Grolman

International Distribution

# Hungarocoat 2022

## Formulation of a water borne direct-to-metal paint

29th of November 2022

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# Introduction Grolman Group

# About us

Grolman
International Distribution

## Established 1855
Today run by the 5th generation of the Grolman family and privately owned

## Specialty Chemicals
Complementary product portfolio provides synergies and multiple cross-selling opportunities

## 43 Countries
Covered by 24 individual sales offices across Europe, Turkey, Northern Africa, India and China

## >200 Employees
Our success is based on a strong dedication and commitment to building an efficient customer-focused organization where customers' needs are an essential driving force

## Solution oriented
Technical market approach to support customers to solve their daily challenges and develop innovative, sustainable solutions

## >20,000 Customers
Excellent market penetration through a very broad customer basis across all focus industries

Grolman is a privately owned, leading European distributor of specialty chemicals

# Industries

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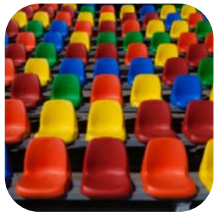
CONSTRUCTION


SEALANTS


PLASTICS


RUBBER


PAPER


PAINTS & COATINGS


PERSONAL CARE


PRINTING INKS & GRAPHIC ARTS


BATTERY


ADHESIVES


MORE INDUSTRIES

# Synergistic Portfolio

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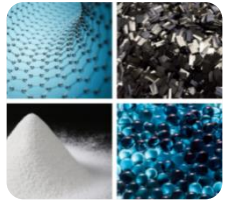

dynea
MOMENTIVE
VENATOR
ARKEMA
POLYSCOPE
fresh thinking, great products

SHIKOKU
eps ENGINEERED POLYMER SOLUTIONS Science Simplified

Additives
Resins
Pigments & Dyes
Perf. Materials & Fillers

Cross-Selling Opportunities

SCHLENK
VENATOR
orion ENGINEERED CARBONS
JOINTCOLOR A Secret Color Garden
BF BRUCHSALER FARBEN

ELEMENTIS A global specialty chemicals company
VENATOR
Nabaltec
MOMENTIVE TECHNOLOGIES
eicl RAW TO REAL

# International Team

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- Group Functions: >60
- Branch Offices: 24
- Technical Sales Managers >90
- Customer Service >50

13 Laboratories:
- Paints & Coatings
- Plastics & Rubber
- Personal Care

# Application Laboratories

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- Support customers and suppliers with guideline formulations
- Close partnership to develop customised solutions
- Lab provides solutions based on our raw material portfolio
- Development projects with suppliers
- Internal Trainings


Multiple cross-selling opportunities

# Grolman Coatings Laboratory

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## Technical support

- Paint formulation development / improvement
- Raw material evaluation
- Pigment & Filler dispersions
- Quality control
- QC method development / improvement
- Partnership with external labs


## Internal or external Trainings

- Basics and advanced in paint technology
- Tailor made customer training

# Grolman Coatings Laboratory

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## Anticorrosive solutions

- Evaluation of anticorrosive paints
  - Properties
  - Performance
  - Commercial aspects
- Flash rusting evaluation
- Neutral Salt Spray test
- Determination of water resistance/permeability
- Formulation support

## Technical Assistance

- Starting point formulation
- Right choice of raw materials
- Improvement of formulation
  - Properties
  - Performance
  - Commercial aspects
  - Rheology studies

# Grolman Coatings Laboratory

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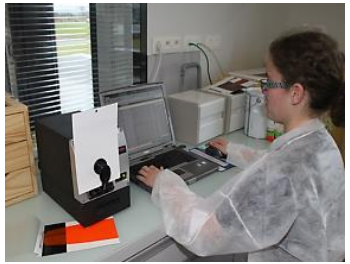
## Colour Service

- Since 2011: Development of new colour database supported by Datacolor technology
- Control analysis of pigments/pigment dispersions
- Opacity measurement & whiteness index on paints
- Evaluation of potential new pigments
- Colour matching (RAL, British standard, etc.)

