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Coatings

and anticorrosion protection

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Coatings and anticorrosion protection

Every fundamental approach to corrosion must take into account the properties of the metal, of the environment, and of the metal – environment interface.

Metal: *composition, structure, heterogeneity, stress, etc.*
Environment: *chemical composition, impurities, temperature, hydrodynamic conditions*
Interface: *reaction kinetics, the nature and distribution of corrosion products, speed of creation and destruction of films.*

The mechanisms of corrosion are complex, and an understanding of them calls upon knowledge from several disciplines, ranging from physics to bacteriology. However, many cases can be resolved by the simple application of concepts that are relatively straightforward, taking into account the impact of the solution applied on all the other characteristics of the workpiece or the installation. The best solution to a corrosion problem is not usually the most high-performance remedy in terms of anticorrosion, but rather the best compromise between the behaviour of the workpiece in relation to its environment, as well as its overall performance within a given technical-economic context.

Application methods

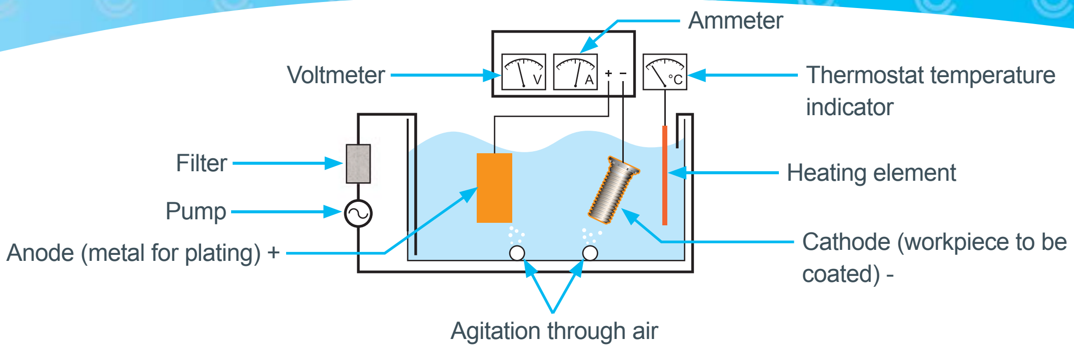
Electrolytic process

The point of this process is to add a specific superficial property - which may be decorative, protective against corrosion, or more generally, physical or mechanical properties that are different from those of the substrate (in terms of hardness, friction, conductivity, adhesion of organic products, barrier layers, etc.).

The filler metal - initially in ionic form in a bath - is subjected to an electrochemical reduction reaction, transforming it to a metal state. This reaction is provoked on the surface of the parts to be coated through the addition of electrons from an external circuit.

The operation takes place within an electrolytic cell comprising the following elements:

- a tank containing the electrolytic bath
- the electrodes immersed in the bath
    - The negatively polarised cathode comprising the workpiece to be coated, and the seat of the reduction reaction resulting in the plating. This electrode can also be the seat of other reduction reactions, including the electrolysis of the water with the release of hydrogen – which can be a source of embrittling for certain substrates.
    - The anode, seat of one or more oxidation reaction(s). This can be soluble or indissoluble. Where it is soluble, it comprises metal for plating and is subject to the opposite reaction of that which is produced at the cathode. Where it is insoluble, the composition of the bath varies continuously throughout the course of the electrolysis.
- the electrical circuit is made up of conductors supplying the electrodes connected to a generator of current.



The electrolytic cell shown is suitable for medium and large sized workpieces. Small workpieces are processed in bulk, in an appliance known as a "**barrel**". Other devices are used for specific applications (out-of-tank plating). Certain installations designed for specific applications look more like machine-tools than electrolytic tanks.

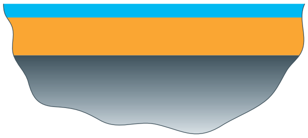
In order to obtain superior corrosion resistance, a conversion treatment is required after coating. This treatment, known as **passivation**, is carried out in trivalent chrome-based baths (Cr3).

