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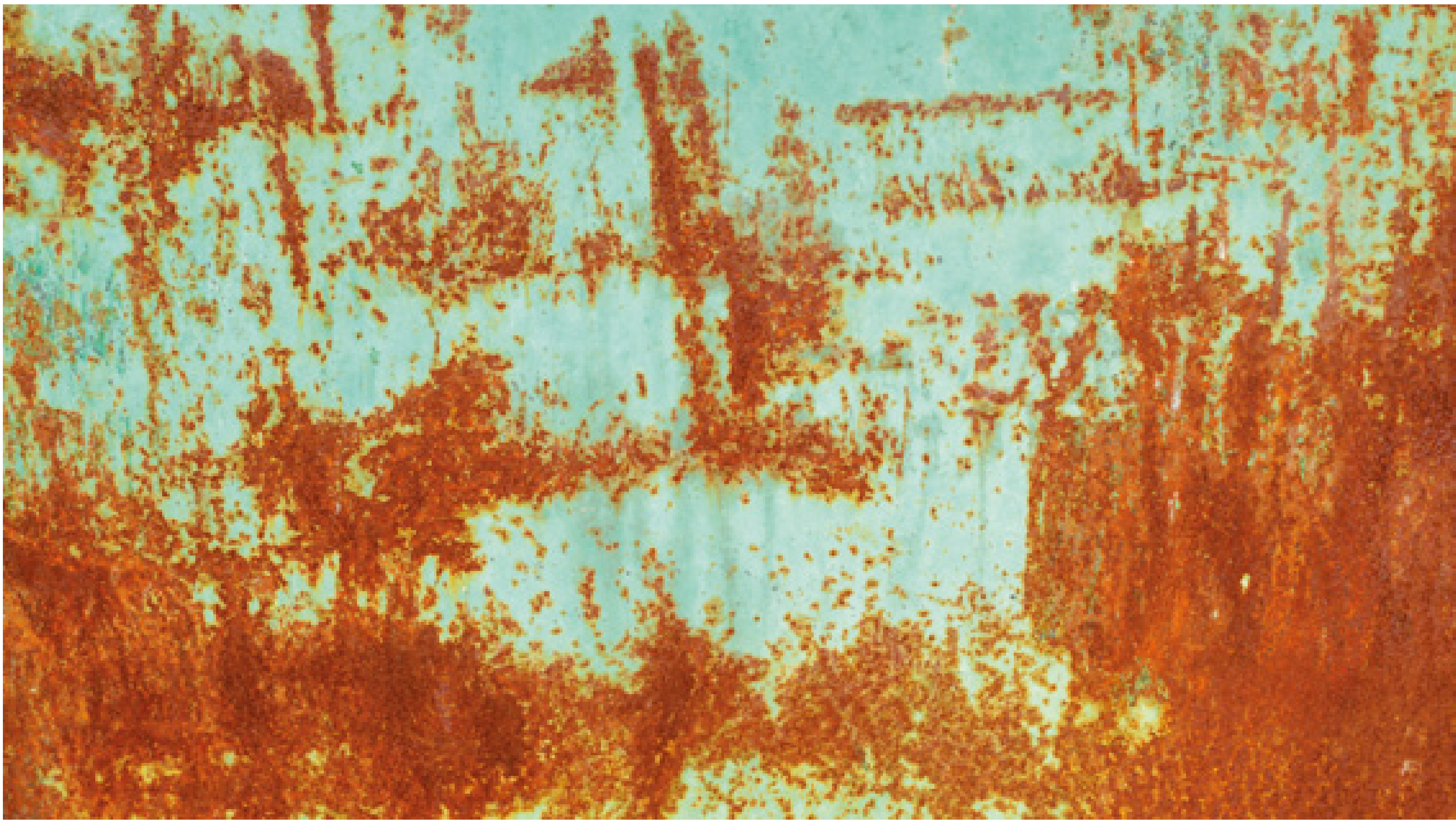


COST-EFFECTIVE CORROSION BARRIERS

Novel epoxy nanoclay composites keep costs down whilst improving performance. By Samuel Kenig, Shenkar College of Engineering and Design, Israel, and Roberto Cafagna, Nanto Cleantech, Italy.

