

# The effect of VpCI chemical pre-treatment on adhesion of organic coatings

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Abstract: Surface preparation is the first step in a coating protection process and the most critical factor affecting the total success of surface treatment. The presence of even small amounts of surface contaminants such as oil, grease and salts can reduce coating adhesion to the substrate. Abrasive blasting is the most often used method for surface pre-treatment before coating. It is a very efficient method, creating uniform surface roughness and cleanliness. But, chemical contaminants that are not readily visible, such as chlorides and sulphates often remain on the surface resulting in premature failure of the organic coating. To overcome that and to provide the best possible contact surface for the applied coating, very often chemical cleaners are used. Today, because of environmental concerns, chemical cleaners for surface preparation are water based products containing a corrosion inhibitor for flash rust prevention after cleaning.

In this paper the influence of three waterborne VpCI chemical cleaners on the adhesion of organic coatings were studied. The mild steel samples were prepared with and without chemical cleaners containing a vapor phase corrosion inhibitor. The study was conducted in a salt spray chamber and humidity condensation chamber, whereas the adhesion was tested before and after accelerated exposure to a corrosive environment. The coating resistance was studied in 3.5% NaCl solution by electrochemical impedance spectroscopy. The results showed that an appropriate water based cleaner could replace solvent based thinner in the surface preparation process after abrasive blasting.

Key words: surface preparation, chemical cleaners, vapor phase corrosion inhibitor, organic coating, adhesion

## **Introduction**

All engineering structures whether in terms of mechanical engineering, shipbuilding, automotive industry or civil engineering, are subject to unintended and harmful damaging processes, i.e., changes that reduce their working life. The most damaging process of this type is corrosion, the chemical deterioration of a material, which can often jeopardize the functionality of the structure.

According to a survey conducted in the United States from 1999 to 2001, the annual cost of corrosion amounted to 275.7 billion US \$, which is about 3.1% of their GDP. The latest NACE IMPACT report revealed that the corrosion cost increased and that the global cost of corrosion is estimated to be US\$2.5 trillion per year, which is equivalent to 3.4% of the global GDP (2013). The survey estimated that almost a third of the damage could have been avoided by using available corrosion control methods [1].

Corrosion prevention methods can be classified into five groups: coating protection, cathodic and anodic protection, corrosion inhibitors, corrosion resistant materials and design considerations [2-3].

If the construction material isn't resistant enough in the foreseen conditions, either the conditions should be changed, or a protective coating should be applied. Applying protective coatings to the product surface is the most widely used method of corrosion protection. The protective property of the coating depends on its type, thickness, degree of density and adhesion ability [4].

Depletion of sources of raw materials and the introduction of stricter environmental regulations launched the greater development of water borne resins, so that today they take their place amongst ecologically acceptable materials thanks to their "friendly" properties, drying methods and industrial use. Waterborne coatings were developed to replace organic solvents with water, which has the obvious advantages of being non-flammable and non-toxic.

The protective coating method is generally a passive corrosion protection method, but it can be emphasised by adding corrosion inhibitors in the protective coating, thus providing both, passive and active protection.

Corrosion inhibitors are chemical substances which when added to a corrosive environment reduces the corrosion rate. A special group of inhibitors are Vapor phase Corrosion Inhibitors (VpCI) that protect metals from atmospheric corrosion. These are organic substances that have high vapour pressure to sublime and thus form a non-corrosive ambient. In contact with the metal surface, a vapour of VpCI condenses into a thin monomolecular film which through ion activity protects the metal from corrosion. The resulting film prevents contact within the fluid and metal and thus prevents ions to migrate from the surface of the metal in the solution [5].

The coating protection job consists of surface preparation, coating application and adequate coating drying. The durability of a protective coating depends greatly upon the degree of surface cleanliness and roughness prior to application. Most coating failures can be attributed to the poor surface preparation and pre-treatment.

The surface preparation could be performed by abrasive blasting (dry or wet), hand and power tool cleaning, chemical cleaning or electrochemical cleaning. All these processes are performed together with a degreasing process, often done by using different solvent-based degreasers and thinners. As environmental and disposal regulations become more and more stringent, the desire for “green” protection technologies is increasing [6].

