

A new way to ensure metal protection with Waterborne Dispersion

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ABSTRACT

Metals and their alloys are excellent materials with high strength and outstanding mechanical properties; they have been used for centuries. However, when they are exposed to a corrosive environment, surface of the steel structures will corrode and thus pose a potential danger to the whole steel structure and reduce its service life. The huge economic impact of the corrosion of metallic structures is a very important issue for all modern societies.

Today, the corrosion protection of metal is often obtained by multi-layer systems involving at least a primer and a top coat. These two coats are often based on different technologies implying solvent borne and water borne binders and formulations. It introduces complexity in the applications and drying equipment and processes.

Arkema has developed a new waterborne acrylic technology that provides by itself a very high protection to corrosion and a good adhesion on a large variety of substrates, under hard conditions. Due to these key features, this new Arkema's technology offers the advantage that it can be used as single Direct To Metal coating (DTM).

In the article, the new properties will be presented, as well as mechanisms and fundamentals which have been used to develop the technology.

1. INTRODUCTION

Within Arkema, the driven factors of our polymer development can be summarised by sustainability and market needs. In the protective coatings market which we target, these factors are linked. When we speak about sustainability, we include of course, the reduction of volatile organic compound (VOC) emissions, but also the fact that we will not use toxic compounds and the fact that the coatings formulated with our binders will increase the durability of the steel structures and so increasing its service life. One other parameter of the sustainability will also be to reduce the number of coating layers applied. Today, the anticorrosive protection is achieved by using, at least, two layers, the primer and the top coat. The principal properties required for a primer are adhesion, corrosion and water resistance (barrier properties). Concerning the top coat, the main properties are exterior UV durability, lack of dirt pickup, chemical resistance and gloss. Developing a binder, that can be used as single Direct To Metal coating (DTM) will fit with this last parameter of sustainability.

Water-borne anticorrosion maintenance coatings are generally more appreciated than solvent-borne ones in order to reduce volatile organic compound (VOC) emissions. Traditionally, the performance of available water-borne anticorrosion coatings has not been able to provide sufficient long time protection for steel structures especially in extremely corrosive environments. However, the development of novel binder technology will allow us to access resins that can be formulated in aqueous systems easily, and form very good hydrophobic and barrier films that are suitable for anticorrosion coating applications. Of course, the other sustainability's parameters described previously will be used to achieve our target of developing a new waterborne acrylic technology that can be used in a one layer (DTM), one compound (1K) and air drying system.

In this paper, we will investigate in the first part, how we develop this new technology, studying the influence of the functional monomers and their polymerisation process, the film formation and reticulation. The second part will be dedicated to how this technology fits with the protective coatings needs.

2. EXPERIMENTAL

2.1. Materials

Three acrylic dispersions have been used for this study. They differ in terms of hydrophoby, functional and cross-linking monomers. Their characteristics are summarized in Table 1.

Acrylic dispersion			WB Acrylic 1	WB Acrylic 2	WB Acrylic 3
Hydrophoby			High	Moderate	High
Process			Standard	New	New
Functional monomers			Yes	Yes	Yes
Cross-linking system			No	No	Yes
Solids content 1h @105°C	ISO 3251	%	43	50	50
Brookfield viscosity @ 23°C	ISO 2555	mPa.s	1200	960	1450
MFFT (+/- 2°C)	ISO 2115	°C	40	23	20
Particle size	ISO 13321	(nm)	100	107	110
pH	ISO 976		8	9	9
T _g °C (DSC)			38	21	19

Table 1: Characteristics of the acrylic dispersions

2.2. Varnishes formulations

The varnish formulations are respectively based on *WB Acrylic 1*, *WB Acrylic 2* or *WB Acrylic 3* added by 15% of coalescent agent for *WB Acrylic 1* and 5% of coalescent agent for *WB Acrylic 2* and *3* (on solid binder). These varnishes have been used to realise the polymeric films.

2.3. Metallic substrates

The metallic substrates used to evaluate the different applicative properties are: Cold rolled steel QD 36 from Q-panels, Cold rolled steel DC04 from Rocholl, Ground finish steel S36 from Q-panels, Aluminium A36 from Q-panels, Electro-galvanized steel DC 01, Hot rolled steel DD11, Fire tinted steel DX51 from Rocholl.