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# Introduction

## Corrosion

# Corrosion

Corrosion: Deterioration of a material by chemical or physicochemical transformation. It is a natural process which converts refined metal to their more stable oxide

Iron corrosion is an oxidoreduction phenomenon with an oxidant (water) and a reductor (iron):

$Fe \rightarrow Fe^{2+} + 2e^-$

$O_2 + 4e^- + 2H_2O \rightarrow 4OH$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O$

# Corrosion – Tests

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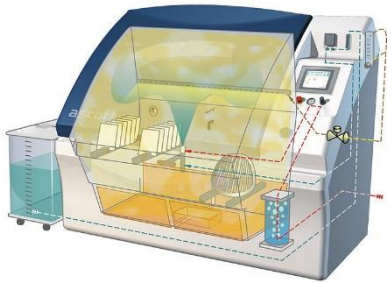
- Main corrosion tests for assessment:
  - ✓ Outdoor exposure:

    A very long real-life test under very severe atmospheric conditions
  - ✓ Accelerated tests

Neutral Salt Spray: ISO 9227, ASTM B117



| Parameters | Values |
|---|---|
| Air pressure | 1 +/- 0,2 bar |
| Salt concentration solution | 50 +/- 5 g/L of NaCl |
| Flow rate | 1,5 +/- 0,5 mL/h |
| pH of salt solution | 8 +/- 0,4 |
| Cell test temperature | 35 +/- 2°C |

# Corrosion – Tests

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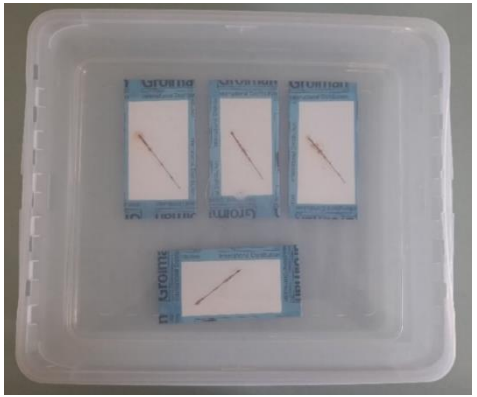
Neutral Salt Spray (NSS) test still requires a long time: 500 hours ↔ 21 days

Our quick internal method for a first screening:

based on Machu test (Qualicoat)



Painted panels are prepared as for a NSS test (protected and scarified) and immersed in a specific solution at room temperature (20 – 25°C vs 37°C for Machu)

Container with test solution and panels is covered to avoid evaporation.

Specific solution:

| Raw Materials | Formula |
|---|---|
| Salt (NaCl) | 50g |
| Hydrogen peroxide (H2O2) 30% | 10g |
| Demineralised water | Quantity needed for 1 litre |

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Tested with different systems and compared to 4 NSS equipment:
48 hours of our internal method ↔ 500 hours of NSS

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# Formulation development

## Raw materials selection

# Raw materials selection

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## Target:

- Develop a cost effective anticorrosion paint for industrial application based on styrene acrylic binder
- Spray gun application, 100µm dry minimum in 1 layer
- Minimum corrosion resistance : 500 hours NSS

## Several studies to select raw materials, focusing on:

- Binder (Competitor vs **EPS 595**)
- Dispersing agents (Competitor vs **Xiran 1440HE**)
- Anticorrosion pigments (most commonly used vs **rima cor** series)
- Fillers (different classical fillers vs **Himafine**)
- Adhesion promotor (without vs with **Coatosil MP200**)
- PVC (30 vs 20)

# Raw materials selection

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## Selection of the water-based polymer emulsion

- To select binders, apply them on a Q-panel and let them dry.
- Select the binder with the least flash-rusting.



# Raw materials selection

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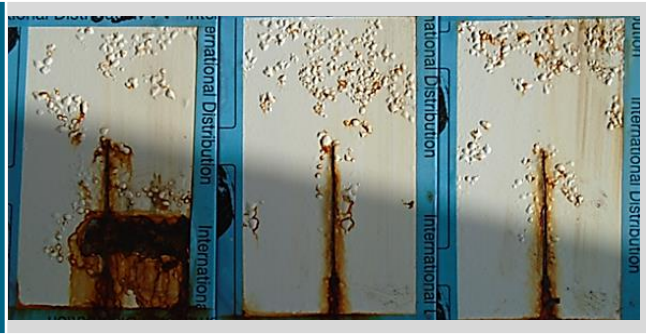
## Selection of the water-based polymer emulsion

Performance evaluation PVC = 30%, SC = 56%

350 hours NSS

| Binder | Competitor | EPS 595 |
|---|---|---|
| Pictures |  |  |

Spray gun application on degreased Q-Panels S36

1 layer, Thickness ≈ 100 -150 µm dry, 3 weeks of drying at room temperature

# Raw materials selection

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## Selection of the dispersing agent

- First check the compatibility with the resin: put a small quantity of resin emulsion on a contrast card, add some drops of the dispersing agent, and mix with a spatula. Any precipitation formation indicates incompatibility, and the dispersing agent shouldn't be used.

