

# BONDERITE M-ZN 1994 R4

Known as Granodine 1994 E-4

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**PRODUCT DESCRIPTION**

BONDERITE M-ZN 1994 provides the following product characteristics:

<b>Technology</b>	Metal Pretreatment
<b>Product Type</b>	Tricationic
<b>Application</b>	Zincphosphating Dip-process
<b>Accelerator</b>	HA
<b>Process components:</b>	
BONDERITE M-ZN 1994 MU1	Make-up
BONDERITE M-ZN 1994 R4	Replenisher
BONDERITE M-AD 565	Neutralizer

BONDERITE M-ZN 1994 is a nitrite-free tricationic phosphating process for steel, galvanised, alloyed coated (Zn/Ni) steel and aluminium (after bath-modification). It generates a fine crystalline coating of manganese containing zinc phosphate.

The crystalline layer has very good corrosion protection properties and is an excellent foundation for subsequent painting or organic coating.

For easier process steering no separate dosing of an accelerator is necessary. The tendency to incrustation is very low.

The coating weight is e.g. 1.8 to 3.0 g/m<sup>2</sup> (depending on process conditions and/or substrate, the value can deviate).

**Application Areas:**

BONDERITE M-ZN 1994 is particularly suited as pretreatment for electrocoat application. Suitable for control with Automatic Control Equipment.

**TECHNICAL DATA**

Appearance:	clear green solution
Density	~1.34 g/cm <sup>3</sup>
pH-value	~1.8

**DIRECTIONS FOR USE****Preliminary Statement:**

Prior to use it is necessary to read the **Material Safety Data Sheet** for information about precautionary measures and safety recommendations. Also, for chemical products exempt from compulsory labeling, the relevant precautions should always be observed. Please also refer to the local safety instructions and contact Henkel for analytical support.

**Bath make-up, for 1,000 L:**

Fill 3/4 of the bath with cold water and add during continuous pump circulation:

BONDERITE M-ZN 1994 MU1    46.0 kg = 32.9 L  
BONDERITE M-AD 565        7.0 kg = 6.3 L  
to adjust the pH-value

Before start up fill the tank to correct work level.

**Operating Data:**

Adjusting the following data could be necessary depending on the phosphatizing process.

Total Acid	22.0 to 30.0 mL
Free Acid	1.0 to 1.8 mL
Zinc	3.4 to 4.3 mL
Accelerator (HA)	0.7 to 1.4 g/L
Temperature	48 to 55 °C
Duration of treatment	120 to 300 sec

**Process Description:**1. Cleaning

Cleaning is preferentially done with a suitable alkaline MPT cleaner (e.g. BONDERITE C-AK xxx plus surfactant BONDERITE C-AD xxxx). For heavily contaminated goods the addition of a BONDERITE cleaning booster may be necessary. For details please refer to the corresponding Technical Data Sheets.

2. Rinsing

Cleaning is followed by rinsing with water. A continuous overflow should be maintained to avoid contamination.

3. Conditioning

We recommend surface conditioner like BONDERITE M-AC 950 or Prepalene X for this. Conditioning provides homogeneous and fine grained zinc phosphate coatings on steel, galvanized and alloy coated steel. Softened or deionized water is best suited for the activating bath. For details please refer to the corresponding Technical Data Sheets.

4. Phosphating with BONDERITE M-ZN 1994

Keep parameters in the recommended range. We suggest to add BONDERITE M-ZN 1994 R4 continuously by a dosing pump. At too high temperatures formation of sludge and coating weight will increase. Sparse coatings and rusting can be the result of working at low temperatures, too high "Free Acid" or with insufficient dosing of BONDERITE M-ZN 1994 R4.

## 5. Rinsing

The rinse after the phosphating zone must be continuously overflowed with fresh water.

## 6. Passivating

Dosing of a passivating product like BONDERITE M-PT 54 NC to the last rinse is recommended. For the make up of this product we recommend soft or deionized water. Depending on the phosphatizing line design, the passivating bath is running at 20 to 40 °C. For details please refer to the corresponding Technical Data Sheets.

## 7. Rinsing with deionized water

Before starting the electrocoating, rinsing with deionized water is recommended.

## 8. Drying (Depending on the process, it may be necessary)

We recommend fast and complete drying at temperatures of 100 to 120 °C in ovens with indirect heating. In agreement with the paint supplier, oven drying may be omitted prior to the application of water based paints.

## Bath Monitoring:

The BONDERITE M-ZN 1994 bath solution is controlled by the following analysis.

### Titration of Total Acid:

- Pipette 10 mL solution into a clean 300 mL Erlenmeyer-flask.
- Add 50 mL deionized water.
- Add 5 drops of indicator phenolphthaleine (0.1 % alcoholic solution).
- Titrate the solution with 0.1 N sodium hydroxide.
- The endpoint will be shown by a colour change from colourless to permanent pink.
- The consumption of 0.1 N sodium hydroxide in mL is equal to the content of total acid.

Specified range: 22 to 30 mL

### Replenishing of the bath:

Add per missing mL and per 1,000 L of bath volume:

BONDERITE M-ZN 1994 R4 2.0 kg = 1.5 L

### Remark:

Correcting with BONDERITE M-ZN 1994 R4 is meant for normal conditions.

Special conditions may require an alternative replenisher.

### Titration of Free Acid:

- Pipette 10 mL solution into a clean 300 mL Erlenmeyer-flask.
- Add 50 mL deionized water.
- Add 5 drops of indicator bromophenolblue (0.04% alcoholic solution).
- Titrate drop by drop with 0.1 N sodium hydroxide solution.
- The endpoint will be shown by a colour change from yellow to blue.
- The consumption of 0.1 N sodium hydroxide in mL is equal to the content of free acid.