Passivation creates a protective barrier of zinc coating (see "Protection principles")

The surfaces to be treated require careful preparation, and the conversion treatments must be carried out after electrolysis. The treatment options are, therefore, complex procedures of which electrolysis represents only one stage. Example of the electrolytic galvanizing range:

1. Chemical degreasing
2. Rinsing
3. Electrolytic degreasing
4. Rinsing
5. Pickling
6. Rinsing
7. Electrolytic degreasing
8. Rinsing
9. Electrolytic galvanizing
10. Rinsing
11. Depassivation
12. Rinsing
13. Passivation
14. Rinsing
15. Blowing
16. Baking

Electrolytic zinc on steel



🟦 Cr3 Passivation (barrier protection)
🟧 Zn coating (sacrificial protection)
⬛ Steel substrate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The various electrolytic treatments offered by LA CLUSIENNE-CLUFIX are listed in the table on the last page of document.

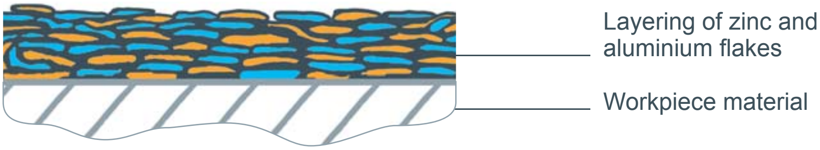
Application methods

Flake process

Flake-type coatings were designed to offer increased resistance to corrosion in comparison with conventional electro-zinc coatings, as well as for their other advantages in the manufacture of small components, and fasteners in particular.

This type of coating is widely used in the automotive industry. Its composition and characteristics also enable friction coefficients to be controlled, where a repeatable control of mechanical torque is necessary (in the case of automated mounting for mass production).

This type of coating is principally composed of zinc flakes, combined with aluminium flakes in certain cases.



The use of zinc flakes rather than zinc dust or powder in the formulation of this material is primordial, because the presence of flakes allows us to obtain an extremely dense coating. Their structuring parallel to the substrate surface during drying and baking considerably improves the protection offered by the coating. The flakes can be connected by an organic or inorganic matrix, depending on the specific materials used.

These coatings are highly conductive, offering steel sacrificial cathodic protection. They are often also given a top coat to strengthen resistance to corrosion as well as barrier effect - in which case the coating ultimately achieved can cease to be conductive.

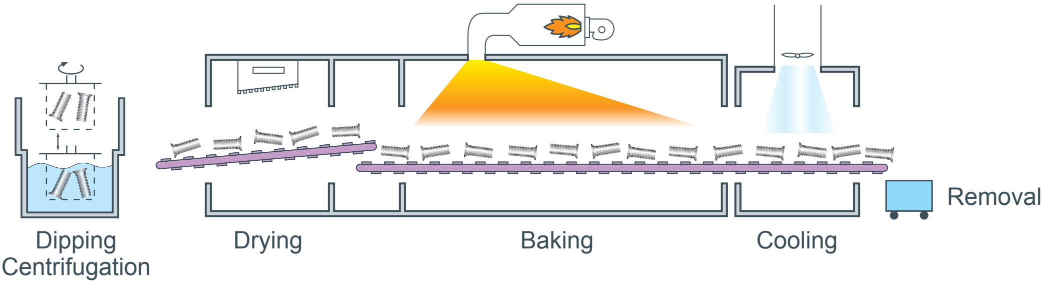
In terms of performance, zinc flake coating offers the following advantages:

- Excellent resistance to atmospheric corrosion
- Reduced ‘white rust’ effect (products of zinc corrosion) or other products of corrosion
- Resistance to salt spray superior to that of many other coatings resulting from conventional processes, such as: electro-galvanizing or sherardizing.
- Protection against numerous “non-aggressive” chemical products and solvents, such as brake fluids and fuel, etc.
- No embrittling through hydrogen because the application is non-electrolytic.
- Generally highly conductive.
- Electroplate protection of the zinc-enriched coating allows satisfactory reduction of bimetallic corrosion on contact with steel, aluminium, zinc and cadmium in most situations.
- Allows complexly-shaped workpieces, with hollows and holes, to be coated with optimal material.
- Reduced thickness makes it possible to obtain corrosion resistance equivalent to that of conventional, more thickly-layered coatings.

The zinc flake coating process (**barrel**) - the most common method- can be broken down into 4 phases:

1) **Preparation** phase, which seeks to remove all dirt, lubricants and oxidation from the workpieces to be treated: this phase can itself be broken down into an alkaline degreasing + drying stage, followed by either mechanical (shotblast) or chemical pickling (phosphate);
2) **Dipping-centrifugation** Phase: the fasteners placed in cylindrical baskets are dipped in a liquid zinc flake bath preparation. The baskets are then subjected to centrifugation, which results in an even coating over the entire workpiece surface. The baskets are then tilted and tossed to empty the hollow bodies, before being centrifugated again;
3) **Drying** phase: the workpieces are tipped out onto a mat in a drying cabinet;
4) **Baking** phase: immediately after drying, the workpieces travel through the baking oven.

