Application of FLG-LD in a polymer matrix in Dollcoat RS 103 and GP 107 nanotechnology-based pre-treatment products

F. Aiello, G. Assanelli, L. Bonoldi, M. Bruscagin, and M. Notari
Eni DowR&D - San Donato Milanese (Milan), Italy

André Bernasconi
DN Chemicals Srl – Milan (Italy) bernasconi@dn-chemicals.com

The partnership between DN Chemicals and Eni has led to the development of some innovative nanotechnology-based products in the Dollcoat series, formulated with FLG-LD in a polymer matrix for multi-metal anti-corrosion pre-treatments. Tests have shown a significant increase in corrosion resistance compared with traditional technologies, as well as high performance on various metal substrates and full compatibility with complex and nanoceramic processes.

Developing a groundbreaking innovation with no market equivalents, one that would surpass existing expertise and necessitate the creation of new technical knowledge, was the goal set during the first meeting of the DN Chemicals-Eni team in January 2022. The project was complex and ambitious from the beginning, with numerous critical issues to address and skills to develop, even in areas that had not been explored by the research group until then.
DN Chemicals, a company specialising in the production of chemicals for coating pre-treatment and water purification, could rely on a solid technological foundation: over twenty years of experience with its Dollcoat SA products based on synthetic oligomers obtained from silanes, the use of atomisation modules developed and refined with partners, Qualicoat and Qualisteelcoat certifications, and approvals from major customers. Incidentally, these certifications would have had to be re-obtained as part of the new project, but with significantly higher performance levels.

© DN Chemicals

Eni brought its consolidated expertise in the production of graphite suspensions for different applications. Similarly, however, these suspensions had to be reformulated and optimised for combined use with the products developed by DN Chemicals. The company's previous experience in the production of stable single-walled carbon nanotube (SWCNT) suspensions also played a significant role.

The project

The concept was to create a polymer matrix in which to disperse the graphite suspension (**Fig. 1**, see also the Technical Insight at the end of the article). The research project, therefore, started with selecting a polymer that:

◆ could be emulsified;
◆ had excellent corrosion resistance;
◆ had excellent mechanical properties, especially when applied in sectors that involve post-forming operations, such as coil pre-treatment;
◆ could promote the adhesion of any type of paint;
◆ was fully compatible with cataphoresis processes.

The identified polymer was then functionalised using specific polysilsesquioxanes, on whose synthesis the Dollmar group, to which DN Chemicals belongs, has developed considerable experience over the years. This first product was marketed under the name Dollcoat RS 103, establishing itself as a radical innovation with the following key characteristics:

◆ no-rinse multi-metal product, usable at room temperature;
◆ very high resistance to pollutants and, therefore, suitability for recirculation in normal pre-treatment operations for months without any deterioration in performance;
◆ also applicable via atomisation modules, provided they are suitably modified;
◆ no sludge formation.

The industrialisation of Dollcoat RS 103, which began at the end of 2022, enabled the further refinement of its formulation and the identification of some simple but effective plant engineering adjustments to optimise technical performance and consumption in extended recirculation processes.

The formulation of Dollcoat GP 107

Simultaneously with the industrialisation of Dollcoat RS 103, the DN Chemicals-Eni team developed Dollcoat GP 107, a product offering even higher performance thanks to the use of an FLG-LD suspension engineered in Eni's laboratories, which was the subject of a joint international patent filed in November 2024.
The aim was not only to develop a product with superior anti-corrosive properties compared with Dollcoat RS 103 while maintaining the general characteristics described above, but also to optimise the pre-cataphoresis process by using a 'conductive' matrix capable of promoting better coverage, particularly on complex geometries. Thanks to the use of electrochemical impedance spectroscopy (EIS), ACET technology and, more recently, Raman spectroscopy, the selection process among the numerous suspensions identified by Eni laboratories was much faster than would have been possible with traditional techniques such as salt spray testing.