2.4. Minimum Film Formation Temperature measurements

The Minimum Film Formation Temperature is measured on a COESFELD device according to the ISO 2115 norm. The MFFT is the temperature at which a continuous, transparent film with no cracks is formed.

2.5. Microscopic evaluation of the film formation

The varnish films applied on glass plates at a wet film thickness of 100µm – dried during 7 days at room temperature 23°C, 50% relative humidity – have been characterised by reflection optical microscopy in order to evaluate the quality of the film formation. The microscope used is a Leica DMRM. The magnification is x200.

2.6. Glass Temperature measurements

The determination of glass transition temperatures – i.e. T_g – is done on a Mettler Toledo DSC1 device. The temperature varies from –40°C to 100°C at a rate of 10°C.min⁻¹.

2.7. Dynamic Mechanical Thermal Analysis – Tensile tests - Differential Scanning Calorimetry

Films:

Varnishes were applied on polypropylene plate at a wet film thickness of 600 µm, dried during 14 days at 23°C, 50% relative humidity.

Conditions for the DMA analysis:

Viscoelastic properties are evaluated by DMA measurements on a RSAII device in traction mode. The temperature is increased from –50°C to 200°C at a rate of 3°C/min and a frequency of 1Hz.

Tensile tests:

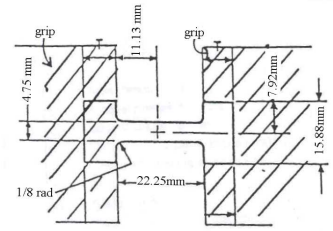
Done on a MTS machine

Temperature: 23°C, Relative Humidity: 50%

Speed: 5 mm/min

Cell: 50 N

Samples geometries: The samples have been cut with a punch



2.8. Water uptake test

WB Acrylics 1, 2 and 3 have been applied on polypropylene plate at a wet film thickness of 600 μm and dried in a climatic chamber at a temperature above 20°C to the MFFT, with a humidity condition decreasing from 90% to 50%. Discs of 29mm diameter are cut in the films prepared and stored during 7 or 14 days at 23°C, 50% relative humidity. The discs are immersed into water at 23°C and the weight evolution during time is measured.

$$\text{Water uptake \%} = \frac{m(t) - m_0}{m_0} \times 100$$

m_0 : Initial weight and $m(t)$ weight in time

3. RESULTS – DISCUSSION

3.1. New waterborne acrylic technology development

In this part, we will describe how our new technology has been built and developed in order to meet key properties for corrosion protection. Many properties can be adjusted and improved in the paint formulation thanks to additives and especially anticorrosive pigments; however our main targeted properties for the binder itself were first an excellent multi-substrate adhesion and excellent barrier properties.

It is well known in the literature that the way to improve adhesion of acrylic dispersions onto metallic substrates is to introduce functional monomers such as acids, amines, sulfonate, phosphate or phosphonate⁽¹⁾. All these functions are highly electronegative and can exchange electrons or create complex with metals and their oxides generating stable chemical bondings. It is also well known in the literature that such monomers are often hydrophilic and will not be incorporated homogeneously into the polymer particle with emulsion polymerization process but will be shared between the aqueous phase, the surface of the particle and the particle⁽²⁾. It is easy to anticipate that this partition will have consequence on the final adhesion.

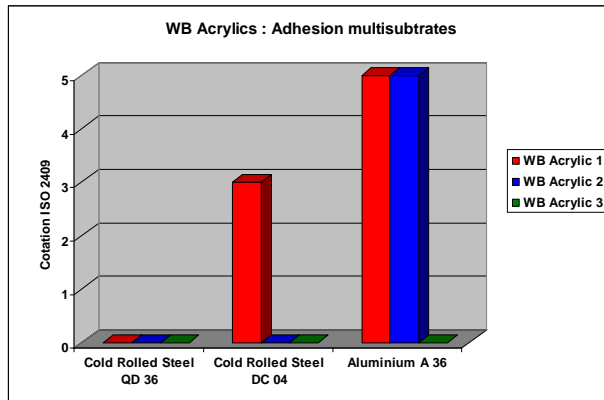
To achieve good barrier properties thanks to a polymer film, it is important to reduce as much as possible the diffusion of water through the film. The two main parameters that can influence it highly are the chemical nature of the polymer and its cross-linking density.