The one environmentally friendly solution is the use of bio-based and water based products for chemical cleaning and degreasing [7]. The other one is an application of a wet abrasive blasting method which uses water as a media this creates a surface roughness and removes the non-visible contaminants in the process. On the other hand, evaporation of water after blasting may create flash rust, to avoid this, it is common to use corrosion inhibitors in the water of wet blasting methods [8]. The third method is high-pressure water jetting, where also flash rust occurrence after cleaning could be a problem. The possible solution for flush rust prevention is the application of sodium tetraborate (borax) in the water as a corrosion inhibitor during water-jetting [9].

All these solutions use corrosion inhibitors in surface pre-treatment. The possible negative effect of using corrosion inhibitors are residuals on the surface after cleaning which could be detrimental to coating adhesion and protection performance. Corrosion inhibitors are used to retard the formation of flash rust on the surface, but residues of these materials on the surface may become contaminants.

In this paper, the influence of three waterborne VpCI chemical cleaners for chemical cleaning and degreasing on the adhesion of organic coatings was studied.

## **Experimental study**

In the experimental part, the influence of three waterborne VpCI chemical cleaners compared to degreasing by a solvent-based thinner on the adhesion of organic coatings was studied. The study was conducted in a salt spray chamber and humidity condensation chamber, whereas the adhesion of coatings was tested before and after accelerated exposure to a corrosive environment. The coating resistance was studied in 3.5% NaCl solution by electrochemical impedance spectroscopy. The electrochemical behaviour at the coating/electrolyte interface is an important factor for determining the protective properties of the coatings.

### **Materials and sample preparation**

The mild steel samples, dimensions 100 x 150 mm, were prepared by abrasive blasting, degreased with solvent and water based chemical cleaners and then protected with two water borne acrylic coatings (with and without a vapor phase corrosion inhibitor). The abrasive blasting was conducted in order to maintain the same surface cleanliness and roughness of the samples. After blasting, the surface was covered by mineral oil, and then degreased using different cleaning agents. Before painting, the cleaners were thoroughly washed from the surface using tap water and a brush. One set of blasted samples remained clean without oil contamination, used as etalons and for comparison of coatings without the influence of chemical cleaning.

The properties of chemical cleaners are given in table 1.

**Table 1.** The properties of chemical cleaners

Label	Type	Density [g/cm <sup>3</sup> ]	dilution ratio	pH	General description
VpCI 414	water borne, VpCI based	1.03-1.05	50:50	10.9-11.4	cleaner and degreaser, heavy-duty temporary coating remover
VpCI 416	water borne, VpCI based	1.03-1.04	50:50	11.5-12.5	heavy-duty water-based alkaline cleaner and degreaser offering unique flash corrosion protection, higher level of corrosion inhibitor
VpCI 418	water borne, VpCI based	1.03-1.04	50:50	11-12	requires pressure washing, leaves no residual film and will not affect adhesion, non-foaming
Thinner	solvent borne	0.78	-	-	Synthetic thinner, mixture of aliphatic and turpentine hydrocarbons

The acrylic coatings used for testing were:

1. Coating A: VpCI 386, is a water-based acrylic primer/topcoat containing organic corrosion inhibitors that successfully provides protection in harsh, outdoor and unsheltered applications.
2. Coating B: VpCI free coating, is a water-based acrylic coating with non-toxic and weather-resistant properties for protection of metal substrates.

The dry film thickness (DFT) of the applied coating was measured according to ISO 2808, using a non-destructive magnetic induction method with an Elcometer 456 instrument by Elcometer Limited Manchester, UK. Measurements of DFT were carried out at ten different locations per sample, table 2.

**Table 2.** Measurements results of coating thickness

Pre-treatment procedure	VpCI acrylic coating (A)	Mean coating thickness, $\mu\text{m}$	VpCI free, acrylic coating (B)	Mean coating thickness, $\mu\text{m}$
Abrasive blasting	1	55.73	1	57.64
Abrasive blasting	2	60.70	2	55.34
Abrasive blasting	3	72.02	3	61.90
Thinner	4	58.53	10	63.58
Thinner	5	61.93	11	53.68
Thinner	6	66.73	12	56.30
414	7	70.43	7	63.37
414	8	64.13	8	66.12
414	9	67.25	9	65.86
416	10	68.05	4	53.66
416	11	68.98	5	53.80
416	12	68.78	6	64.12
418	13	65.87	13	61.02
418	14	63.36	14	57.03
418	15	62.99	15	57.41

### Testing in salt spray chamber

Neutral salt spray chamber test (5 % NaCl solution, 35 °C) was conducted according to ISO 9227 for a duration of 100 hours to determine the resistance to salt fog atmosphere. Before salt spray testing, the painted panels were horizontally scribed through the paint film to expose the base metal (ISO 7253). The testing was conducted in Ascott cabinet, model S450.

