

## Effect of Flake Nickel Powder on the Permeation Resistance of Fluorocarbon Coatings: Postprint

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### Abstract

Fluorocarbon coatings containing flake nickel powder at various volume fractions were subjected to salt spray testing, electrochemical testing and analysis, and water vapor transmission rate tests to investigate the effect of flake nickel powder volume fraction on the anti-permeability performance of fluorocarbon coatings. The results indicate that the coating exhibited optimal comprehensive properties at a nickel powder volume fraction of 5%, while the anti-permeability performance decreased with increasing nickel powder volume fraction when the volume fraction exceeded 15%.

### Full Text

## Influence of Flaky Nickel Powder on Permeation Resistance of Fluorocarbon Coatings

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**Abstract:** The influence of flaky nickel powder as pigment on the permeation resistance of fluorocarbon-based coatings was investigated through salt spray tests, electrochemical impedance spectroscopy (EIS), and measurement of water vapor transmission rate. The results demonstrate that among all formulations tested, the coating with a volume fraction of 5% flaky nickel powder exhibited

the best comprehensive performance; however, its resistance to water permeation degraded significantly for coatings with higher volume fractions of flaky nickel powder up to 15%.

**Keywords:** materials failure and protection, flaky nickel powder, fluorocarbon coating, salt spray test, EIS, permeation resistance

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## 1. Introduction

The corrosion protection mechanism of organic coatings primarily involves shielding against corrosive media and inhibiting the corrosion process. Incorporating pigments into metal anticorrosion coatings is a common method to reduce coating permeability. Pigments act as passivating or shielding agents that block contact between corrosive media and the substrate, while some metallic pigments also provide cathodic protection [1] to enhance anticorrosion capability.

Flaky pigments are lamellar powders with a high aspect ratio that form overlapping layered arrangements within the coating matrix, which extends the diffusion path for corrosive media, enhances shielding effectiveness, and improves both permeation resistance and anticorrosion performance. Materials used as flaky pigments include glass flakes [2,3], mica, graphite, and metals. Among these, flaky metal pigments such as zinc, aluminum, and zinc-aluminum alloy powders provide both shielding effects and cathodic protection, and are widely applied in anticorrosion coatings [4]. Jin Xiaohong et al. [5] compared the performance of lamellar zinc powder with conventional spherical zinc powder, finding that lamellar zinc powder could reduce the required dosage to one-third that of spherical zinc powder without compromising anticorrosion performance in zinc-rich primers. S. González et al. [6] reported that epoxy coatings containing 10% volume fraction of aluminum powder (hereinafter referred to as volume fraction) provided excellent protection for carbon steel, a benefit attributed to both the cathodic protection afforded by the aluminum powder and the precipitation of its reaction products within coating pores.

The incorporation of nickel powder as a flaky pigment in organic coatings has been reported previously [7,8]. Nickel powder offers moderate cost and ferromagnetic properties, and when added as a functional filler to coatings, it provides electromagnetic shielding effects [9]. This study investigates the influence of nickel powder content on the permeation resistance of fluorocarbon coatings using salt spray testing and electrochemical impedance analysis.

## 2. Experimental

### 2.1 Materials and Coating Preparation

The nickel powder used in this study was a standard water-based flaky nickel powder with a lamellar morphology and particle size of 30-50  $\mu\text{m}$  [Figure 1: see original paper]. The substrate was Q235 steel that had been sandblasted, with dimensions of 150 mm  $\times$  70 mm  $\times$  3 mm. Butyl acetate served as the solvent. Predetermined amounts of fluorocarbon resin (LF200) and solvent were mixed with polyamide wax, then stirred in a disperser at 1800 r/min for 5 min before adding the flaky nickel powder and continuing agitation for 20 min to prepare fluorocarbon coatings with specified pigment volume fractions. The curing agent was isocyanate (type 3390, 90% solid content), with a base-to-curing-agent ratio determined by  $\text{NCO}:\text{OH} = 1:1$  (molar ratio). Five formulations were prepared with nickel powder pigment volume fractions of 0%, 5%, 15%, 25%, and 35%.