3.1.1. Polymer structures-properties evaluation

3.1.1.1. Functional monomers

The choice and the level of the functional monomers are really key parameters in order to develop a polymer which can achieve multi-substrates adhesion. However if their incorporation is not well controlled their effect on adhesion will be very poor. For each of the functional monomer selected, we optimized the conditions of polymerisation (process of introduction as well as pH in case of ionisable ones) in order to locate the maximum amount at the surface of the particle where it will be the more efficient to improve adhesion. All functional monomers that polymerize in the water phase, and so not linked to the polymer or buried inside the particle, will not contribute to the adhesion. The *WB Acrylic 1* where the polymerisation of the functional monomers is not well controlled shows a bad multi-substrate adhesion. On the opposite when the polymerisation of the functional monomers is well controlled which is the case of the *WB Acrylic 2*, we recover adhesion on cold rolled steel. To achieve a good multi-substrates adhesion we also need to optimise the level and the nature of these functional monomers. This is the case of the *WB Acrylic 3*. All the multi-substrates adhesion results are illustrated on the Graph 1 and have been done on the varnishes after

7 days of drying. Following the ISO 2409 method, a quotation of zero means perfect adhesion and a quotation of five means complete loss of adhesion.



Graph 1: Cross test adhesion on Cold Rolled Steel & Aluminium for varnishes based on WB Acrylics

The trend has been also confirmed using the pull off test (ISO 4624). The results summarised in the Table 2, have been obtained on the varnishes applied on cold rolled steel QD 36 at a dry film thickness of 50 µm. The pull off adhesion has been done after only 24 hours of drying at 23°C, 50% relative humidity.

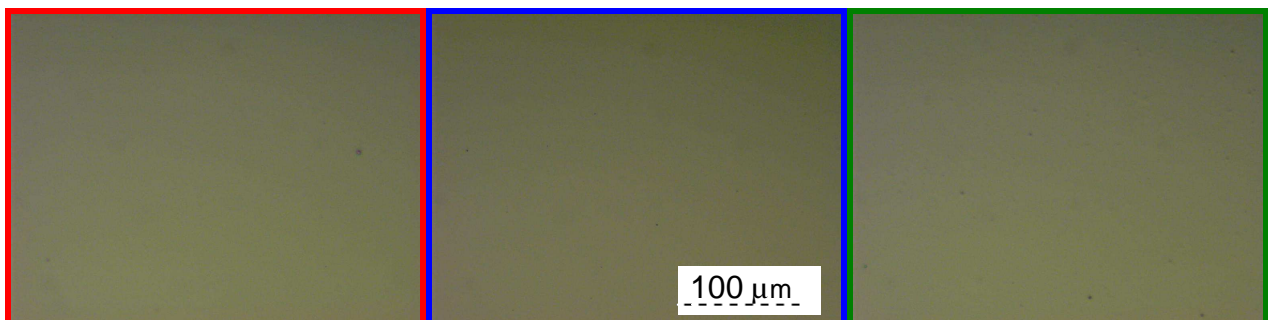
Samples	Strength at break (N)	Fracture pattern
WB Acrylic 1	173 +/- 25	The varnish is completely removed from the substrate
WB Acrylic 2	316 +/- 110	Only a part of varnish is removed from the substrate
WB Acrylic 3	615 +/- 10	Only a part of varnish is removed from the substrate

Table 2: Varnishes - Pull off test adhesion on Cold Rolled Steel (QD 36) after 24 hours drying- DFT 50µm

3.1.1.2. Film formation and cross-linking

If the adhesion has been identified as a key property in our application, it is not the only one. In terms of anticorrosive properties, and to protect the metallic substrate the role of the binder is to ensure high barrier properties against water. To reach the target, we played on the hydrophoby of the polymer backbone, on film formation and cross-linking.

The film formation of our three binders has been observed by microscopy (pictures 1, 2, 3), and it confirms that all our binders *WB Acrylic 1*, *2* and *3* have a good film formation.

