Environmentally Friendly Fluoropolymer Coatings for Oil field Applications

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Abstract

In the mid-1990s, new environmental restrictions forced changes in many industries, but especially in offshore drilling and metal finishing. These changes required modifications to fluoropolymer coatings then in use that would improve chemical resistance and lower volatile-organic-compound emissions. Today, after more than 5 years in service, the new coatings have actually proven to be an improvement over their solvent-borne predecessors.

Background

Fluoropolymer coatings have been used in the oil-drilling and chemical-processing industries since the late 1960s. Applications include fasteners, valves, wellheads, blowout preventors, and downhole tools. These coatings provide low coefficient of friction with good chemical/corrosion resistance. They are applied at 1 mil, nominal, per coat and cured in an oven at 450°F. (Phosphate conversion coatings as a pretreatment are often added when coating carbon steel.) The early coatings were, high in VOCs because the carrier was organic solvent. The also had poor resistance to bases and caustics.

Introduction

The fluoropolymer coatings used in offshore drilling ran into problems around 1995, when the industry started using control fluids based on non-hazardous propylene glycol (replacing hazardous ethylene glycol). These fluids contained a corrosion inhibitor that raised the pH to 9 or higher. About the same time, deeper drilling led to an increase in wellhead temperatures, in some cases to as much as 400°F. The powerful combination of high pH and temperature caused commonly used fluoropolymer coatings to dissolve.

Meanwhile, the Environmental Protection Agency (EPA) imposed tougher guidelines for air quality. The new emission limits affected many industries, in the amount of Volatile Organic Compounds they could emit from their facility on a daily basis.

Industry turned to the manufacturers of fluoropolymer coatings. There was an urgent and immediate need to formulate coatings that retained the performance of the existing products, but with better chemical resistance and with lower VOCs.

New Formulas

Waterborne fluoropolymer coatings are not new. Waterborne coatings were used primarily for consumer products associated with food contact. However, these coatings were designed as a release agent for food products, they did not meet the requirements of the oil and chemical process industries.

Manufacturers of coatings used their experience with the food-contact products to adopt the technology to develop coatings for industrial applications. In 1998, the first of the new family of waterborne low-VOC fluoropolymer coatings went on line at numerous coaters in the Houston area. It was not long before it was proven the new formulas (1424/524) performed as well as the old ones (1440/Med Blue and 1014/524), but had better chemical resistance (Table 1), improved salt-fog resistance ASTM B-117 (1) (Figure 1) and better Kesternich Din 50018(2) performance (Figure 2). Soon, major oil tools companies changed their specifications from the old solvent-borne coatings to the new waterborne formulas.

The Negative

The major drawback for the new waterborne coatings is their use temperature. Solvent-borne coatings can withstand temperatures from -426°F to +500°F. The new coatings are limited to temperatures from -40°F to +400°F. Nevertheless, this reduced temperature range accommodates 98% of the current applications.

The old formulas are still in limited use today, and it is likely there will always be some call for use in extreme cold or hot conditions.

Further Developments

With wellhead temperatures increasing with depth, a newer generation of waterborne coatings is being developed to withstand the more hostile drilling environments. These fluoropolymer coatings incorporate polyphenylene sulfide (PPS) as their binder resin. PPS is an engineering material that has resistance to all solvents up to 400°F. PPS-based fluoropolymer coatings also have outstanding abrasion resistance. The combination of extreme performance makes these newest coatings viable for the oil patch.

Conclusion

The fluoropolymer coating industry has met, and in some cases, exceeded the demands of new environmental regulations. With ever-increasing concerns about the environment, it is expected that government regulations will continue to change.

As a result, the petrochemical and coating industries will have to continue to improve coating technology.

References

(1) ASTM B117 (Latest revision) “Standard Practice for Operating Salt Spray (fog) Apparatus” (West Conshohocken, PA: ASTM)

(2) Din 50018 (Latest revision), “Test Method in Damp Heat Alternating Atmosphere Containing Sulfur Dioxide” (Berlin, German: DIN)

(3) ASTM D1308-79 “Chemical Spot Test” (West Conshohocken, PA: ASTM)