Phases 2 to 4 are then repeated, as many times as there are layers of plating. Two layers of plating for a Grade A coating; three layers of plating for a Grade B coating. The maximum size of these parts, for the barrel method, is up to 150 mm x 20 mm in diameter, for a weight of around 0.5 kg.



For larger dimensions and weights, the barrel process is no longer appropriate and the **jig** coating process is used. The parts are positioned on jigs. The jigs are dipped in a liquid zinc flake bath. Then, the parts thus coated undergo a draining-centrifugal process designed to eliminate all excessive liquid. The maximum acceptable size of parts is up to 1100 x 500 mm for a weight of 30 kg.

There is a third type of plating method, known as **spraying**. The parts (brake discs, etc.) are placed on jigs before being treated by spraying. This treatment gives them increased protection against corrosion, and a finish that is more aesthetically pleasing.

The various flaked treatments offered by LA CLUSIENNE-CLUFIX are listed in the table on the last page of document.

Control of the friction coefficients of zinc flake coatings is guaranteed:

- either solely through the intrinsic qualities of the layers deposited - in which case we speak of zinc flake with integrated lubricant
- or by the addition of an extra protective film or topcoat to the layers of zinc flake to guarantee friction coefficient control.

The friction coefficients of the zinc flake zincs offered by LA CLUSIENNE-CLUFIX are listed in the table on the last page of this document.

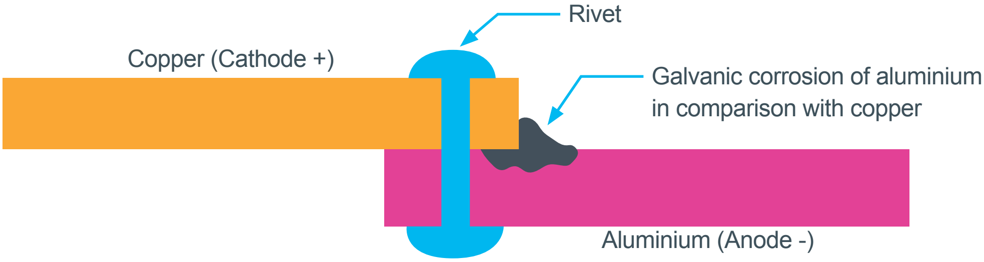
The workpieces commonly zinc flake coated are as follows:

- Threaded fasteners, in particular, those of strength grades 10.9 and 12.9
- Stamped pieces, springs, fasteners for the automotive industry, household appliances and construction industry.
- High-strength steel (≥ 1000 N/mm2 in particular) and cemented workpieces, for surface protection without any risk of embrittling through hydrogen.
- Sintered steel, cast steel and cast iron parts
- Complexly-shaped workpieces, with holes and hollows
- Connectors with multiple screw threads, e.g. locking parts and hose connectors

The potential created when the metal comes into contact with a solution depends on both the metal and the solution. Two different metals or alloys in contact with the same environment will generally take two different potentials. If these two metals are electronically connected, the difference in their potential will give rise to electrochemical reactions and to the circulation of electrical current.

The most negative (least noble) metal is therefore positively polarized and the most positive metal is negatively polarized. In the vast majority of cases, this set-up corresponds to an increase in the corrosion rate of the most corrodible metal (the most negative), and a reduction in the corrosion rate of the least corrodible metal (the most positive). The severity of the corrosion of the least noble metal depends on several factors:

- The difference in potential between the two metals: The higher this value is, the more powerful the electromotive force of the phenomenon. The values to be taken into consideration correspond to the potentials of metals and alloys constituting a pair in relation to the environment in question. These potentials are experimental in size, and must be distinguished from the standard potentials of thermodynamics tables. The experimental potentials are strongly influenced by such parameters as temperature, agitation and aeration. Moreover, some metals can take two different potentials in relation to the same environment, depending on whether they are active or passive (stainless steel coming into contact with seawater, for example). These considerations demonstrate that it can be difficult to foresee trends without having recourse to experimentation, because many parameters are liable to reverse the polarities of certain galvanic pairs. The table opposite shows the galvanic pairs of the principal metals.