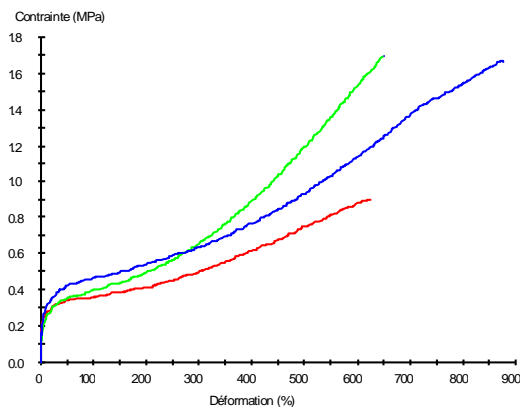


Picture 1: Film formation of varnish based on *WB Acrylic 1*

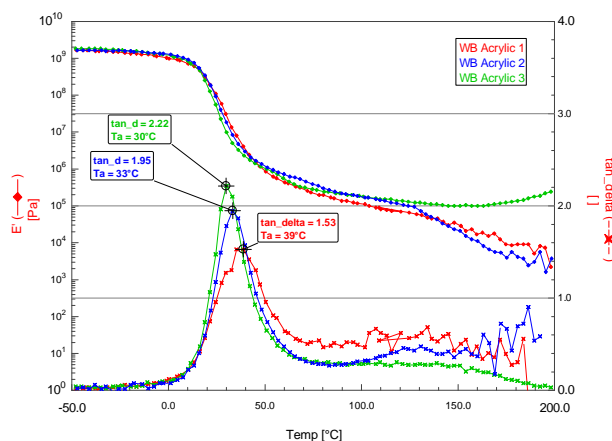
Picture 2: Film formation of varnish based on *WB Acrylic 2*

Picture 3: Film formation of varnish based on *WB Acrylic 3*

Dynamic Mechanical Thermal analysis as well as tensile tests, carried on plasticized films in order to eliminate difference of Tg effects, helped us to characterize the level of cross-linking that we could develop in our three generations of dispersions. We see that *WB Acrylic 1* and *2* are not cross-linked and that the introduction of a cross-linking system in *WB Acrylic 3* is effective thanks to the plateau we have on the modulus and the reinforcement of the stress when we elongate the film of polymer.



Graph 2: Tensile tests on varnishes film based on WB Acrylics



Graph 3: The Dynamic Mechanical Thermal on varnishes film based on WB Acrylics

Cross-linking is important to develop barrier properties however it shouldn't be in competition with the film formation otherwise we would lose all the benefit of cross-linking and would damage the barrier properties. The compromise, we need to achieve between the two phenomena is well explained in the literature^(3,4); film formation is characterized by a diffusion time (time for which the diffusion is optimal without any cross-linking agent) and cross-linking is characterized by a reaction time (time when every polymer chain has one cross-linking and has lost all mobility). The ratio $\text{Time}_{\text{diff}}/\text{Time}_{\text{react}}$ describes well the system and in order to have a homogeneous cross-linking within the film it is important that the time of reaction is not too short compared to the time of diffusion.

We have quantified by different means cross-linking and film formation of the three generations of binder. We carried on chemical resistance, water uptake test, Electrochemical Impedance Spectroscopy (EIS) study, and Salt Spray resistance and we will now discuss the results.

Chemical resistance test

The varnishes based respectively on *WB Acrylic 1*, *2* and *3*, have been applied on steel (S36) at a dry film thickness of 60 μm and dried during 7 days at 23°C, 50% relative humidity. The chemical resistance has been done using as solvent Methyl Ethyl Ketone (MEK) with a 1Kg mechanical hammer. The results are summarised in the Table 3.

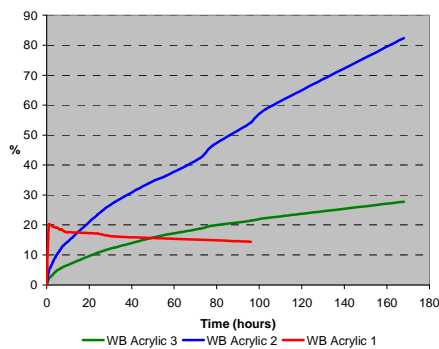
The very poor result obtained with *WB Acrylic 1* is probably due to the very poor adhesion of the varnish on the steel and in that case we can't measure its chemical resistance. Otherwise, for the two other dispersions which don't present any problem of adhesion, we clearly see an improvement of the chemical resistance when the system is cross-linked.