Small quantities of functionalised nanoclays hold great potential for the performance of conventional paint systems. Exfoliation, chemical compatibility and orientation are critical to enhance the barrier properties, resulting in improved corrosion resistance and fire retardancy. The novel coatings discussed in this article entail that a variety of different substrates can benefit from these properties.

The technology of nanoclay polymer composites is currently generating a great deal of interest due to its potential cost-effective advantages in reinforcement, fire retardancy and barrier properties [1-6].

Nanoclays (NCs) appear in nature in condensed structures. When properly exfoliated to single platelets, that possess a thickness of 1 nanometre (nm) with an aspect ratio of close to 500, they assume a surface area of 750 m^2/g. Uniform dispersion of the NCs platelets requires them to be chemically compatible with the host system.

Due to their enormous surface area, only small amounts of the nanoparticles are needed to significantly enhance properties. The emergence of commercial NCs (montmorillonite type) has opened up new avenues for

Figure 1: TEM micrograph of Nano1 NCs at 3% concentration (bar size – 20 nm).

RESULTS AT A GLANCE

→ Exfoliation, compatibility and orientation of nanoclays (NCs) are key factors for anti-corrosion primers and intermediates and for the barrier properties of epoxy coatings.

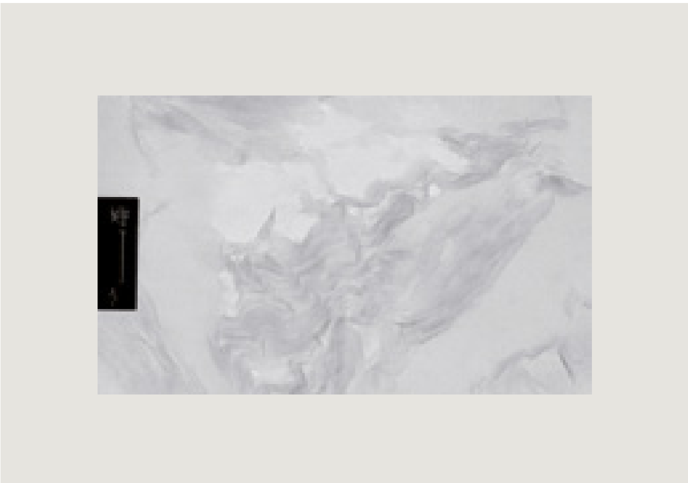
→ The optimal concentration and treatment of NCs in neat epoxy resin substantially reduced oxygen and water permeation.

→ 1-2% of treated NCs gave the best results in salt spray testing in terms of blister formation, electrical and chemical resistance and adhesion.

→ Small amounts of nanoclays may enhance anti-corrosion performance and fire retardancy.

anti-corrosion and fire retardant paints due to the high barrier to oxygen and humidity that NCs can impart to conventional paint formulations.
In this study, the effectiveness of NCs as barrier elements to corrosion agents (oxygen and humidity) and the effect of NCs surface treatment on the barrier properties were investigated to obtain anti-corrosion and flame retardant paints. The objective was to evaluate the effectiveness of NCs as barrier elements to corrosion agents (oxygen, humidity) in epoxy paints and to study the effect of NC concentration on the barrier properties of epoxy paint systems. The paints containing NCs were evaluated as primers and intermediate layers for steel elements, and compared with epoxy paints of the same composition but without the compatibilised NCs.

Figure 2: TEM micrograph of "Cloisite 25A" NCs at 5% concentration (bar size – 20 nm).