### Testing in humidity chamber

The testing in a humidity chamber was conducted according to ISO 6270-2 for a duration of 100 hours with the aim to determine the resistance of samples to wet - hot climate conditions (RH = 100 %, 40 °C). The testing was conducted in C&W Humidity cabinet, model AB5.

### Adhesion test

Adhesion of the coating was measured using a Cross-cut adhesion test, before and after corrosion testing in a salt spray and humidity chamber, with Zehntner device ZMG 2151 and 2 mm spacing of cut, according to ISO 2409.

### Electrochemical impedance spectroscopy

The protective properties of the applied coatings were examined by EIS measurements using a VersaSTAT 3 Potentiostat/Galvanostat (AMETEK Scientific 131 Instruments, Princeton applied research, Berwyn, PA, USA). The measurements were performed for each plate after 24 hours in 3.5% NaCl solution at room temperature (23±2) °C.




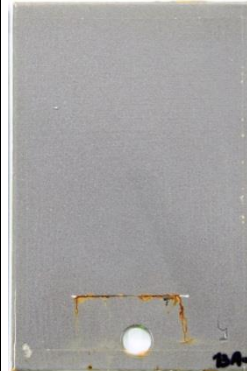


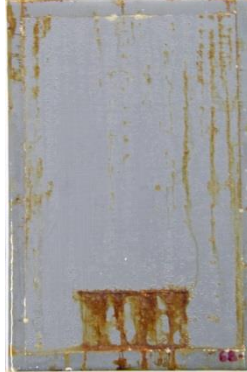
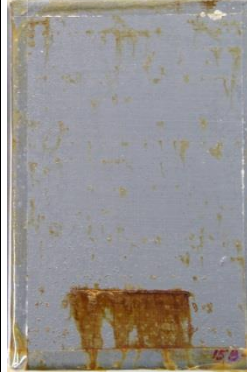
EIS was performed at OCP with a 10 mV sinusoidal amplitude in the frequency range from 100 kHz to 0.1 Hz. The working electrode was the tested plate, while Hastelloy C276 was the reference electrode. The area of the working electrode was 32 cm<sup>2</sup>. For interpretation of the obtained data, the ZSimpWin Version 3.2 software was used.

## **Results and discussion**

### Salt spray chamber results

After 100 hours of salt spray chamber testing, the samples were evaluated in accordance to ISO 4628, by measuring the corrosion around the scribe in accordance to ISO 7253 and by Cross-cut adhesion testing according to ISO 2409. For successful protection, samples must be free of visible surface changes and signs of corrosion, with no adhesion loss and corrosion around the scribe lower than 1.5 mm according to ISO 12944-6. The corrosion around the scribe was measured at eight points and then the averaged value was calculated.

Testing results are presented in figure 1.

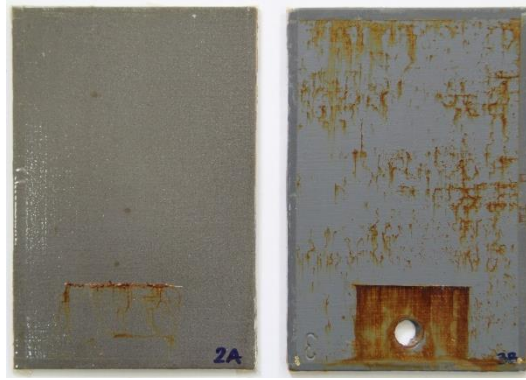
	Thinner	414	416	418
VpCI 386 acrylic coating				
	66,73 μm; Gt = 0	67,25 μm; Gt = 1	68,78 μm; Gt = 0	65,87 μm; adhesion loss
Acrylic coating, VpCI free				
	63,58 μm; Gt = 1	59,10 μm; Gt = 2	64,12 μm; Gt = 1	61,02 μm; Gt = 2

**Figure 1.** Samples after 100 hours of salt spray chamber testing

After the corrosion test in the salt spray chamber, the samples 13A-1 and 6B-1 applied on the surface cleaned by chemical cleaner 416, showed the best adhesion results, which are equal to samples 6A and 10B applied on the surface cleaned by thinner.