Varnishes based on	MEK Resistance (s)
WB Acrylic 1	< 10
WB Acrylic 2	40
WB Acrylic 3	90

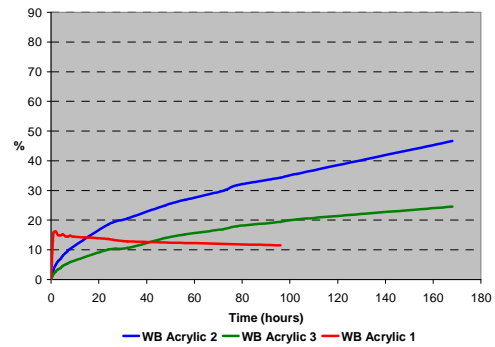
Table 3: Chemical resistance double rubs with MEK

Water uptake test

The *WB acrylic 1* shows a very quick water uptake followed by a partial solubilisation (this explains the shape of the red curve - Graph 3 and 4), this behaviour is probably due to the fact that the introduction of functional monomers was not optimized and gave high quantity of hydrophilic oligomers free in the polymer film. These ones are easily extracted from the film and it contributes to quick degradation of the polymer film. We obtain nearly the same results after 7 days and 14 days of drying. On the *WB Acrylic 2* we observe a big difference in terms of water uptake between 7 and 14 days of film drying, this could be explained by the film formation (after 7 days the film is not fully formed, the inter-diffusion of polymer chains to ensure a good autohesion between particles is not completed). Nevertheless this binder gives us a medium water uptake (around 50% after 14 days drying). The best result is obtained with the *WB Acrylic 3* which has a good compromise between film formation and cross-linking. Indeed we obtain no big difference between 7 and 14 days of drying and we achieve the lowest level of water uptake (around 25%). Compared to what we observe with *WB acrylic 2*, it seems to be interesting to have this quick development of good film formation and also cross-link in order to have high barrier properties and not to rely only on full film formation, since ultimate polymer diffusion may need several weeks.



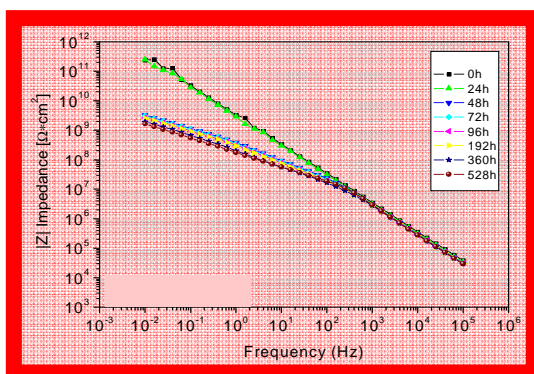
Graph 3: WATER UPTAKE Immersion into water @ 23°C of films after 7 days of drying



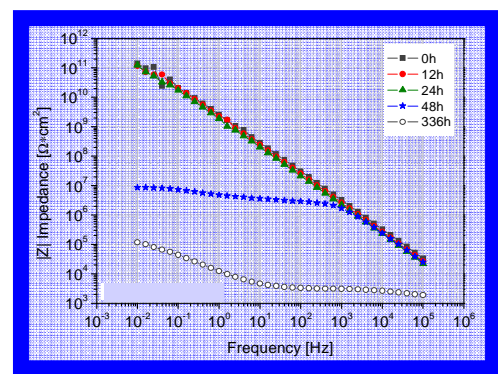
Graph 4: WATER UPTAKE Immersion into water @ 23°C of films after 14 days of drying

Electrochemical Impedance Spectroscopy (EIS)

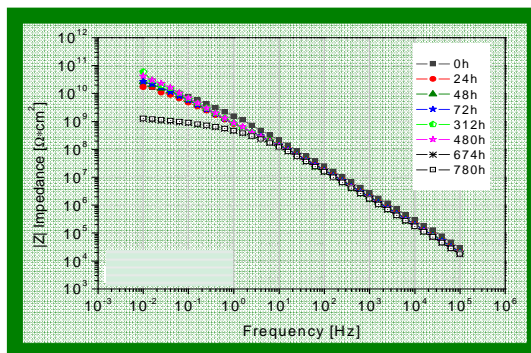
The protective properties of the clear coating (varnishes applied at 50 μ m dry on QD 36) were studied by electrochemical impedance spectroscopy measurements (EIS) obtained in aqueous 0.3% Na₂SO₄ solution which can simulate an aggressive corrosive environment. The EIS measurements were obtained in general on intact coatings (without artificial defects) at the free corrosion potential using a potentiostat and FRA equipment, signal amplitude 10 mV, frequency range 100KHz-0.01 Hz and testing area about 15 cm². A classical three electrodes arrangement was used. An Ag/AgCl (+0.205 V vs SHE) electrode and a platinum wire were used respectively as reference and counter electrode. The cell was obtained fixing a plastic tube on the sample surface. This test has been realized by Flavio Deflorian's team at the University of Trento (Italy)