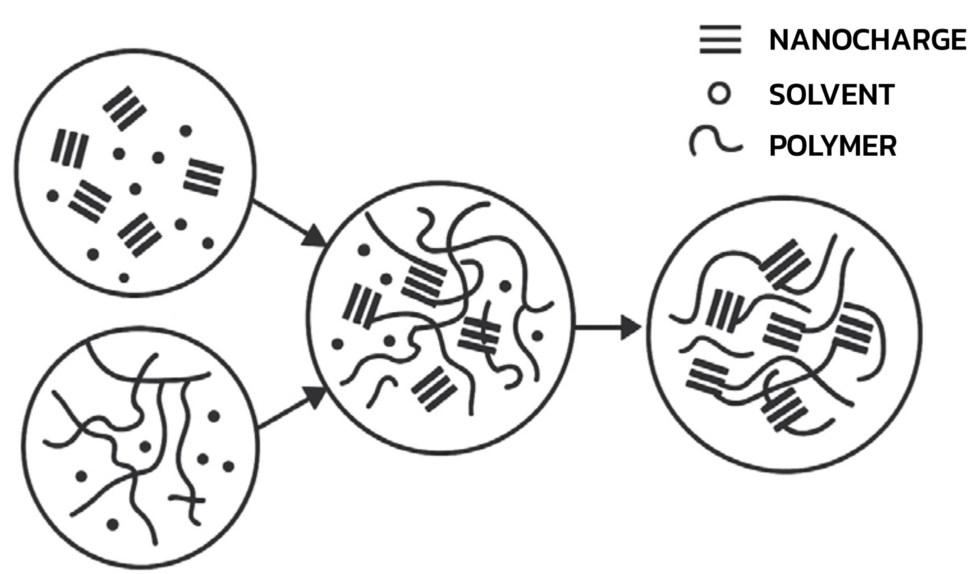


Figure 1 - The polymer matrix for the dispersion of the graphite suspension.

The application of Dollcoat GP 107

Over the last two years, Dollcoat GP 107 has been tested on four industrial plants, two of which are equipped with atomisation modules and one with a chemcoater for coil pre-treatment. Like Dollcoat RS 103, Dollcoat GP 107 is a no-rinse product that can be used on any type of metal alloy using relatively simple processes. An example is a pre-treatment cycle consisting of alkaline degreasing, two rinses, phosphodegreasing with Dollcoat SA 127, two further rinses (the last of which with demineralised or osmotised water), and nanotechnology application with Dollcoat RS 103 or Dollcoat GP 107. Naturally, more complex process cycles deliver a corresponding degree of corrosion protection. The strong synergy created between the nanoceramic processes and the subsequent application of Dollcoat GP 107 is also worth noting.

Corrosion protection performance on various metal substrates

The performance levels achievable on industrial plants treating different metal substrates are shown in **Table 1**. The comparison highlights the significant increase in performance achieved with this new family of products compared with conventional polysilsesquioxane-based technologies. The industrial process used for all metal substrates included multi-metal alkaline degreasing, nanoceramic conversion, and the application of products from the Dollcoat line.

	Jcorr (A/cm²)	Corrosion rate (mm/Y)	Rp (Ω)
CRS – DOLLCOAT SA 118	2,35 E-06	0,0272385	933
CRS – DOLLCOAT RS 103	1,11 E-06	0,0129135	1473
CRS – DOLLCOAT GP 107	3,86 E-07	0.00448725	7049
HDG – DOLLCOAT SA 118	3,58 E-06	0,041	489
HDG – DOLLCOAT RS 103	4,32 E-07	0,00051	2200
HDG – DOLLCOAT GP 107	8,16 E-08	0,000948	3600
Al – DOLLCOAT SA 118	8,60 E-07	0,0098	2846
Al – DOLLCOAT RS 103	3,86 E-09	0,0000359	42155
Al – DOLLCOAT GP 107	1,77 E-09	0,0000125	68120

Table 1: Performance comparison between traditional polysiloxane-based technologies and Dollcoat technology.

The polarisation resistance (Rp) values show a marked increase from Dollcoat SA 118 to Dollcoat RS 103, with the overall increase approaching one order of magnitude for Dollcoat GP 107. The presence of graphene also significantly reduces ‘porosity’, thus considerably reducing water uptake, as shown by the ACET analysis in **Fig. 2**.