SUMMARY OF RESULTS I-14756

TABLE - 1

CHEMICAL RESISTANCE of 1424/524*	CHANGES IN 1424/524 AFTER 24 HRS. EXPOSURE
HCl (concentrated) @ room temp.	none
HCl (pH 2) room temp.	none
HCl (pH 2) 125 F	none
NaOH (50%) room temp.	none
NaOH (pH 12.5) room temp.	none
NaOH (pH 9.5) 125 F	none
MEK room temp.	Slight mark
Toluene room temp.	Slight mark
Castrol Hydraulic Fluid 200 F	Gloss decrease; 25.6 to 24.1 after exposure. No loss in coating integrity
HW-540 200 F	Gloss decrease; 29.9 to 10.3 after exposure. Color lightened slightly. No loss in coating integrity.
HW-640 200 F	Gloss decrease; 29.5 to 23.1 after exposure. Color lightened slightly. No loss in coating integrity.
Salt Spray B-117 1296 hours	15% rust, bubbling, white corrosion
Kesternich DIN 50018 43 cycles	15% rust, bubbling, adhesion loss

* Chemical spot test per ASTM D1308-79 (3)

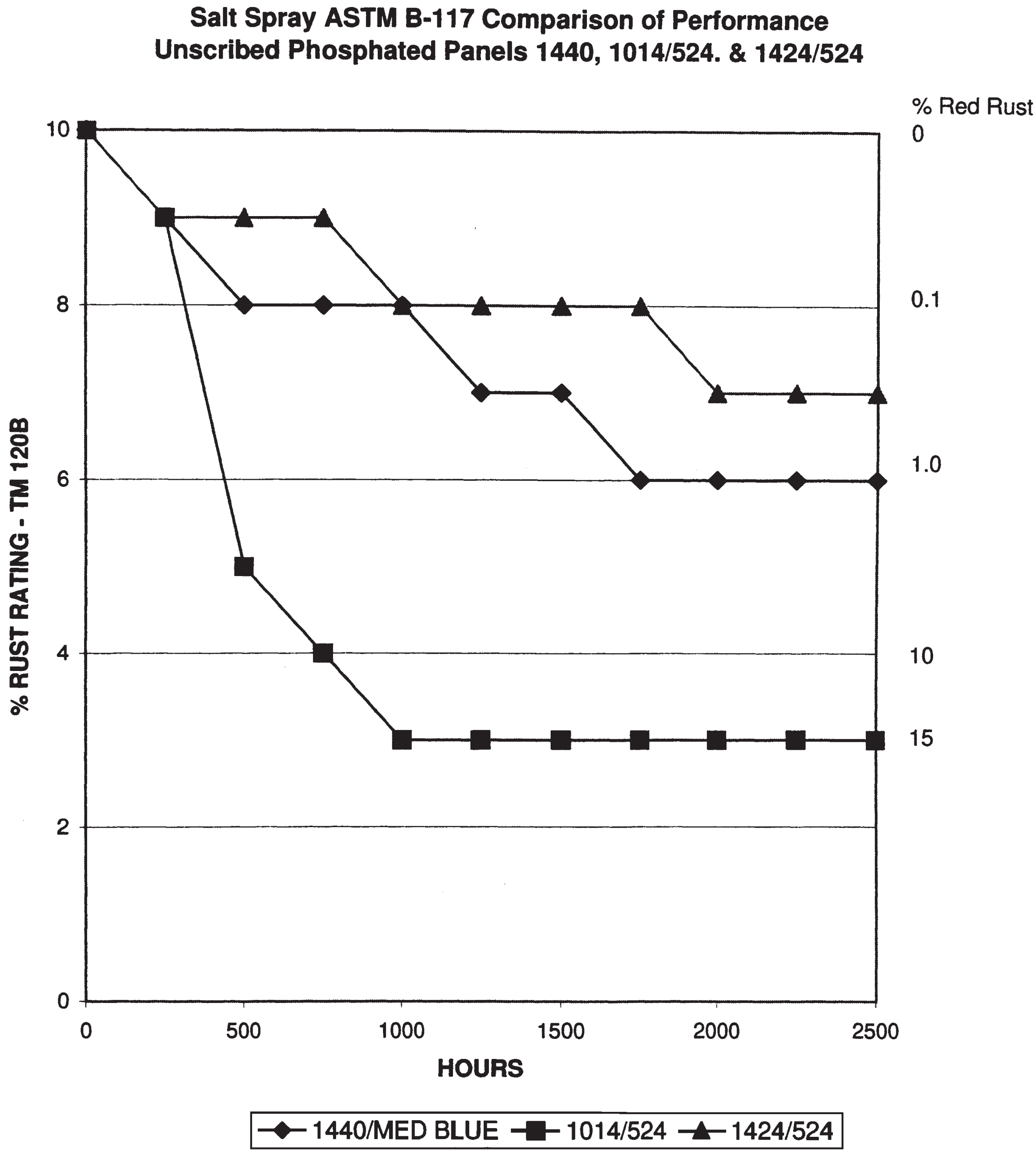
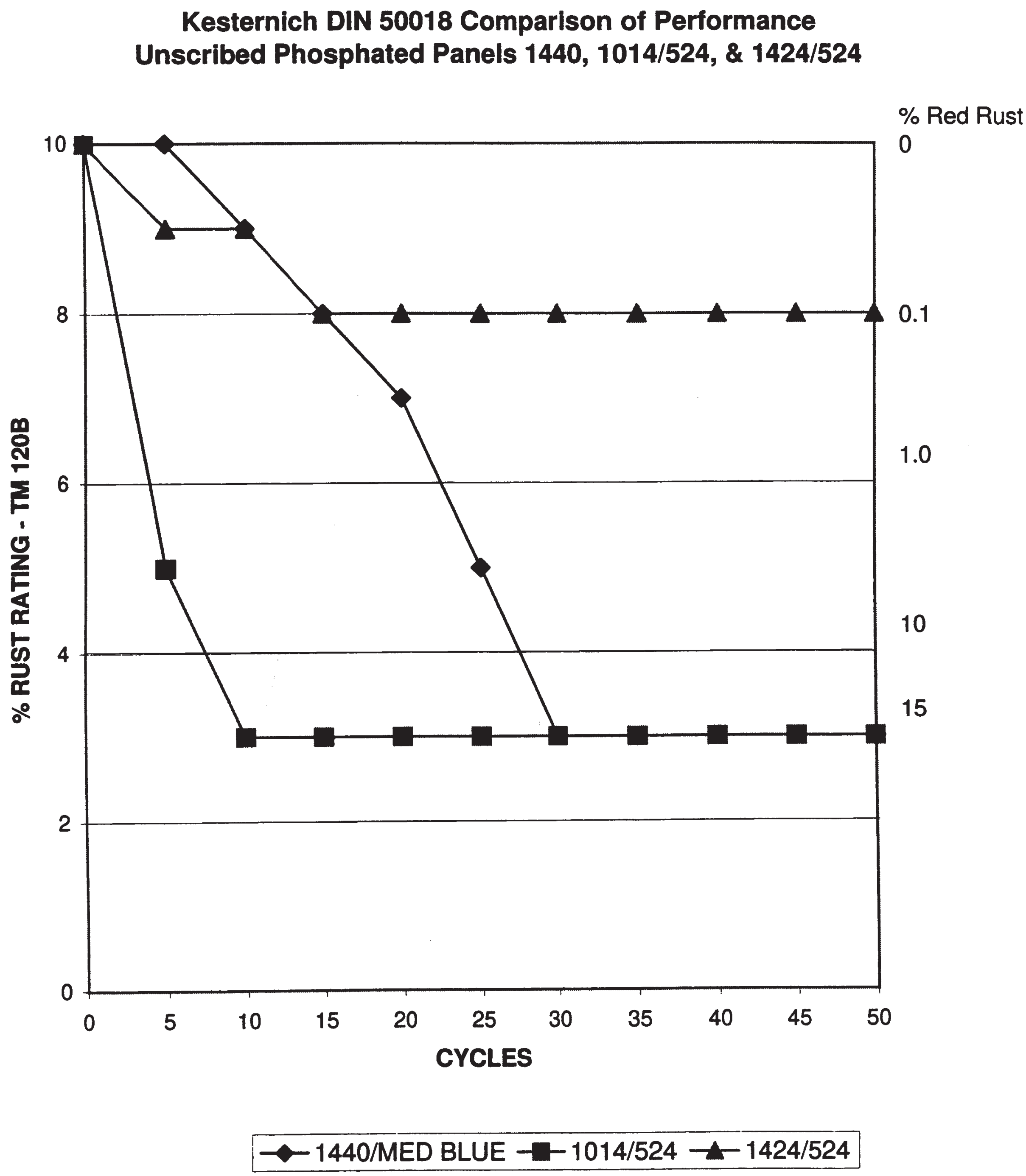

Salt Spray ASTM B-117 Comparison of Performance
Unscribed Phosphated Panels 1440, 1014/524. & 1424/524
% Red Rust
0
0.1
1.0
10
15
10
8
6
4
2
0
% RUST RATING - TM 120B
0
500
1000
1500
2000
2500
HOURS
1440/MED BLUE
1014/524
1424/524

FIGURE - 1



Kesternich DIN 50018 Comparison of Performance
Unscribed Phosphated Panels 1440, 1014/524, & 1424/524
% Red Rust
0
0.1
1.0
10
15
10
8
6
4
2
0
% RUST RATING - TM 120B
0
5
10
15
20
25
30
35
40
45
50
CYCLES
1440/MED BLUE
1014/524
1424/524

FIGURE - 2