Graph 5: WB Acrylic 1



Graph 6: WB Acrylic 2



Graph 7: WB Acrylic 3

The impedance spectra for *WB Acrylic 3* (Graph 7) has shown extremely high impedance, in the order of a 10^{11} Ohm.cm², at the low frequency just after immersion, which is an indication of very good barrier properties. Furthermore, the coating seems to remain stable after several hours of analysis. The ingress of aggressive ions and/or water coming from the electrolyte through the coating layer might have caused the slight reduction in the impedance modulus ($|Z|$) after 674 hours. To a certain extent, 10^9 Ohm.cm² can be qualified as a high value of impedance. With *WB Acrylic 1* (Graph 5), the behaviour is quite different. At the beginning the impedance is very similar to the *WB Acrylic 3*, but drops quickly after 48h of exposure. We can suppose, for this kind of material, a more defective structure with possible ionic paths through the coating causing the failure of the system. *WB Acrylic 2* (Graph 6) shows again very high impedance starting values for short immersion time, but the impedance drops reaching very low values (around 10^7 Ohm.cm²) after a few days of immersion. The conclusion is that *WB Acrylic 1* and *WB Acrylic 2* have less reliable protective properties in comparison with *WB Acrylic 3*.

Salt Spray resistance

The measure of corrosion resistance has been done on coated metal at 35°C with a salted solution (50g/l) into a corrosion chamber following the norm ISO 9227.

The previous EIS 's results were confirmed by continuous Salt Spray tests. The varnishes based on *WB Acrylic 1*, *WB Acrylic 2*, *WB Acrylic 3* were applied on steel S36 from Q panel at a dry film thickness of 40- 50µm, dried during 14 days at 23°C, 50% RH, and put into the continuous Salt Spray



Picture 4: WB Acrylic 1



Picture 5: WB Acrylic 2



Picture 6: WB Acrylic 3

Continuous Salt Spray results after 185 hours exposure

The corrosion results after 185 hours of exposure (Picture 4, 5, 6) clearly indicate excellent anticorrosion properties for the varnish based on *WB acrylic 3*.

3.1.2. CONCLUSIONS

In this part, we showed that the choice, level and polymerisation process of the functional monomers are key in order to achieve the right level of multi-substrates adhesion. When the polymerisation is not well controlled (*WB acrylic 1*) the direct effect is clearly linked with the loss of adhesion. On the opposite when the level and polymerisation of the functional monomers is well controlled the benefit on

adhesion has been clearly identified. This is the case of *WB acrylic 2* with an optimum with *WB acrylic 3*. Concerning the high level of barrier properties that help us to reduce the corrosion of metallic substrates, we demonstrated that the good balance between film formation and cross-linking allows us to well protect the metal. The combination and control of these parameters in the design of the polymer permits us to generate our new waterborne acrylic technology SECHA (SElf-Crosslinking Hydrophobic Acrylic). The optimum of this series has been obtained with the *WB Acrylic 3*.

3.2. How this new technology fulfils the market and customers requirements

We demonstrated in the previous part of the article that our new technology SECHA (*WB Acrylic 3*), has quite promising properties. The properties requested for an application on metal and in particularly as Direct To Metal (DTM) application could fit with the intrinsic properties of *WB Acrylic 3*.

- Low VOC level
- Excellent barrier proprieties
- Very good film formation
- Good adhesion on different metallic substrates
- Good Gloss
- Good durability

In this part, we will go deeply into the final applicative properties at the user's end. To realise that, we formulated a white gloss paint and tested it.

3.2.1. White gloss paint formulation

The white gloss paint has been made according to the formulation presented in the Table 4. This formulation didn't contain any anticorrosive additives or anticorrosive pigments. The pigment concentration in volume (PVC) has been fixed at 15 %.