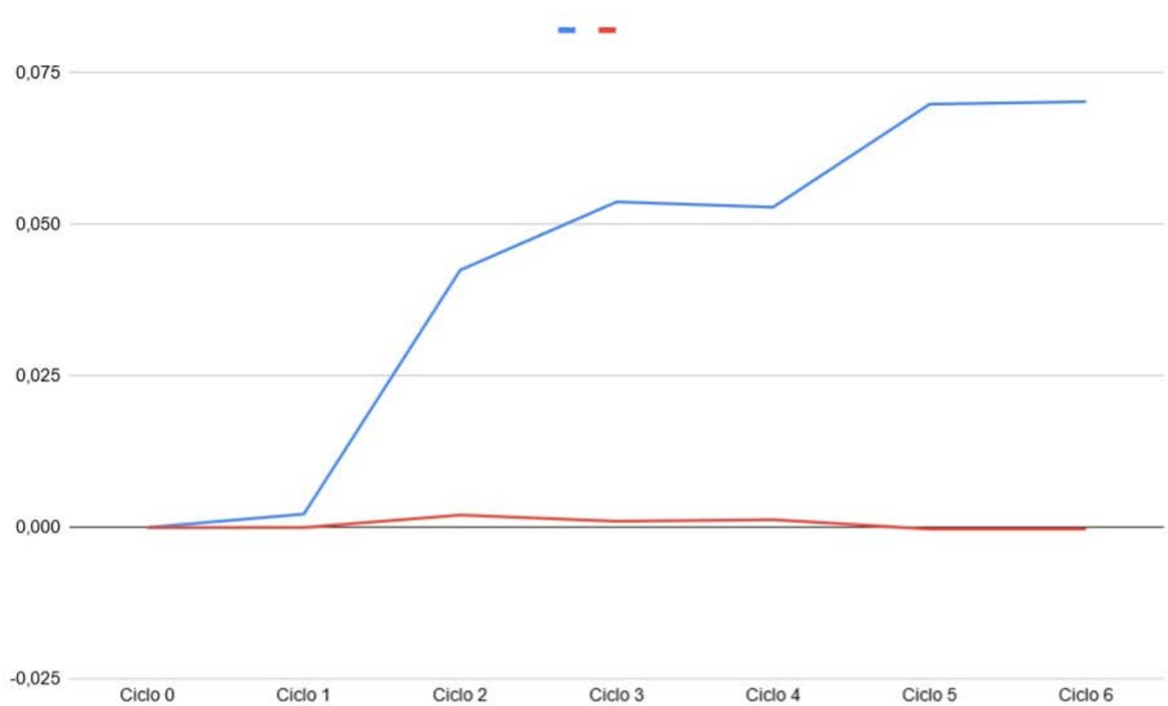


Figure 2 - Results of the ACET analysis relating to water uptake.

The same panels were then coated with polyester powder, either directly or after applying a primer or cataphoresis layer, and subsequently tested using both the ACET and neutral salt spray methods. Due to space constraints, we cannot report all test results, but the comparison we find most interesting is between the panels coated with polyester powder alone and those subjected to both cataphoresis and polyester powder application, as shown in **Table 2**.

Panel	Coating type	Total thickness (µm)
1	KTL + polyester powder	70-90
2	KTL + polyester powder	60-80
3	KTL + polyester powder	65-75
4	KTL + polyester powder	55-70
5	polyester powder	55-70
6	polyester powder	40-60
7	polyester powder	50-60
8	polyester powder	55-70

Panel	Reference standard	1	2	3	4	5	6	7	8
504 h									
Blistering	DIN EN ISO 4628-2	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)
Delamination (mm)	DIN EN ISO 4628-8	0,6	0,5	0,6	0,7	0,6	0,6	0,9	0,3
Degree of rusting	DIN EN ISO 4628-3	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0
Cross-hatch test	DIN EN ISO 2409	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0
720 h									
Blistering	DIN EN ISO 4628-2	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)	0 (S0)
Delamination (mm)	DIN EN ISO 4628-8	1,2	1,0	1,0	1,3	1,6	1,9	2,5	1,2
Degree of rusting	DIN EN ISO 4628-3	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0	Ri 0
Cross-hatch test	DIN EN ISO 2409	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0	Gt 0

Table 2: Comparison between panels coated with polyester powder alone and with cataphoresis followed by polyester powder application.

The results show substantial equivalence among the panels at least up to corrosion category C3H. In category C4H, the panels coated exclusively with polyester powder still maintain high performance compared with those also treated with cataphoresis.
It is important to highlight the decisive role of the paint used: during this industrial test, the first series of panels showed widespread blistering and significant signs of corrosion after only 250 hours in neutral salt spray. The ACET analysis revealed very high water uptake, correlated with reduced salt spray resistance performance. With a different batch of the same paint, however, the water uptake value decreased by about an order of magnitude and, as a result, the impedance loss dropped from 65% to 6.5% (**Table 3**).