EXPERIMENTAL

Proper exfoliation and orientation of the nanoclay platelets is expected to reduce permeability in the paint system. Reduction of permeability is attributed to the tortuous path available for diffusion of gases (oxygen) and liquids (water). Reducing permeability can inhibit the corrosion of metal structures. The study was composed of two parts. In the first part, the NCs were incorporated into neat epoxy systems. In the second part, the NCs were compounded into primer and intermediate epoxy paint formulations. The same basic epoxy resin and curing agent were used in the two stages.
The epoxy resin used was based on diglycidyl ether of bisphenol A (DGEBPA) and a curing agent based on polyamidoamine. Two different NCs were used, one hydrophobic and one hydrophilic. Two novel NCs were also prepared from pristine NCs. The first was prepared by intercalation in non-organic solvent (Nano 1) and the second by an organic solvent (Nano 2). Compounding the dry NCs into epoxy or paint was by intensive mixing (0.5–9% by weight). Vacuum was applied to remove volatiles. Then the curing agent was added and mixed in using a ratio of 1 part curing agent to 4 parts epoxy. The paints were applied using a doctor blade apparatus. For oxygen permeability tests the paint samples were 180 to 250 microns thick and for water permeability tests the samples were 700 to 800 microns thick. The oxygen barrier of the nanocomposite paints was evaluated according to ASTM D 3985 at 25 °C, 0% relative humidity and 1 atmosphere of oxygen. The humidity barrier was tested according to ASTM E 96, at 38 °C and 90% relative humidity. Compounding of the dry NCs into epoxy or paint was by intensive mixing (1–5% by weight). The paint was applied by brush. The epoxy resin NCs morphology was followed by (TEM) Transmission Electron Microscopy. Salt spray testing (700 to 2000 hrs) was performed according to ASTM B-117 using 10 x 10 cm steel specimens coated with various paints formulations. Blister formation was followed by visual inspection. Electrical impedance measurements were taken following salt spraying. Finally, the wet adhesion was measured following 1000 hrs in an aqueous solution of both alkaline and acidic conditions.

SURFACE TREATMENT KEY FOR GREATEST BARRIER PROPERTIES

The reduced permeation of oxygen and humidity through the paint layer is expected to result in corrosion inhibition of metallic structures. In the case of the nanoclay platelets having a high aspect ratio (500 to 1000), the reduction in permeability is due to the tortuous path for gas

Table 1: Oxygen permeability of epoxy/NCs coatings (normalised to 200 microns).

Composition	Oxygen permeability cc/m²/day
Epoxy – 0% NC	38.8
Epoxy – 5% 25A	48.8
Epoxy – 5% 30B	10.5
Epoxy – 5% Nanto 1	27.1
Epoxy – 3% Nanto 1	7.9
Epoxy – 5% Nanto 2	29.1

diffusion (oxygen and humidity). To achieve the highest barrier properties, the condensed NC structure should be exfoliated to the highest possible level (single platelets) and the single platelets homogeneously dispersed parallel to the surface. Consequently, the current study focused on the effect of nanoclay surface treatment with respect to the epoxy paint system, on the permeability to oxygen and humidity.

HYDROPHILIC NANOCLAY INCREASES OXYGEN AND HUMIDITY BARRIER

In stage 1, neat epoxy/NCs were studied with respect to the effect of NCs having various treatments for the NCs at different NC concentrations. *Table 1* summarises the oxygen permeability of various epoxy/NC combinations.
As can be seen in *Table 1*, the best results were obtained with the hydrophilic NC treatments (Nanto1 and 30B). In the case of 3% NCs in Nanto1 a 5-fold reduction in oxygen permeability was achieved. The hydrophobic surface treatment (25A) exhibited the worst barrier performance, as it was incompatible with the epoxy system. The effectiveness of the Nanto 1 treatment compared with the commercial organo-ammonium ion treatment was confirmed by Transmission Electron Microscopy (TEM). TEMF micrographs indicated that the Nano1 treatment gave an exfoliated structure while the organo-ammonium hydrophobic treatment resulted in an agglomerated morphology. As can be seen in *Figure 1*, the Nano1 treatment at 3% NCs indicated good exfoliation and parallel tortuous path morphology.