INGREDIENTS	Weight	Volume		
millbase				
1 WATER	63,00	63,00		
2 BIOCIDES	1,85	1,79		
3 DISPERSING AGENT	5,39	5,08		
4 TITANIUM DIOXYDE	213,37	52,04		
5 DEFOAMER	1,00	0,99		
Dispers under high shear				
6 WB ACRYLIC 1 ou 3	633,45	609,09		
7 COALESCENT AGENT	15,96	17,74		
8 WATER	33,19	33,19		
9 THICKENER 1	1,50	1,43		
10 THICKENER 2	4,01	3,86		
11 WATER	27,27	27,27		
Total	1000,00	815,49		

PAINT CHARACTERISTICS :		DRY FILM CHARACTERISTICS :	
Density (g/cm ³)	1,23	Solids Density (g/cm ³)	1,53
Weight % Solids (%)	53,69	PVC (additive included) (%)	14,84
Volume % Solids (%)	43,00	PVC (minus additive) (%)	15,00
VOC (water incl.) (g/l)	20		

Table 4: White gloss paint formulation and specifications

3.2.2. Level of volatile organic compound (VOC) in our paint

Following the paint formulation prepared previously we can easily achieve the level of volatile organic compound (VOC) below 50 g/l, and in our case we were at 20g/l.

3.2.3. Cross test adhesion

The good results obtained with *WB Acrylic 3* on varnish have been confirmed and extended to the white gloss paint. All the multi-substrates adhesion results are illustrated on the Table 5 and have been done after 7 days of drying. Following the ISO 2409 method, a quotation of zero means perfect adhesion.

	Cold Rolled Steel QD 36	Cold Rolled Steel DC 04	Aluminium A 36	Electro-galvanized steel DC 01	Hot rolled steel DD11	Fire tinted steel DX 51
Multi-substrates adhesion of the paint based on <i>WB acrylic 3</i> (ISO 2409)	0	0	0	0	0	0

Table 5: White gloss paint adhesion on different metallic substrates

3.2.4. Gloss

The level of gloss we achieved with the paint fits with the market requirement, indeed we obtain: 60UB at 20° (angle measurement) and 80 UB at 60° (angle measurement).

3.2.5. Corrosion protection

Due to the high level of barrier properties of *WB Acrylic 3*, we manage to maintain an excellent corrosion protection and this without the addition of any anticorrosive pigments. To give a comparison we used as reference *WB acrylic 1* formulated in the white gloss paint according to the Table 4.



Picture 7: WB Acrylic 1



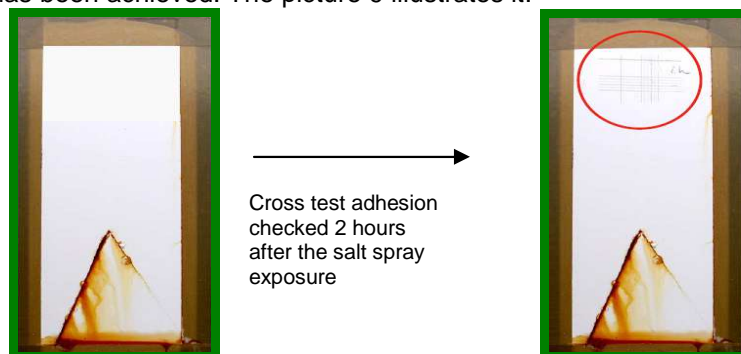
Picture 8: WB Acrylic 3

Continuous Salt Spray results after 240 hours exposure

The corrosion results (Picture 7 & 8) obtain on continuous salt spray test after 240 hours of exposure; show a very good protection of *WB Acrylic 3* against the corrosion.

3.2.6. Wet adhesion

In order to complete the market and customers requirements, the adhesion of paint has been tested in a more sever condition. We tested what we call the wet adhesion. This wet adhesion has been realised following the ISO 2409 method and 2 hours later the 240 hours salt spray test. The panels are stored at 23°C, 50% relative humidity during these 2 hours. In this condition, we still maintain the perfect adhesion as a quotation of zero has been achieved. The picture 9 illustrates it.



Picture 9: Wet cross test adhesion on white paint based on WB Acrylic 3

4. CONCLUSIONS

In conclusion, we demonstrated that playing with the right parameters which were the hydrophobicity of the polymer backbone, the influence of the process, the functional monomers, and the good balance between film formation and cross-linking; we were able to develop a new waterborne technology that provides excellent multi-substrate adhesion and excellent barrier properties by itself.

We demonstrated also that this type of technology fits with the final end user application in terms of protective metal. Indeed our new waterborne acrylic technology (SECHA) can be used in paint as a single layer for Direct to Metal (DTM), in one component system (1K), for air drying application for protective coatings.

Acknowledgements

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