Example of galvanic corrosion for a riveted assembly of aluminium and copper sheets, without insulation. There is corrosion, because the dissolution potential of the aluminium is lower than that of copper.

- The surface ratio between the two metals: the least favourable case is that of a large cathodic surface (the most positive metal) electrically connected to a small anodic surface (the most negative metal). The corrosion rate of the most negative metal can be multiplied by 100, or even 1000. An assembly consisting of sheets of iron held by copper rivets is far more resistant to corrosion than the opposite set-up (copper sheets and iron rivets).
- The conductivity of the corrosive environment influences the location of deterioration. Galvanic corrosion can occur even in very resistant environments. In such cases, it happens at the point where the two metals touch. Conversely, the attack is located less in the conductive environment.
- The corrosion resistance of the most noble metal- regardless of its potential - has considerable influence on the behaviour of bimetallic torque. If the noblest metal corrodes, its corrosion products risk, through their movement, accelerating the corrosion of the most corrodible metal. For example, the products of copper corrosion can corrode aluminium. The result is that the copper-aluminium pair (which has a lesser difference in potential than the gold-aluminium pair) is, however more dangerous – because gold, which is incorrodible, does not present this risk.

A few ways of fighting against this corrosion: choose metallic pairs in which the elements are as close as possible in the table opposite; avoid an unfavourable surface relationship; avoid, as far as possible, direct contact between two different materials (by using a seal, insulator, coating, etc.).

Protected paired cathodic metal (more noble) - Corroded metal considered to be anodic (less noble) +	Platinum	Gold	Stainless steel 18-9	Silver	Mercury	Nickel	CuZn23Ni22 alloy	Copper	Copper-Aluminium Cu Al10	CuZn brass CuZn39Pb	Bronze CuSn12	Tin	Lead	Fe Ni25	Aluminium-Copper AlCu4Mg	Cast iron	Carbon steel	Screw-cutting light alloy	Light cast alloy	Aluminium A5	Carbon steel for heat treatment XC80	Al Mg alloy	Cadmium	Pure iron	AlMgSi alloy	Chrome	Al Zn Mg alloy	Sn Zn white metal	Zinc	Manganese	Magnesium
Platinum	0																														
Gold	130	0																													
Stainless steel 18-9	250	120	0																												
Silver	350	220	100	0																											
Mercury	350	220	100	0	0																										
Nickel	430	300	180	80	80	0																									
CuZnNi alloy	450	320	200	100	100	20	0																								
Copper	570	440	320	220	220	140	120	0																							
Copper-Aluminium	600	470	350	250	250	170	150	30	0																						
Brass CuZn	650	520	400	300	300	220	200	80	50	0																					
Bronze CuSn	770	640	520	420	420	340	320	200	170	120	0																				
Tin	800	670	550	450	450	370	350	230	200	150	30	0																			
Lead	840	710	590	490	490	410	390	270	240	190	70	40	0																		
Fe Ni25	930	800	680	580	580	500	480	360	330	280	160	130	90	0																	
Aluminium Copper	940	810	690	590	590	510	490	370	340	290	170	140	100	10	0																
Cast iron	950	820	700	600	600	520	500	380	350	300	180	150	110	20	10	0															
Carbon steel	1000	870	750	650	650	570	550	430	400	350	230	200	160	70	60	50	0														
Screw-cutting light alloy	1000	870	750	650	650	570	550	480	400	350	230	200	160	70	60	50	0	0													
Light cast alloy	1065	935	815	715	715	635	615	495	465	415	295	265	225	135	125	115	65	65	0												
Aluminium	1090	960	840	740	740	660	640	520	490	440	320	290	250	160	150	140	90	90	25	0											
Carbon steel for heat treatment	1095	965	845	745	745	665	645	525	495	445	325	295	255	165	155	145	95	95	30	5	0										
Al Mg alloy	1100	970	850	750	750	670	650	530	500	450	330	300	260	170	160	150	100	100	35	10	5	0									
Cadmium	1100	970	850	750	750	670	650	530	500	450	330	300	260	170	160	150	100	100	35	10	5	0	0								
Pure iron	1105	975	855	755	755	675	655	535	505	455	335	305	265	175	165	155	105	105	40	15	10	5	5	0							
AlMgSi alloy	1105	975	855	755	755	675	655	535	505	455	335	305	265	175	165	155	105	105	40	15	10	5	5	0	0						
Chrome	1200	1070	950	850	850	770	750	630	600	550	430	400	360	270	260	250	200	200	135	110	105	100	100	95	95	0					
Al Zn Mg alloy	1275	1095	975	875	875	795	775	655	625	575	455	425	385	295	285	275	225	225	160	115	130	125	125	120	120	25	0				
Sn Zn white metal	1360	1230	1110	1010	1010	930	910	790	760	710	500	560	520	430	420	410	360	360	295	270	265	260	260	255	255	160	135	0			
Zinc	1400	1270	1150	1050	1050	970	950	830	800	750	630	600	560	470	460	450	400	400	335	310	305	300	300	295	295	200	175	40	0		
Manganese	1470	1340	1220	1120	1120	1040	1020	900	870	820	700	670	630	540	530	520	470	470	405	380	375	370	370	365	365	270	245	110	70	0	
Magnesium	1950	1870	1700	1600	1600	1520	1500	1380	1350	1300	1180	1150	1110	1020	1010	1000	950	950	885	860	855	850	850	845	845	750	725	590	550	480	0