The rust creep for all tested coating is lower than required maximum of 1.5 mm, according to ISO 12944-6.

Figure 2 presents the sample views after 100 hours of salt spray testing of the coatings applied on the clean, abrasive blasted surfaces (without oil contaminants). VpCI 386 coating showed better corrosion protection properties, without rusting and blistering occurrence after salt spray testing. This is possibly because of the corrosion inhibitor effect in the coating. Both the coatings were applied on the surface with the same mean roughness ( $R_z=37 \mu\text{m}$ ) and in the same mean thickness ( $DFT_{2A}=60.70 \mu\text{m}$ ,  $DFT_{3B}=61.90 \mu\text{m}$ ).



**Figure 2.** Samples prepared by abrasive blasting and protected by coating: 2A = VpCI 386, 3B = VpCI free, after 100 hours of salt spray chamber testing

The summarised results according to ISO 4628 after salt spray chamber testing are presented in table 3.

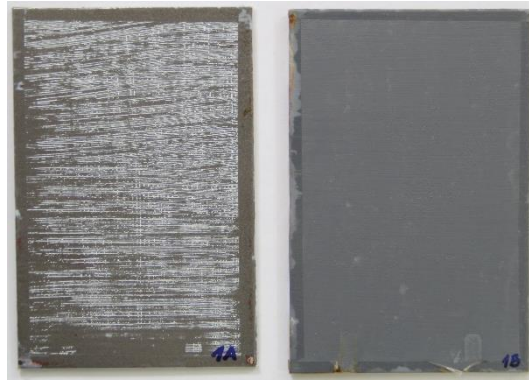
**Table 3.** Salt spray chamber testing results

Tested sample	ISO 4628-2	ISO 4628-3	ISO 4628-4	ISO 4628-5	ISO 7253
	Blistering	Rusting	Cracking	Flaking	Corrosion around the scribe [mm]
2A	0	Ri 0	0	0	0.15
6A	0	Ri 0	0	0	0.21
9A-1	0	Ri 0	0	0	0.28
12A-1	0	Ri 0	0	0	0.17
13A-1	0	Ri 1	0	0	0.23
3B	3 (S2)	Ri 3	0	0	0.16
10B	3 (S2)	Ri 2	0	0	0.18
9B -1	4 (S2)	Ri 2	0	0	0.10
6B -1	4 (S2)	Ri 1	0	0	0.10
15B - 1	3 (S2)	Ri 2	0	0	0.10

### Humidity chamber results

After 100 hours of humidity chamber testing, the samples were evaluated in accordance to ISO 4628 standard and by measuring Cross-cut adhesion, according to ISO 2409 standard.

Figure 3 presents the coatings 1A and 1B applied on a clean, abrasive blasted surface (without oil contaminants) after 100 hours of testing in a humidity chamber. Tested VpCI free acrylic coating (1B) showed blistering, while on the VpCI coating (1A) only color changes were observed.



**Figure 3.** Samples prepared by abrasive blasting and protected by coating: 1A = VpCI 386, 1B = VpCI free, after 100 hours of humidity chamber testing

Humidity testing results are presented in table 4.

