quality should help ensure a defect-free film.

**ULTRA-HIGH SOLIDS PRODUCTS OFFER SAFETY AND DURABILITY**

A key property is the ability to apply the coating to the specified thickness without the risk of sagging or runs. This allows the applicator plenty of scope for over-application without causing any defects produced by a high film thickness. It should then be possible to apply such a coating at high film thickness without affecting its performance in its given environment and conditions. A higher film thickness does not necessarily equate to better or longer performance, as some coatings become more brittle and may crack, particularly under onerous conditions. A ‘flexible DFT’ single-coat lining system has to tackle this challenge by providing adequate film flexibility and cohesiveness, even at higher dry film thicknesses. Another issue to consider is that of safety, particularly with tanks or vessels that would be classed as confined spaces under health and safety legislation. Solvent-borne coatings are becoming less desirable due to the extra precautions and measures required to deal with them, and so the use of solvent-free or ultra-high solids products is becoming the norm. A few of these ultra-high solids products have the added benefit of providing inherently better edge coverage due to the naturally higher viscosity compared with traditional solvent-borne products. The higher the film thickness at the edges, the greater the expected durability of the coating in these areas, and consequently, the greater the longevity of the coating.

A NEW BREED OF LINING FORMULATIONS SHOWS EARLY SUCCESS

In response to the changing needs described above, the use of glass and ceramic particles in conjunction with a novel phenolic novolac resin system has led to a new formulation platform for coatings that are capable of withstanding higher pressure, higher temperatures, and a broader range of cargo. This platform also enables a quick-curing, single-coat application for a faster return to service. As well as providing a better barrier (a more ‘tortuous path’) for any moisture or chemical present in the cargo to migrate through the film, the ceramic and glass particles help by providing toughness and moderating the mismatch in the coefficient of thermal expansion with steel substrates. The novel novolac resin system is key to providing the additional film cohesiveness and film-forming quality, fast curing, user friendliness and compatibility with single coat application.

The new technology platform is now being translated into real products. The first such ‘next generation’ HTHP lining has been well received since its market launch in 2013, finding multiple (and growing) applications, from HTHP process water vessels to high temperature crude storage. Expansion of the platform to the demanding subsea processes arena is expected soon. This HTHP lining has already made inroads into the North American market since its launch in that region, being particularly welcomed by customers looking to protect storage tanks, vessels and piping in sec-

### Table 1: Cure study of the new HTHP lining, Nova-Plate 325.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Test</th>
<th>6 hours</th>
<th>1 day</th>
<th>2 days</th>
<th>3 days</th>
<th>7 days</th>
<th>8 days</th>
<th>14 days</th>
<th>21 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nova-Plate 325</td>
<td>Δ DFT (µ)</td>
<td>170</td>
<td>30</td>
<td>13</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Nova-Plate 325</td>
<td>Shore D</td>
<td>63</td>
<td>80</td>
<td>83</td>
<td>N/A</td>
<td>B3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Nova-Plate 325</td>
<td>Barcol</td>
<td>24</td>
<td>26</td>
<td>30</td>
<td>N/A</td>
<td>32</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A: Coating already cured after 24 hours based on limited change in dft and hardness.

### Table 2: Recoat study of Nova-Plate 325.

<table>
<thead>
<tr>
<th>Panel</th>
<th>Tested</th>
<th>1 coat system</th>
<th>1 day recoat</th>
<th>2 days recoat</th>
<th>7 days recoat</th>
<th>14 days recoat</th>
<th>21 days recoat</th>
<th>28 days recoat</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>DFT (µ)</td>
<td>787</td>
<td>622/391</td>
<td>597/239</td>
<td>554/384</td>
<td>582/203</td>
<td>607/384</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average pull-off tensile strength (psi)</td>
<td>3943</td>
<td>2922</td>
<td>4024</td>
<td>&gt;4079</td>
<td>3916</td>
<td>&gt;4079</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average mode of failure</td>
<td>Cohesion</td>
<td>Cohesion in topcoat</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>DFT (µ)</td>
<td>762</td>
<td>706/358</td>
<td>643/251</td>
<td>605/333</td>
<td>533/361</td>
<td>653/333</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average pull-off tensile strength (psi)</td>
<td>&gt;4079</td>
<td>3888</td>
<td>3997</td>
<td>&gt;4079</td>
<td>3984</td>
<td>&gt;4079</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average mode of failure</td>
<td>Cohesion</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td>Cohesion in primer</td>
<td>Adhesion between coats</td>
</tr>
</tbody>
</table>
The HTHP lining was applied by plural application to hot-rolled steel panels. Following applications, panels were tested for cure, recoat times using adhesion testing, cathodic disbondment, and immersion testing in simulated seawater and DI water. All tests were conducted with a one-coat system of each test, with the exception of recoat testing, which was tested for a two-coat system.