- Use the most efficient one in order to reduce its concentration in the formulation.

  Do trials with several types of dispersing agents using the same amount and select the one which induces the smallest viscosity.

# Raw materials selection

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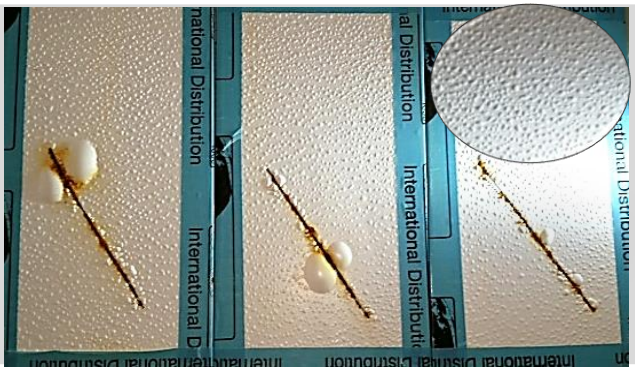
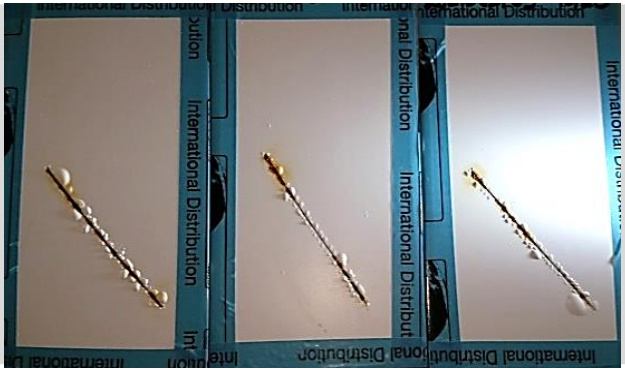
48 hours using our internal method:

| Dispersing agent | Competitor | Xiran 1440HE |
|---|---|---|
| Pictures |  |  |

Xiran 1440HE improves the corrosion resistance especially with regard to blistering, whether on the scratch or in full panel (Cf. pictures).

# Raw materials selection

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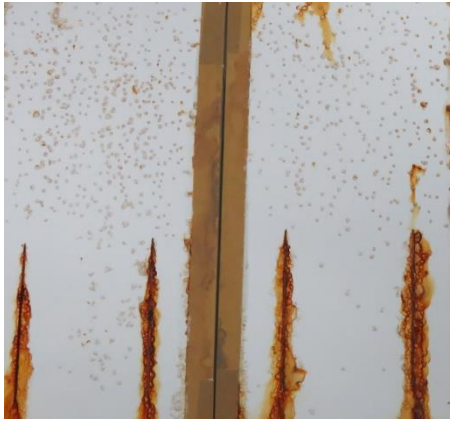
## Selection of the fillers

- Pay attention to the surface treatment

Trials with competitor filler
(Calcined Kaolin with silane treatment)

Trials with **Himafine**
(Calcined Kaolin)



# Raw materials selection

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## Selection of the anti-corrosion pigment

- The anti-corrosion pigment needs to be easily wetted (you will use less dispersing agent)
- The anti-corrosion pigment must be without soluble species, but it must be more soluble than species formed with Fe (Zinc or aluminium phosphates are more soluble than iron phosphates)

Phosphates:

$3Fe^{2+} + 2PO_4^{3-} \rightarrow \underline{Fe_3(PO_4)_2}$ ↓ $\qquad Fe^{2+} + HPO_4^{2-} \rightarrow \underline{FeHPO_4}$ ↓

- rima cor products are the results of the lab's development of synergy mixtures based on Aluminium Triphosphate

# Raw materials selection

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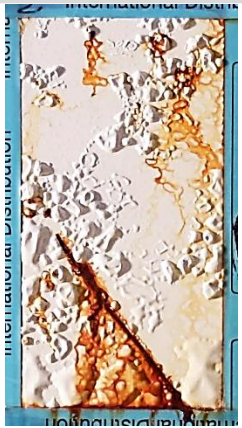
## Selection of the anti-corrosion pigment