Coating application was performed via air spraying at 0.6 MPa pressure. The coated panels were cured at room temperature for 7 days. The dry film thickness was  $(75 \pm 10) \mu\text{m}$  for salt spray testing and  $(95 \pm 10) \mu\text{m}$  for electrochemical testing.

### 2.2 Performance Testing of Composite Nickel Powder Fluorocarbon Coatings

The microstructure of the nickel powder was observed using an XL30 ESEM-FEG environmental scanning electron microscope (SEM). Coating adhesion was tested according to national standard GB/T 9286-1998, flexibility according to GB/T 1731-1993, and impact strength according to GB/T 1732-93. Salt spray testing was conducted per GB/T 1771-2007 using continuous spray mode with a 5% NaCl (mass fraction) solution at  $(35 \pm 2)^\circ\text{C}$ .

Coating samples were analyzed by X-ray diffraction (XRD) using a DMAX/2400 diffractometer ( $\text{CuK}\alpha$ , 40 kV, 100 mA). Electrochemical impedance spectroscopy (EIS) was measured using a 273A system at open-circuit potential over a frequency range of 100 kHz-10 mHz with a 10 mV amplitude sinusoidal signal. A three-electrode cell configuration was employed with a platinum auxiliary electrode, saturated calomel reference electrode (SCE), and coated substrate as the working electrode (effective area  $\sim 12.56 \text{ cm}^2$ ). The corrosive medium was 3.5% NaCl solution. Impedance data were analyzed using ZSimpWin software.

The oil absorption of nickel powder was tested according to GB 5211.15-88. Water vapor transmission rate was measured using an STW-8/120D instrument per GB/T 1037 at 30% humidity and  $25^\circ\text{C}$ , with a sample area of  $33 \text{ cm}^2$ .

### 3. Results and Discussion

#### 3.1 Mechanical Properties of Coatings

Table 1 presents the mechanical properties of coatings with different nickel powder volume fractions. The results show that coating adhesion, flexibility, and impact strength exhibited no significant variation with increasing nickel powder volume fraction. These properties are fundamentally determined by the fluorocarbon resin itself, and even the addition of 35% nickel powder did not degrade these characteristics.

#### 3.2 Salt Spray Testing

Figure 2 [Figure 2: see original paper] shows the appearance of coated panels with different nickel powder volume fractions after 500 h of salt spray testing. All coatings exhibited varying degrees of blistering and corrosion along the scribe marks. The 0% and 5% volume fraction coatings showed relatively smaller blistered areas. The 0% coating panel displayed over 60% blistering area, consisting mostly of micro-blisters along with 6% small blisters and 3% medium blisters; large blisters appeared in isolated locations with maximum corrosion creep width of 7–8 mm. The 5% volume fraction coating panel exhibited the smallest blistered area adjacent to the scribe, approximately 10%, with a maximum corrosion creep width of only 3 mm. The 15% volume fraction coating showed severe corrosion, with over 80% blistering area along the scribe, more than 6% large blisters, approximately 30% surface rusting, and a maximum corrosion creep width of 5 mm. Panels with 25% and 35% pigment volume fractions exhibited severe surface rusting, with complete surface corrosion. During the 500 h salt spray test, the 5% panel developed few blisters, while the 0% and 15% panels showed progressively expanding blistered areas. The 25% and 35% panels began developing rust spots within 48 h and showed severe surface rusting after 120 h. These results indicate that a small addition of nickel powder (5% volume fraction) improves the salt spray resistance of fluorocarbon coatings, but excessive addition reduces corrosion resistance. High loadings above 25% volume fraction result in extremely poor salt water corrosion resistance.

To further investigate the role of flaky nickel powder during salt spray testing, XRD analysis was performed on the 5% nickel powder coating near the scribe area before and after testing [Figure 3: see original paper]. The XRD spectra were identical before and after salt spray exposure, showing only sharp peaks of pure nickel, indicating that the nickel powder in the coating was not corroded by the salt solution and continued to provide a barrier effect.