As can be seen in the TEM micrograph in *Figure 2*, for the commercial nanoclay 25A (5% NCs), partial agglomeration of the NCs takes place with no parallel arrangement of the NC platelets which leads to increased oxygen permeabilities.
Table 2 depicts the humidity permeability of the epoxy nanocomposite coatings. In this case only the Nanto 1 NCs were studied with respect to their concentration effect. *Table 2* shows a more than 9-fold reduction in humidity permeation as a result of using 3% of the Nanto1 NCs. At lower (1%) and higher (5%) concentrations, the barrier properties are reduced compared with the optimal NCs level (3%).

Table 2: Water permeability of epoxy/nanoclay coatings.

Composition	Thickness (microns)	Water permeability in g/m²/day
Epoxy – 0% Nantol	700	1.727
Epoxy – 1% Nantol	800	0.244
Epoxy – 3% Nanto	800	0.127
Epoxy – 5% Nantol	800	0.199

NANOCLAYS REDUCE BLISTERING AND INCREASE ELECTRICAL RESISTANCE

In stage 2 of the study, epoxy paint formulations based on DGEBPA and polyaminoamide curing agent were used containing a variety of fillers [7]. NCs based on Nano1 treatment were used throughout the second stage. As the viscosity of the paint formulation is higher than the neat epoxy resin, the viscosities of the various formulations were evaluated as a function of the NC concentration compared with the epoxy paint that did not contain NCs, in addition to the number of blisters formed and electrical resistance following salt spray exposure (700 hours of exposure).
Table 3 describes the composition and attributes of the primer formulation. It shows that the viscosities of the primer formulation increased significantly with NC concentration. Furthermore, the number of blisters formed following salt spray was reduced with increasing NC concentration to 1% and 2%. In addition, electrical resistance increased by two orders of magnitude with an increase of NCs to 1 and 2% by weight.
Table 4 summarises the results for the intermediate formulation. For the intermediate formulation, the viscosities increased even more than for the primer formulation with increased NC concentration. The effect of the NCs on blister formation is very significant along with the increase in electrical resistance. The next attribute to be investigated was the pull off of the intermediate formulation as a function of various NCs in dry and wet adhesion following immersion for 1000 hours in water. *Table 5* describes the dry adhesion results for dry as well as wet adhesion for Nanto1 and "Cloisite 30B" NCs at a concentration of 1% and 2%. As is evident, Nanto-treated NCs have an advantage for dry as well as wet adhesion pull off.
Following exposure to water, selected formulations were immersed in basic as well as acidic conditions according to Standard EN ISO 2812-1. Accordingly, panels were immersed for 7 days in 10% caustic soda solution and 10% sulphuric acid solution. Experimental results indicated that all specimens coated with paints containing NCs did not form blisters while all specimens coated with paints without NCs show blistering. Finally, corrosion resistance in salt fog and humidity conditions was investigated according to ISO 9227 for 700 and 2000 hours. As can be seen in *Table 6*, following 700 hours exposure no blisters developed in the primer containing NCs or in the NC-free formulation. However, following 2000 hours of exposure the advantage of the primer formulation containing NCs is evident, with no formation of blisters.

FUNCTIONALISED NANOPARTICLES ENHANCE FLAME RETARDANCY

As NCs provide good barrier attributes to oxygen it may also be effective for fire retardancy (FR). Hence, novel fire retardant coatings were developed based on functionalised NCs. The FR series could be used in a variety of applications such as civil, industrial and marine structures, as the coatings are suitable for applying on different substrates such as steel, wood, composites and concrete.

Table 3: Primer composition - viscosity - resistance - blisters.

Composition	% NC	Visc. (1) mPaS	Thickness micron	No. blisters (2)	Resistance Ω cm²
Neat	-	27,000	150	4	9x107
Nanto1	1.0	37,100	140	2	5x109
Nanto1	2.0	52,400	142	2	1x109

(1) Rotational viscosity at 10 rpm (2) After 700 h salt spray
(3) After 700 h salt spray at 80 microns thickness

Table 4: Intermediate Composition - viscosity - resistance - blisters.