**Table 4.** Humidity chamber testing results

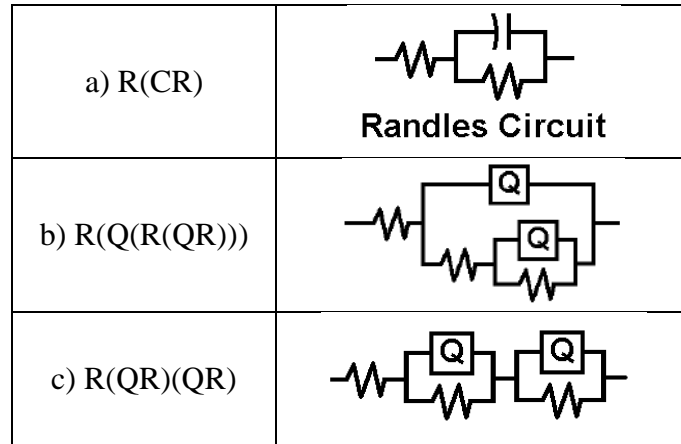
Cleaning agent	Tested sample	ISO 4628-2	ISO 4628-3	ISO 4628-4	ISO 4628-5	ISO 2409
		Blistering	Rusting	Cracking	Flaking	Adhesion
Blasted	1A	0	Ri 0	0	0	0
Thinner	5A	0	Ri 0	0	0	0
414	8A-1	0	Ri 0	0	0	2
416	10A-1	0	Ri 0	0	0	2
418	14A-1	0	Ri 0	0	0	adhesion loss
Blasted	1B	3 (S2)	Ri 0	0	0	0
Thinner	12B	4 (S2)	Ri 0	0	0	2
414	7B-1	3 (S2)	Ri 0	0	0	2
416	4B-1	2 (S2)	Ri 0	0	0	3
418	13B-1	3 (S2)	Ri 0	0	0	2

The samples protected by VpCI acrylic coating showed better behaviour in a humidity chamber compared to acrylic coating without corrosion inhibitors at which severe blistering was observed. Also, blistering negatively reflected on adhesion of the coating. The best results in the humidity chamber were obtained on sample 1A prepared by abrasive blasting (etalon).

#### Electrochemical impedance spectroscopy (EIS)

The impedance spectra was measured after 24 hours of exposure to 3.5% NaCl solution, and then analysed by fitting with a suitable equivalent circuit model. The impedance data of tested acrylic coatings were fitted by the Randles equivalent electric circuit (Figure 4a) and equivalent electric circuits for porous coating (Figure 4b and 4c). The Randles equivalent circuit is a combination of a capacitor and two resistors, often used for modelling the non-porous coating behaviour. The charge transfer resistance and double layer capacitance elements appear for a porous coating system with corrosion occurring on the metal surface [10-12].





**Figure 4.** Electrical equivalent circuits [10-12]

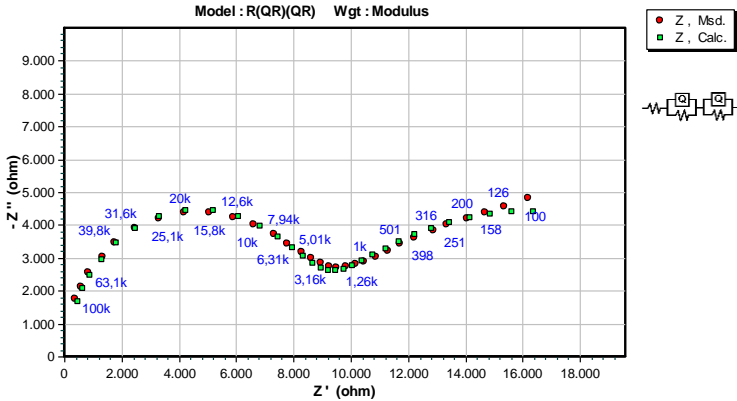
The EIS data, namely solution resistance ( $R_1$ ), coating resistance ( $R_2$ ), charge transfer resistance ( $R_3$ ), coating capacitance ( $C_c$ ), constant phase element of the coating ( $CPE_1$ ) and constant phase element of the double layer ( $CPE_2$ ) with empirical constant  $n_1$  and  $n_2$ , are given in Table 5.