#### 3.3 EIS Test Results and Analysis

Figure 4 [Figure 4: see original paper] presents Bode and Nyquist plots for various coatings after different immersion times in 3.5% NaCl solution. For the fluorocarbon coating without nickel powder (0%), the initial impedance modulus remained high at approximately  $10^{10} \Omega \cdot \text{cm}^2$ . After 3–7 days of immersion, the

impedance modulus decreased slightly, but the Nyquist plot still showed only one time constant, indicating solution ingress into the coating. After 312 h, a distinct second capacitive arc appeared in the Nyquist plot and the impedance modulus dropped significantly to  $10^6 \Omega \cdot \text{cm}^2$ , indicating that the solution had reached the substrate and entered the mid-immersion stage. Subsequently, the impedance modulus increased to  $10^8 \Omega \cdot \text{cm}^2$ , then decreased slightly after 672 h. This behavior may be attributed to corrosion product formation at the coating-substrate interface, which temporarily inhibited corrosion propagation, but as time progressed, localized corrosion continued to develop, causing the impedance values to decline.

The 5% nickel powder coating maintained a high impedance modulus of  $10^9$ - $10^{10} \Omega \cdot \text{cm}^2$  throughout the entire immersion period, with no second time constant observed in the Nyquist plots, indicating that it remained in the initial immersion stage without solution penetration to the substrate, thus demonstrating excellent corrosion resistance and permeation resistance.

The 15% nickel powder coating exhibited an impedance modulus below  $10^6 \Omega \cdot \text{cm}^2$  at the low-frequency end after only 0.5 h of immersion, indicating poor protective capability. Two time constants appeared in the Nyquist plot after 6 h, suggesting that corrosive media had already begun penetrating the coating and that through-coating transport channels had formed, initiating substrate corrosion. The coating impedance modulus continued to decrease throughout the immersion period with continuously shrinking capacitive arcs, indicating progressive corrosion development.

The 25% nickel powder coating showed an impedance modulus below  $10^5 \Omega \cdot \text{cm}^2$  from the beginning of immersion (0.5 h), and the significant reduction in impedance modulus and substantial contraction of capacitive arcs after 3 h indicated coating failure. The 35% nickel powder coating exhibited similar behavior, with low impedance modulus after 0.5 h of immersion, indicating premature failure. In fact, visible large-area rusting appeared on the surfaces of both 25% and 35% coatings after 24 h of immersion.

To analyze the evolution of coatings during immersion, equivalent circuit models were used to fit the impedance data. Based on the specific conditions of coatings at different stages, three equivalent circuits shown in Figure 5 [Figure 5: see original paper] were employed [10]. Due to the dispersive effect of nickel powder in the coating, constant phase elements were used instead of capacitive elements to simulate coating capacitance. Figure 5a represents the initial immersion stage when the coating provides good shielding and effectively isolates the corrosive medium from the substrate, showing only one capacitive arc in the Nyquist plot, where  $R_s$  represents solution resistance, constant phase element  $Q_c$  corresponds to coating capacitance, and resistance  $R_c$  represents coating resistance. Figure 5b represents the mid-to-late immersion stage when corrosive media begin to penetrate the coating, resulting in a second time constant, where  $R_p$  represents the resistance of coating surface micropores,  $Q_{dl}$  represents the double-layer capacitance beneath the coating, and  $R_{corr}$  represents the resis-

tance of electrochemical reactions occurring when solution penetrates through the coating to the metal surface. Figure 5c represents the late immersion stage when corrosive media reach the metal surface, showing a low-frequency slope in the Bode plot corresponding to diffusion processes of corrosive species, indicating a new diffusion layer formed by accelerated corrosion reactions at the interface, represented by Warburg impedance  $Z_w$ .

Figure 6 [Figure 6: see original paper] shows the variation of coating resistance with immersion time for different formulations. Coatings with 15%, 25%, and 35% nickel powder volume fractions consistently exhibited relatively low coating resistance. The 0% coating maintained relatively high coating resistance but showed an overall declining trend with a distinct valley followed by recovery and subsequent decline; the 15% coating displayed similar behavior. Throughout the immersion period, the 5% coating resistance, after an initial decrease, remained at a high level of  $10^9 \Omega \cdot \text{cm}^2$  after 6 h, exceeding that of the 0% coating by one order of magnitude and showing no declining trend. Coating resistance is an important indicator of a coating's ability to resist permeation by corrosive media and can be used to evaluate protective performance. The high and stable coating resistance of the 5% nickel powder fluorocarbon coating indicates that an appropriate nickel powder addition provides the best resistance to corrosive media permeation.