Sample	Max Z (W*cm²)	Min Z (W*cm²)	Delta Z (%)	Water uptake (%)
Batch A	1.79E+10	3.80E+09	6.5	0.03
Batch B	6.12E+09	2.53E+03	65	1.80
KTL+Batch A	6.16E+07	5.29E+07	0.84	0.020
KTL+Batch B	2.40E+07	1,61E+07	2.4	0.038

Table 3: ACET test results on two batches of the same paint.

Application with a chemcoater

Another available application is the pre-treatment of aluminium coils using chemcoaters. The chosen benchmark was a competing Cr^{3+}-based product. **Table 4** demonstrates that the use of Dollcoat RS 103 enhances polarisation resistance by almost an order of magnitude, while Dollcoat GP 107 provides a substantial increase of around four orders of magnitude.

	Jcorr (A/cm²)	Corrosion rate (mm/Y)	Rp (Ω)
Cr^{3+} -based product	3,38 E-06	0,038	800
DOLLCOAT RS 103	2,23 E-07	0,034	3500
DOLLCOAT GP 107	1,62 E-09	0,0000188	2000000

Table 4: Application of Dollcoat RS 103 and Dollcoat GP 107 on aluminium coils using a chemcoater.

Fields of application

This new class of products has many fields of application, especially those that require at least C3H corrosion resistance with a single coat of polyester powder. Besides contract coaters, these include industries such as household appliances, coil coating, architectural aluminium (coils and profiles), automotive components, pre-cataphoresis/anaphoresis, aluminium or steel wheels, and earth-moving, agricultural, and construction machinery (ACE). Dollcoat RS 103 is already Qualisteelcoat approved up to corrosion category C4H, and approval for category C5H is currently underway. Qualisteelcoat and Qualicoat approvals are also expected to be obtained for Dollcoat GP 107.

Conclusions

This new Dollcoat family introduces innovative technologies to the market that provide significantly enhanced anti-corrosion performance without requiring complex processes or the use of heavy metals like chromium, including in trivalent form. These products have very high pollutant resistance, allowing application by spraying through conventional nozzles, with the product being recirculated for months; they can also be applied using atomisation modules or by immersion. Their use in combination with nanoceramic conversions has proven particularly synergistic, delivering optimal corrosion protection.

Few Layer Graphite-Liquid Dispersion: innovation in the production and application of few layer graphite

Thanks to its consolidated experience in the dispersion of nanoparticles in lubricating fluids, Eni has developed an advanced technology for producing few layer graphite, called Few Layer Graphite-Liquid Dispersion (FLG-LD). The resulting dispersion acts as an additive for coating systems, which can impart specific properties depending on the intended application.

FLG-LD technology description

The core of the FLG-LD technology lies in a liquid phase (water or organic solvent) exfoliation process carried out using typical high shear mixers. The dispersion obtained is achieved using the following components:

- exfoliation promoters, for the controlled reduction of the number of graphite layers;
- surfactants, to ensure the stability of the FLG dispersion in the liquid medium;
- boosters and specific additives, selected according to the intended end use (e.g. for antimicrobial, anti-corrosion, or anti-fouling paints and coatings).

In terms of process management, it should be noted that the operating conditions are extremely simple: the process takes place at atmospheric pressure and without external heating. The application of specific mixing methods and the use of selected additives effectively prevent FLG from recombining into its original graphite structure.

The FLG-LD dispersion is characterised by planar dimensions on a micrometre scale (200-1,000 nm) and a nanometric thickness (≈ 6-10 nm) corresponding to the number of carbon layers (≈ 20-30). This structural configuration is the main strength of this technology, as it is extremely effective in generating a 'protective/active' surface within the treated component. Graphite was chosen as the main raw material over ready-to-use graphene to optimise both management procedures and the health, safety, and environmental (HSE) aspects of the finished product. In summary, the FLG-LD production process is based on low-cost components, does not involve significant energy consumption as it takes place at room temperature and atmospheric pressure, and does not present any particular health, safety, or environmental issues during handling, production, and packaging.