Below the red line, the metal listed in the vertical column will be attacked:

- the metal combined is not subject to galvanic corrosion – on the contrary, it benefits from a protective effect
- the galvanic effect is influenced by the interaction between the surfaces of the two metals in contact – if the surface of the metal considered is the smallest, its corrosion increases, and vice versa

unit : mV

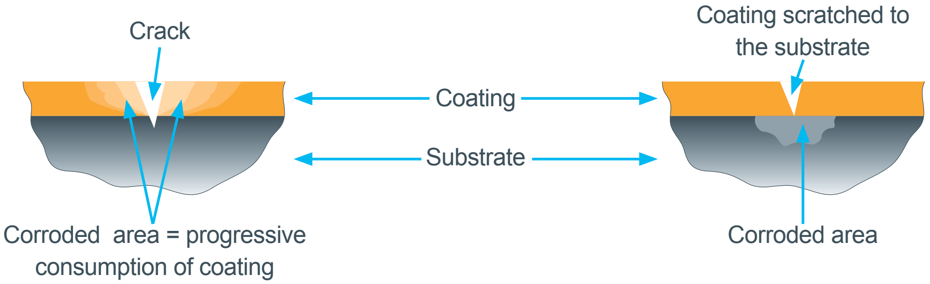
Protection principles

Sacrificial

The coating corrodes rather than the substrate, because the coating is less ‘noble’ than the substrate. If the coating is locally damaged down to the substrate by scratching or scoring, the substrate will remain protected as long as it is adequately surrounded by the coating.

Barrier

The coating is nobler than the substrate – it is therefore extremely resistant to corrosion. If the coating is locally damaged down to the substrate by scratching or scoring, the coating will no longer protect the substrate, which will immediately become corroded.



In the event of electrolytic galvanizing with a chrome trivalent (Cr3) based passivation, the passivation creates a protective barrier of zinc (chrome being nobler than zinc) and the zinc plating creates a sacrificial protection for the steel (zinc being less noble than steel).

Measurement of coating performance

In practice, the effectiveness of a finish is expressed in terms of its resistance to corrosion. This resistance is in turn expressed in terms of hours of exposure, in accordance with standardized tests known as ’salt spray tests’.

The salt spray test entails the exposure of surface treated workpieces to a salt spray chamber in which a controlled aggressive saline environment reigns.

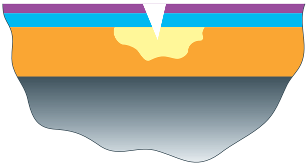
Resistance to corrosion is expressed in terms of the number of hours without the appearance of white rust, and then red rust.

White rust (WR):

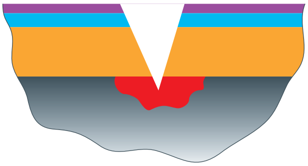
White rust corresponds to the corrosion of the zinc layer.

Red rust (RR):

Red rust corresponds to the corrosion of steel – in other words, where no coating remains on the steel.