Panels were also tested after 24 and 48 hours’ cure in 80 per cent and 87 per cent sulphuric acid, along with 37 per cent hydrochloric acid, for six months.

**EXPERIMENTAL**

**Cure within 24 hours**

The system was checked for cure at ambient temperature (Table 1). It was concluded that the HTHP lining had fully cured in approximately 24 hours, confirmed by testing after 48 hours via the limited change in DFT and hardness.

**Good intercoat adhesion**

Panels were recoated at one, three, seven, 14, and 21 days, and then tested for adhesion using a self-alignment adhesion tester. The lining showed good intercoat adhesion through 21 days (Table 2).

**Cathodic disbondment**

Coatings cured at ambient temperature were tested 14 days after applications were completed. Testing was conducted per ASTM G8, with 6” x 12” x 1/8” panels, in the following electrolyte: 1% w/w of sodium chloride, sodium carbonate, and sodium sulphate in DI water. Each panel was attached to a magnesium anode, and all of the panels exhibited an average voltage drop of -1.38 V vs. Ag/AgCl reference electrode throughout the 30 day test. Following 30 days of testing, the panels were radial scribed around the holiday, and the coating was picked at with a knife.

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**Table 3: Results of CD testing Mg anode, ambient.**

<table>
<thead>
<tr>
<th>System</th>
<th>Panel</th>
<th>DFT (µ)</th>
<th>Average disbonded radius (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nova-Plate 325</td>
<td>A</td>
<td>699</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>655</td>
<td>7.0</td>
</tr>
</tbody>
</table>

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There will be greater demands on linings to cope with greater temperatures and pressures."

3 questions to Lee Spoar

Do you think that coatings must be even more heat and pressure resistant in the near future? In my own opinion, yes. As mentioned in the report, the trends are definitely on an upward curve and so I think that there will be greater demands on linings in the future to cope with greater temperatures and pressures that are being utilised in the extraction and processing of oil/gas.

How corrosion resistant is the new coating? The new coating has very good corrosion resistance. This is essential for a coating that must protect the steel in the event of a disruption of the film – normally in the form of damage. Cathodic testing has shown good resistance to undercutting from the scribe aided by excellent adhesion to the substrate.

What further application fields are feasible for this coating? This product has also been tested and approved according to NORSOK M501 Rev. 6 System 7C for elevated temperatures in sea water immersion, so the potential for high temperature subsea immersion is now realised. The coating’s key properties are high temperature and pressure resistance, good resistance to abrasion and good chemical resistance. Applications where these conditions are an issue would provide potential for use.

The HTHP lining showed an average disbonded radius of 8.3 mm (Table 3, Figure 1).

No ill effects from immersion
The system had two panels that were 2/3 immersed in DI water and two panels that were 2/3 immersed in simulated seawater, in 2 litre glass jars at 99 °C in a hot water bath, for six months. Following testing in DI water, no effect on the HTHP lining was found. The only direct effects of the immersion testing in simulated seawater were some colour and gloss changes. (Table 4, Figures 2 and 3).

Acid resistance
For this testing, both sides of the panels were coated with a single application of the HTHP lining: one side was given a second coat the following day to achieve both 24 and 48-hour cure times. The coating was applied to reach a dry film thickness range between 500 and 1,000 microns. Results showed that after six months of immersions in both sulphuric acid (see Figure 4) and hydrochloric acid, the coating performed well at both 24 and 48-hour cure times, with no blisters or etching of the system, only heavy discolouration was observed.

A NEW LINING THAT OFFERS GREAT POTENTIAL FOR CHALLENGING ENVIRONMENTS
When cured at ambient temperature, the HTHP lining can be returned to service within 24 hours (for certain HTHP scenarios). When cured in this way, the lining exhibited strong intercoat adhesion when recoated up to 21 days. Other beneficial results were minimal cathodic disbondment, with an average disbonded radius of 8.3 mm, and no observable change in the coating other than colour and gloss when immersed in simulated seawater. When immersed in DI water for 6 months, the lining showed no effect. The HTHP lining can be put into strong acid service (i.e. 87% sulphuric acid and 37% hydrochloric acid) after a 24-hour cure period.

Table 4: Results of immersion testing at 99 °C.

<table>
<thead>
<tr>
<th>System</th>
<th>Panel</th>
<th>DI water immersion</th>
<th>Simulated seawater immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DFT side X (µ)</td>
<td>DFT side Y (µ)</td>
</tr>
<tr>
<td>Nova-Plate 32S A</td>
<td>640</td>
<td>627</td>
<td>No effect</td>
</tr>
<tr>
<td>B</td>
<td>678</td>
<td>668</td>
<td>No effect</td>
</tr>
</tbody>
</table>
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