Water transport in coatings can alter the polymer's dielectric constant, thereby changing its capacitance. The Brasher-Kingsbury equation [11]  $\phi = \frac{C_t - C_0}{C_0} \lg 80$  can be used to calculate water absorption in coatings, where  $\phi$  represents the volume fraction of water transmitted into the coating, and  $C_t$  and  $C_0$  represent the capacitance at time  $t$  and initial capacitance, respectively. Substituting the coating capacitance values obtained from equivalent circuit fitting into this equation yields the variation of water absorption volume concentration with immersion time for different coatings. The fitted results for water absorption versus time are shown in Figure 7 [Figure 7: see original paper]. The final stable water absorption of the 5% and 15% nickel powder coatings was lower than that of the 0% coating, indicating that these additions of flaky nickel powder inhibited water permeation. For the 25% and 35% coatings, the barrier effect against water permeation was weak due to rapid coating failure.

### 3.4 Water Vapor Transmission Rate Testing of Coating Films

The water vapor transmission rate of a material, defined as the mass of water vapor transmitted per unit time through a unit area, characterizes its barrier performance. Fluorocarbon coatings with various nickel powder volume fractions and thicknesses of  $(50 \pm 5) \mu\text{m}$  were tested for water vapor transmission rate, with results listed in Table 2.

### 3.5 Determination of Critical Pigment Volume Concentration (CPVC) for Flaky Nickel Powder

The critical pigment volume concentration (CPVC) refers to the PVC value at which the binder resin just completely wets all pigment particles during PVC increase. When the pigment PVC exceeds CPVC, the resin is insufficient to fully wet the pigment and fill inter-pigment voids, leading to degraded comprehensive coating performance and increased medium permeability.

The oil absorption (OA) of a pigment refers to the mass of linseed oil (in grams) required to completely wet 100 g of pigment into a paste. Based on pigment oil absorption, the CPVC value can be calculated using the formula  $CPVC = 1/(1 + OA \cdot \rho)$ , where  $\rho$  represents the pigment density ( $\text{g}/\text{cm}^3$ ).

Experimental measurement determined the oil absorption of flaky nickel powder to be 60 g, yielding a calculated CPVC value of 14.8%, which is consistent with experimental results. When nickel powder volume fraction is below CPVC, permeation resistance is stronger than that of clear coating and increases with volume fraction; however, when nickel powder volume fraction exceeds CPVC, permeation resistance decreases significantly. To ensure good comprehensive coating performance, pigment volume concentrations of 0.2-0.7 times the CPVC value are recommended [13]; the 5% PVC used in this study falls within this range.

In summary, salt spray testing, electrochemical analysis, water vapor transmission rate measurements, and CPVC determination of nickel powder all consistently demonstrate that a 5% nickel powder addition yields optimal comprehensive performance with good corrosion resistance and permeation resistance. Additions exceeding 15% surpass the CPVC value of nickel powder (14.8%), resulting in decreased permeation resistance. At excessive nickel powder concentrations, the fluorocarbon resin acting as binder becomes relatively insufficient to fully wet the nickel powder, and the increased pigment volume concentration raises coating viscosity, making defect formation more likely and reducing permeation resistance.

## 4. Conclusion

The fluorocarbon coating with 5% nickel powder addition exhibited superior permeation resistance compared to the nickel-free fluorocarbon coating. The coating with 15% nickel powder was near the critical volume fraction, showing poor corrosion resistance but slightly better permeation resistance than the 5% coating. Coatings with 25% and 35% nickel powder additions, exceeding the critical pigment volume concentration (14.8%), demonstrated poorer permeation resistance than the nickel-free coating, with rapid failure observed for both formulations. Appropriate nickel powder addition (5% PVC) enhances coating permeation resistance, while additions exceeding the critical volume fraction (14.8% PVC) degrade permeation resistance.

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