**Table 5.** EIS results after 24 hours immersions in 3.5% NaCl

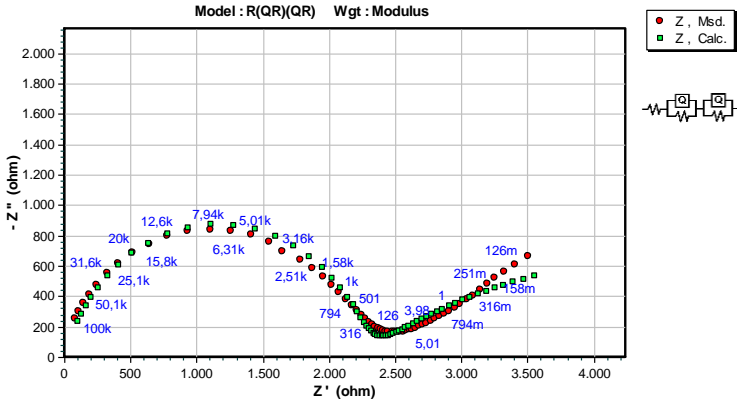
Sample	$R_1$ [ $\Omega\text{cm}^2$ ]	$R_2$ [ $\Omega\text{cm}^2$ ]	$R_3$ [ $\Omega\text{cm}^2$ ]	$C_c$ [ $\text{F}/\text{cm}^2$ ]	$CPE_1$		$CPE_2$	
					$Q_1$ [ $\text{F}/\text{cm}^2$ ]	$n_1$	$Q_2$ [ $\text{F}/\text{cm}^2$ ]	$n_2$
(Blasted) 3A-1	91.9	$3.096 \times 10^5$	-	$9.561 \times 10^{-10}$	-	-	-	-
(Blasted) 2B	100	$3.77 \times 10^3$	$1.854 \times 10^3$	-	$3.760 \times 10^{-8}$	0.88	$2.942 \times 10^{-5}$	0.6
(Thinner) 4A	30.8	$7.786 \times 10^5$	-	$9.515 \times 10^{-10}$	-	-	-	-
(Thinner) 11B	100	$2.659 \times 10^4$	$5.772 \times 10^4$	-	$2.479 \times 10^{-6}$	0.74	$2.180 \times 10^{-8}$	0.89
(414) 8B-1	100	$4.508 \times 10^3$	$2.241 \times 10^3$	-	$6.014 \times 10^{-4}$	0.35	$5.835 \times 10^{-6}$	0.83
(414) 7A-1	31.2	$1.593 \times 10^4$	$8.121 \times 10^3$	-	$9.754 \times 10^{-7}$	0.63	$1.173 \times 10^{-9}$	0.98
(416) 11A-1	79.5	$4.150 \times 10^6$	-	$7.567 \times 10^{-10}$	-	-	-	-
(416) 5B-1	100	$4.144 \times 10^4$	$4.342 \times 10^4$	-	$1.698 \times 10^{-8}$	0.61	$3.758 \times 10^{-8}$	0.87
(418) 15A-1	100	$1.105 \times 10^3$	$5.002 \times 10^6$	-	$1.313 \times 10^{-8}$	0.99	$9.794 \times 10^{-10}$	0.99
(418) 14B-1	44.9	$2.099 \times 10^4$	$1.596 \times 10^5$	-	$2.980 \times 10^{-8}$	0.82	$6.405 \times 10^{-5}$	0.43

After 24 hours of immersion in 3.5% NaCl, the highest coating resistance was noticed on VpCI acrylic coating applied over surface prepared by blasting and decreased by VpCI 416 cleaner. The VpCI coating showed overall better protection properties compared to coating without corrosion inhibitor in 3.5% NaCl solution.

The representative Nyquist diagrams of two tested acrylic coatings applied over blasted surface and decreased with VpCI cleaner are showed in Figure 5.



a)



b)

**Figure 5.** The Nyquist diagram of tested coatings after 24 hours immersion in 3.5% NaCl: a) Sample 7A-1, b) Sample 8B-1

## Conclusions

Choosing the proper surface pre-treatment method is not only the issue which effects durability of coating protection, but also environmental concerns.

The results of this study are summarized as follows:

- The best results are achieved on samples where the coating is applied on a clean (not-oiled) blasted surface.
- Water-based VpCI 416 cleaner showed degreasing results equal to cleaning with solvent-based thinner. VpCI 416 performed better cleaning efficiency and little (only in humidity chamber) or no negative influence on coating adhesion compared to VpCI 414 and 418 cleaners. Generally, the cleaners should be thoroughly removed from the surface by repeating the rinsing process before painting.
- VpCI acrylic coating showed better protection properties in the salt spray and humidity chamber compared to VpCI free acrylic coating. Effect of corrosion inhibitor in the coating is visible due to no rusting of the substrate compared to coating without corrosion inhibitor.
- EIS measurement revealed that VpCI coating applied on VpCI 416 cleaned surface before painting showed the highest resistance to 24 hours immersion in 3.5% NaCl.

Following the results from this study, water-based cleaners could be an effective and environmentally acceptable alternative to traditional solvent-based degreasing agents for surface cleaning before coating protection.

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