Performance evaluation in styrene acrylic, PVC = 21%, SC = 45,5%

500 hours NSS

| Anticorrosion pigment | Liquid corrosion inhibitor | rima cor SWM | $ZnPO_4$ |
|---|---|---|---|
| % of pigment | 6,5 | 4,5 | 4,5 |



Spray gun application on degreased Q-Panels S36

1 layer, Thickness ≈ **50 µm** dry, 3 weeks of drying at room temperature

# Raw materials selection

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## Selection of the coloured pigments

- Use very slightly soluble pigments
- Give priority to mineral pigments (iron oxide pigments help to prevent corrosion because the reaction $Fe/Fe^{2+}$ moves in the direction $Fe^{2+}$ → Fe)
- Avoid all pigments with organic treatment (for an easier dispersibility)
- Organic pigments are generally to be avoided, if it is not possible they should have as few as possible soluble species
- $TiO_2$ should have no treatment or a mineral one
- Ferroxide, $TiO_2$ Tioxide TR92

# Raw materials selection

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## Selection of the anti-flash rusting agent

- Avoid surfactants
- Give priority to products which react with $Fe^{2+}$ or $Fe^{3+}$ like sulfonates, phosphates, phosphonates, …which form the strongest bonds and create insoluble complexes with the iron.

Ex: Alkyl phosphate

$$Fe^{2+} + R\text{-}O\text{-}PO_3{}^{2-} \leftrightarrows Fe(R\text{-}O\text{-}PO_3)$$

Formation of insoluble iron alkyl phosphate complexes (importance of the pH value)

- rima flash JDO

# Raw materials selection

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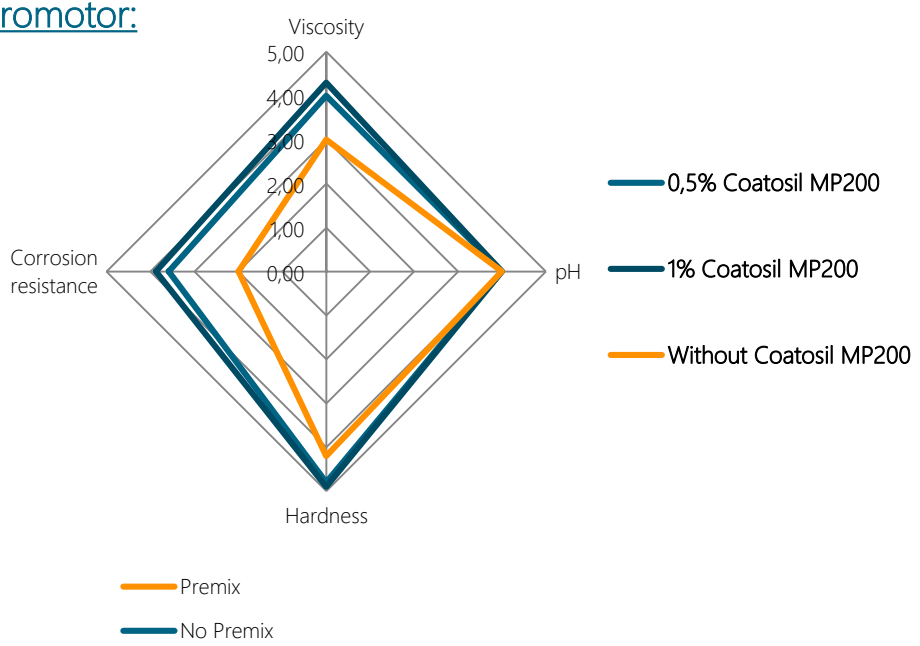
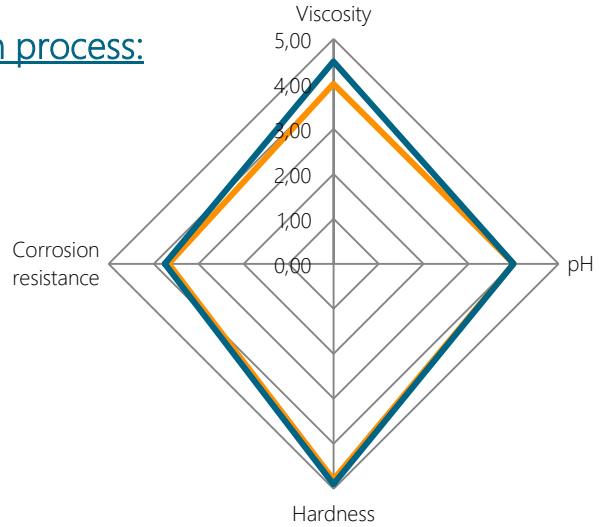
## Selection of the adhesion promotor:




## Incorporation process:



# Raw materials selection

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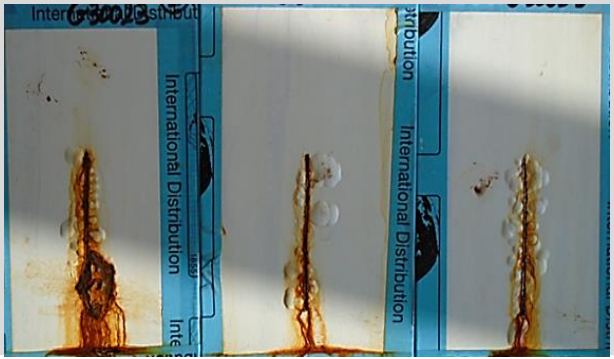
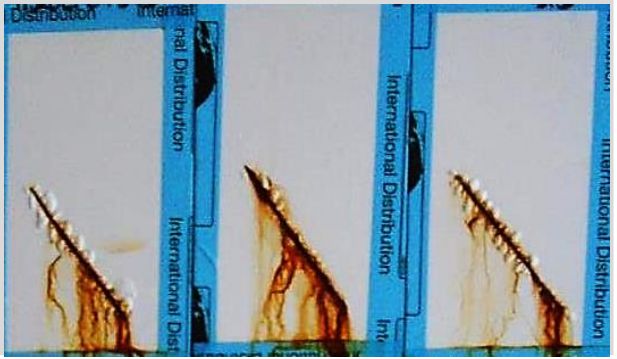
## Determination of PVC

<u>350 hours NSS test:</u>

| PVC | 30% | 20% |
|---|---|---|
| Pictures |  |  |

Spray gun application on degreased Q-Panels S36
1 layer, Thickness ≈ **100 µm** dry, 3 weeks of drying at room temperature

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# Formulation examples

# Formulation - examples

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| Old formulation: | | | New formulation: | |
|---|---|---|---|---|
| Quantity (%) | Raw Material | Function | Raw Material | Quantity (%) |
| 10,80 | Water | Solvent | Demineralized water | 25,90 |
| 0,70 | Poly acrylate NH4 Salt | Dispersing agent | High molecular weight block copolymer with pigment affinic groups | 1,0 |
| 0,50 | Vegetal oil | Antifoaming agent | Mineral oil | 0,05 |
| | | Anti Flash Rust | Nitrite free corrosion inhibitors mixture – **rima flash JDO*** | 0,50 |
| 4,40 | BaSO4 | Filler | | |
| 2,20 | Talc | Filler | Calcined Kaolin – **Himafine*** | 4,00 |
| 22,00 | TiO2 | Pigment | **$TiO_2$ Tioxide TR92** | 11,00 |
| 4,70 | Ca silicate / borate | Anticorrosion pigment | Al triphosphate based – **rima cor SWM*** | 4,50 |
| 52,00 | Anionic acrylic styrene copolymer NH4 neutralized | Binder | Modified styrene acrylic – **EPS 595*** | 50,00 |
| | | Adhesion promoter | Epoxy silane – **Coatosil MP200*** | 0,15 |
| 2,20 | Di Isobutyl Ester | Coalescing agent | Augéo SL 191 | 2,00 |
| | | Neutralizing agent | Amino methyl propanol | 0,50 |
| 0,50 | Associative acrylic | Thickener | Associative polyurethane | 0,20 |
| | | Biocide | Combination of MIT/BIT and Bronopol | 0,20 |
| **100,00** | | **TOTAL** | | **100,00** |

# Formulation - examples

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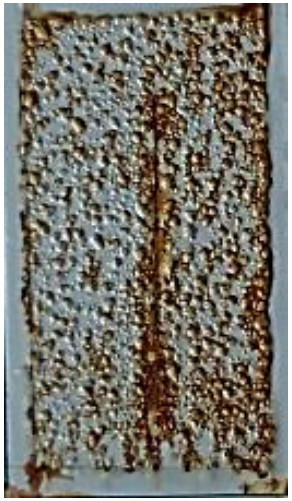
Old formulation:



New formulation:


| | | |
|---|---|---|
| pH: | 7,5 | 8,8 |
| NSS time exposure: | 144 hours | 576 hours |
| PVC: | 30 | 20 |

Spray gun application on degreased Q-Panels S36
1 layers, Thickness ≈ 80 µm dry, 3 weeks of drying at room temperature

# Formulation - examples

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## Cost effective water based anticorrosion paint project:

Styrene acrylic anticorrosion DTM paint PVC = 20,5%, SC = 46%

Grinding process

| | Raw Materials | Function | % |
|---|---|---|---|
| Grinding | Demineralised water | Solvent | 10,00 |
| | Organo-modified siloxane polymer | Antifoaming agent | 0,30 |
| | **Xiran 1440HE*** | Dispersing agent | 1,20 |
| | **rima flash JDO*** | Anti-flash rust | 1,00 |
| | Amino methyl propanol | Neutralising agent | 0,30 |
| | **Himafine*** | Filler (calcined kaolin) | 4,40 |
| | **rima cor SWM New *** | Anticorrosion pigment | 4,40 |
| | **Tioxide TR92*** | Pigment (Titanium dioxide) | 11,00 |
| | Demineralised water | Solvent | 8,00 |
| Let down | **EPS 595*** | Styrene acrylic binder (50% SC, MFFT = 20 – 25 °C) | 48,70 |
| | **Coatosil MP 200*** | Adhesion promotor | 0,12 |
| | Augeo SL 191 | Coalescing agent | 0,95 |
| | Demineralised water | Solvent | 9,25 |
| | BIT | Biocide | 0,20 |
| | Rheolate 666 | HEUR thickener | 0,18 |
| | | **TOTAL** | **100,00** |

# Formulation - examples

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## Cost effective water based anticorrosion paint project:

Styrene acrylic anticorrosion DTM paint PVC = 20,5%, SC = 46%

Grinding process

Results after 48 hours of our internal testing method:


Final formulation:

Spray gun application on degreased Q-Panels S36

1 layers, Thickness ≈ 80 µm dry, 3 weeks of drying at room temperature

# Formulation - examples

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## Cost effective water based anticorrosion paint project:

Styrene acrylic anticorrosion DTM paint PVC = 17%, SC = 47%

Dispersion process

| | Raw Materials | Function | % |
|---|---|---|---|
| Grinding | Demineralised water | Solvent | 10,00 |
| | **Xiran 1440HE*** | Dispersing agent | 1,20 |
| | **rima flash JDO*** | Anti-flash rust | 1,00 |
| | Amino methyl propanol | Neutralising agent | 0,30 |
| | **Himafine*** | Filler (calcined kaolin) | 4,50 |
| | **rima cor SWM 60MC*** | Slurry of anticorrosion pigment | 4,50 |
| | **Tioxide TR92*** | Pigment (Titanium dioxide) | 11,00 |
| | Demineralised water | Solvent | 3,00 |
| Let down | **EPS 595*** | Styrene acrylic binder (50% SC, MFFT = 20 – 25 °C) | 55,00 |
| | **Coatosil MP 200*** | Adhesion promotor | 0,15 |
| | Texanol | Coalescing agent | 6,00 |
| | Demineralised water | Solvent | 3,00 |
| | BIT, CMIT/MIT | Biocide | 0,20 |
| | Rheolate 666 | HEUR thickener | 0,15 |
| | **TOTAL** | | **100,00** |

# Formulation - examples

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## Cost effective water based anticorrosion paint project:

Styrene acrylic anticorrosion DTM paint PVC = 17%, SC = 47%

Dispersion process


Spray gun application on old cladding

2 layers, Thickness ≈ 100 µm dry, 3 weeks of drying at room temperature

# Conclusion

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Using:

- EPS 595 binder
- Xiran 1440HE dispersing agent
- rima cor & rima flash anticorrosion products
- Himafine filler
- Coatosil MP200 epoxy silane
- Tioxide TR92 titanium dioxide


allow the formulation of a high quality water borne direct-to-metal paint.

# Grolman

International Distribution of Specialty Chemicals

## We want to sell Chemicals to Save the Planet.

Innovation Partner for Circular Diversity

ENTREPRENEURS SINCE 1855


**GROLMAN GOES NET ZERO.**