FLG-LD as an anti-corrosion solution for surface pre-treatment

Eni's collaboration with DN Chemicals has resulted in the development of a corrosion protection coating designed to safeguard metal surfaces from aggressive environmental corrosive agents. A dedicated FLG-LD formulation was utilised for this purpose, composed solely of FLG and process aids, which DN Chemicals subsequently incorporated into the final version of this anti-corrosion coating.

continues on the next page

The product entered the industrialisation phase in 2023 on several plants operating in various sectors, such as contract coating, electrical panel manufacturing, and coil coating. All pre-treated metal substrates (the main ferrous or aluminium alloys and HDG) were consistently characterised using EIS and ACET electrochemical techniques, RAMAN spectroscopy, and SEM microscopy. They also underwent accelerated corrosion tests in salt or acetic mist (ISO 9227), depending on the substrate.

Exploring new opportunities

Carbon Capture and Storage (CCS) technology

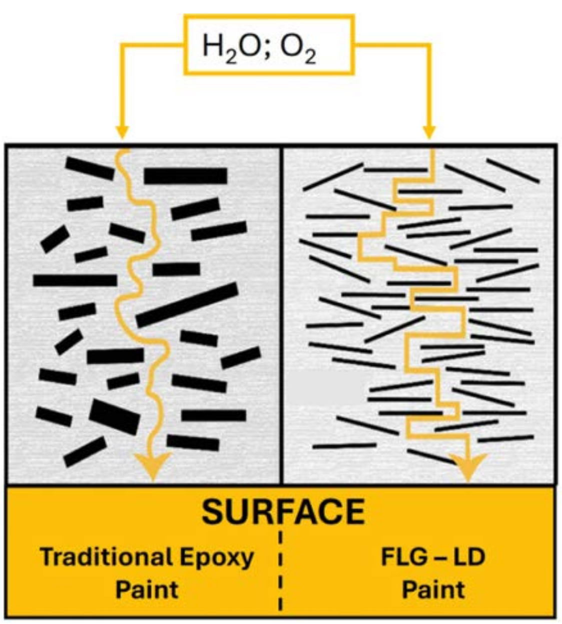
The design and construction of wells for CCS projects demand increased efforts in selecting appropriate materials capable of enduring harsh CO_2 environments. Currently, CO_2 injection conditions include:

- low temperatures;
- presence of impurities (e.g. H_2O);
- abrasion and wear.

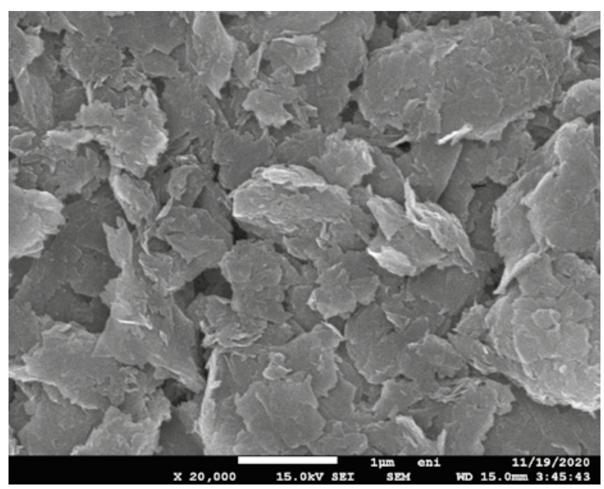
As expensive corrosion-resistant alloys (CRAs) are commonly used in CCS for completion pipes and string accessories, research on internal pipe lining systems could potentially lead to significant cost savings by reducing the time needed to procure materials and equipment. FLG-LD could be considered an option alongside leveraging in-house developed solutions, but it requires assessment due to the considerably more severe well conditions than those it was originally designed for.

Drinking water

The upcoming EU regulation mandates new coating methods for products intended for contact with water. In this context, 'Hf-free coatings' will be used to prevent the release of hazardous metals (e.g., Bi, Ce, Hf, Mo, Pr, Sr, Ti, Y, and Zr). The regulation aims to eliminate harmful substances to protect drinking water supplies from contamination. Manufacturers, therefore, must adjust their production processes to comply with the new guidelines on coating for enhanced safety. DN Chemicals, using Dollcoat GP 107 along with selected powder coatings, has already industrialised a high-performance anti-corrosion process for the sanitary water sector that removes the need for coating.



The image shows one of the properties resulting from the use of FLG-LD in polymer matrices: reduced matrix porosity and, consequently, improved corrosion resistance of the final workpiece.



FLG-LD observed by scanning electron microscopy.