Composition	% NC	Visc. (1) mPaS	Thickness micron	No. blisters (2)	Resistance Ω cm²
Neat	-	26,600	160	20	2x1010
Nanto1	1.0	51,400	135	3	8x1011
Nanto1	2.0	85,700	130	5	1x1011

(1) Rotational viscosity at 10 rpm (2) After 700 h salt spray
(3) After 700 h salt spray at 150 microns thickness

The use of functionalised nanoparticles allows the replacement (fully or partially) of traditional fire retardant materials (ammonium polyphosphate, halogenated substances) with reduced cost and increased performance with respect to smoke emission reduction and enhanced flame retardancy.

ANTI-CORROSION PERFORMANCE AND FIRE RETARDANCY

Experimental results indicated that exfoliation, compatibility and orientation of the NCs are the decisive factors for anti-corrosion primers and intermediate. Optimal treatment and concentration of NCs in neat epoxy resins exhibited a 5-fold reduction in oxygen permeation and a 9-fold reduction in water permeation. In epoxy primers and intermediates, 1% to 2% of Nanto 1 NCs demonstrated the best results following salt spray with respect to the inhibition of blister formation, enhanced electrical resistance, enhanced chemical resistance and improved adhesion.

Low levels of nanoclays (3%) were needed to enhance the barrier properties of epoxy-based paints. The exfoliation, chemical compatibility and orientation of the nanoclays in the paint matrix are the decisive factors affecting the barrier properties of epoxy coatings. Steel specimens coated with optimally treated NCs demonstrated excellent resistance to salt spray testing for 2000 hours. These results indicated that small amounts of optimised NCs led to a paint system that

Table 5: Dry and wet adhesion pull off strength of intermediate paint formulations.

	Dry adhesion (MPa)			Wet adhesion (MPa)
	Value 1	**Value 2**	**Average**	
Without nanoclays	17.0	17.0	17.0	12.0
1% Nanto 1	13.4	15.0	14.2	16.4
1% "Closite 30B"	5.2	6.0	5.6	3.6
2% Nanto 1	15.0	17.0	16.0	19.0
2% "Closite 30B"	5.0	5.0	5.0	4.8

Table 6: Corrosion resistance in salt fog and humidity chamber.

	Corrosion test in artificial atmosphere/ salt spray test according to ISO 9227		
	700 hours	2000 hours	Performance improvement
Primer Epox NPC 9001 WITH NCs	no blistering	no blistering	+ 300%
Primer Epox NPC 9001 W/O NCs	no blistering	diffuse blistering rust around the incision area Test FAILED	

“Nanoclay is commonly applied in industrial assets of heavy industry.“

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3 questions to Roberto Cafagna

1. What are the most common fields of application of nanoclay next to anti-corrosive and fire-retardant coatings? *Nanoclay is commonly applied in industrial assets of heavy industry. There are oil and gas, marine, high value infrastructure and energy. Other very common fields of application of nanaclay are the automotive and aerospace sector as well as business to consumer coatings such as electronic, high abrasion resistant coatings, UV resistant coatings and high barrier coatings.*

2. How much did the electrical resistance increase? *In case of a primer, which is 80 microns thick, the electrical resistance increases from* $9x10^{7}$ *to* $5x10\ \Omega/cm^{2}$*. For the intermediate, which is 150 microns thick, it grows from* $2x10^{10}$ *to* $8x10^{11}\ \Omega/cm^{2}$*.*

3. What are the best methods to ensure that nanoclay is properly exfoliated? *The best methods are a surface treatment that is compatible with the matrix and high shear mixing.*

can be classified as Class C5M - high corrosion resistance according to the UNI EN ISO 12944 standard. These results indicate that small amounts of nanoclay in paints may enhance the anti-corrosion performance of conventional coatings and paints. The effectiveness of the novel treatment led to a patent on high-barrier paints [8]. The oxygen barrier properties of NCs were exploited for fire retardant coatings using specially functionalised NCs.

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