- 🟪 Optional top coat (electrolytic or flake galvanizing)
- 🟦 Passivation (electrolytic galvanizing)
- 🟧 Zn coating (sacrificial protection)
- ⬛ Steel substrate
- 🟨 White rust (corrosion of zinc)
- 🟥 Red rust (corrosion of steel)



Coatings offered (non exhaustive list)

Electrolytic treatment	Compliance ELV & RoHS	Colour	Friction coefficients	Resistance of treatment to corrosion on a sliding scale of 1 to 10									
				1	2	3	4	5	6	7	8	9	10
Zinc Nickel	O	Blue	> 0.25							▨	▨	▨	
Black Zinc Nickel	O	Black	> 0.25							▨	▨	▨	
Zinc Nickel + RF*	O	Blue	0.12 - 0.18							▨	▨	▨	
Zinc Nickel + Lub**	O	Blue	0.09 - 0.15							▨	▨	▨	
Black Zinc Iron	O	Black	> 0.25					▨	▨	▨			
Zinc Chrome 3 + RF*	O	White	0.12 - 0.18					▨	▨				
Zinc Chrome 3	O	White	> 0.20			▨	▨	▨					
Zinc Chrome 3 + Lub**	O	White	0.09 - 0.15			▨	▨	▨					
Green Zinc	N	Green	> 0.25		▨	▨	▨						
Yellow Zinc	N	Yellow	> 0.25	▨	▨	▨	▨	▨					
Black Zinc	N	Black	> 0.25	▨	▨	▨							
White Zinc	O	White	> 0.25	▨	▨	▨							

* RF = Reinforced Finish - organic-mineral & silica-based, which improves resistance to corrosion and reduces the friction coefficient
** Lub = Lubricant Finish which reduces the friction coefficient

Zinc flake coating	Compliance ELV & RoHS	Colour	Friction coefficients	Resistance of treatment to corrosion on a sliding scale of 1 to 10									
				1	2	3	4	5	6	7	8	9	10
Geomet® 500 Grade A*	O	Silver grey	0.12 - 0.18						▨	▨	▨		
Geomet® 500 Grade B**	O	Silver grey	0.12 - 0.18								▨	▨	▨
Geomet® 321 PLUS Grade A*	O	Silver grey	> 0.18						▨	▨	▨		
Geomet® 321 PLUS Grade B**	O	Silver grey	> 0.18								▨	▨	▨
Geomet® 321 PLUS XL Grade A*	O	Silver grey	0.06 - 0.09						▨	▨	▨		
Geomet® 321 PLUS XL Grade B**	O	Silver grey	0.06 - 0.09								▨	▨	▨
Geomet® 321 PLUS L Grade A*	O	Silver grey	0.08 - 0.14						▨	▨	▨		
Geomet® 321 PLUS L Grade B**	O	Silver grey	0.08 - 0.14								▨	▨	▨
Geomet® 321 PLUS VL Grade A*	O	Silver grey	0.09 - 0.14						▨	▨	▨		
Geomet® 321 PLUS VL Grade B**	O	Silver grey	0.09 - 0.14								▨	▨	▨
Geomet® 321 PLUS ML Grade A*	O	Silver grey	0.10 - 0.16						▨	▨	▨		
Geomet® 321 PLUS ML Grade B**	O	Silver grey	0.10 - 0.16								▨	▨	▨
Geomet® 321 PLUS M Grade A*	O	Silver grey	0.12 - 0.18						▨	▨	▨		
Geomet® 321 PLUS M Grade B**	O	Silver grey	0.12 - 0.18								▨	▨	▨
Deltaprotekt® KL100 Grade A*	O	Silver grey	0.12 - 0.18						▨	▨	▨		
Deltaprotekt® KL100 Grade B**	O	Silver grey	0.12 - 0.18								▨	▨	▨
Deltaprotekt® VH300 Grade A*	O	Colourless	0.12 - 0.18						▨	▨	▨		
Deltaprotekt® VH300 Grade B**	O	Colourless	0.12 - 0.18								▨	▨	▨
Deltaprotekt® VH 301 GZ Grade A*	O	Colourless	0.08 - 0.14						▨	▨	▨		
Deltaprotekt® VH 301 GZ Grade B**	O	Colourless	0.08 - 0.14								▨	▨	▨
Deltaprotekt® VH 302 GZ Grade A*	O	Colourless	0.10 - 0.16						▨	▨	▨		
Deltaprotekt® VH 302 GZ Grade B**	O	Colourless	0.10 - 0.16								▨	▨	▨

* Grade A = coating weight > 24 g/m² for thickness of between 5 and 7 microns
** Grade B = coating weight > 36 g/m² for thickness of between 8 and 10 microns

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