### Titration of Free Acid with pH-meter:

- Pipette 10 mL solution into a clean 300 mL Erlenmeyer-flask.
- Add 50 mL deionized water.
- Dip in the electrode.
- Titrate drop by drop with 0.1 N sodium hydroxide solution until the pH-value 3.6 is reached.
- The consumption of 0.1 N sodium hydroxide in mL is equal to the content of free acid.

Specified range: 1.0 to 1.8 mL

### Remark:

The specified free acid range refers to the measurement with pH-meter. The measurement with indicator bromophenolblue shows 0.3 to 0.7 mL higher results, depending on the fluoride content in the bath.

### Correction of Free Acid content:

If the free acid content is too high, correct it with diluted BONDERITE M-AD 565 with running circulating pump.

Add per 0.1 mL of excess free acid and per 1,000 L bath volume:

BONDERITE M-AD 565 0.4 kg = 0.35 L

BONDERITE M-AD 565 shall be added slowly and diluted (e.g. 1/4) into an area of the bath with strong bath agitation to have a very good mixing and avoid locally an over-neutralization (sludge-building).

Under normal conditions a too low content of free acid will not occur therefore a correction would not be necessary.

### Titration of Total Cations:

- Pipette 2 mL of a filtrated bath-solution into a clean 300 mL Erlenmeyer-flask
- Add 50 mL deionized water.
- Pipette 20 mL of ammonia buffer solution pH 10 and 20 mL of 0.01 m Titriplex III (EDTA).
- Add little Eriochrome black T.
- Titrate drop by drop with 0.01 m magnesium sulfate solution.
- The endpoint will be shown by a colour change from blue to light red.
- Calculation:  
20 mL - consumption of magnesium sulfate solution in mL is the total cations pointage.

### Titration of Zinc Content:

Continue with the same solution used for titration of total cations.

- Add 10 drops dimercaptopropanole solution.
- The solution turns blue again.
- Titrate drop by drop with 0.01 m magnesium sulfate solution.
- The endpoint will be shown by a colour change from blue to light red.
- The added mL of 0.01 m magnesium sulfate multiplied by the factor TF 0.33 is equal to zinc in g/L.

Specified range: 3.4 to 4.3 mL = 1.1 to 1.4 g/L Zn<sup>2+</sup>

### HA-determination:

- Pipette 50 mL bath solution into a clean 250 mL



glasbeaker.

- Add 150 ml deionized water.
- Dip in the electrode.
- Titrate drop by drop with 0.1 N sodium hydroxide solution until the pH-value 3.8 is reached (titration 1).
- refill the burette
- Add 10 ml acetone (pH decrease).
- Titrate drop by drop with 0.1 N sodium hydroxide solution until the pH-value 3.8 is reached (titration 2).

Calculation:

ml of titration (titration 2) x 0.072 = g/l HA

Specified range: 0.7 to 1.4g/L

**Remark:**

HA is contained in the replenisher solution and comes with it into the phosphate bath. If the HA amount in this solution is not enough to reach the specified range, appropriate measures in the course of the process sequence have to be initiated.

**Control of Iron Content:**

Depending of the amount of steel surface in the production rate, an accumulation of iron-2 in the phosphate bath is possible. The amount of Fe-2 shall not exceed 200 ppm (mg/l). The iron-2 content can be controlled with test strips, e.g. from company Merck (Merckoquant 1.0004. iron test). It is o.k. to control the Fe-2 content only once or twice per day, each at the end of a production-shift.

If the amount of 200 ppm Fe-2 will exceed, please inform the Henkel representative.

**Desludging:**

The sludge formed in the BONDERITE M-ZN 1994 bath must be removed regularly. We recommend working continuously with filter press, or better nowadays direct filtration with filter press.

**Filling-up:**

After desludging or a partial loss of solution fill up with water, mix thoroughly and recheck the bath parameters.

Add per missing mL of total acid and per 1,000 L of bath volume:

BONDERITE M-ZN 1994 MU1 1.6 kg = 1.1 L  
BONDERITE M-AD 565 0.4 kg = 0.35 L

**Classification:**

Please refer to the corresponding **Material Safety Data Sheets** for details on:

**Hazards identification**

**Transport information**

**Regulatory information**

**Materials for analysis:**

Free acid, total acid and HA-determination:

Pipette 10 mL (2)  
Pipette 50 mL (2)  
Erlenmeyer-flask 300 mL (2)  
Glasbeaker 250 mL (2)  
Burette 25 mL (2)  
Distilled water  
0.04% alcoholic solution of Bromophenole blue  
0.1 % alcoholic solution of Phenolphthaleine  
0.1 N Sodium hydroxide solution  
Dropping bottle 25 mL (2)  
pH-meter  
Aceton p.A  
Messzylinder

Total cations / zinc content:

glass funnel, diameter 80 mm  
folded filter, half diameter 18.5 cm  
Beaker 250 mL  
Pipette 2 mL  
Pipette 20 mL  
Erlenmeyer-flask 300 mL  
Burette 25 mL  
Dropping bottle 25 mL  
Spatula  
0.01 M solution of Titriplex III (EDTA)  
0.01 M solution of magnesium sulfate  
buffer solution pH 10 for complexometric analysis  
Eriochrome black T (mixture with sodium chloride 1:99)  
20 % alcoholic 2,3-dimercaptopropanol-solution (store below 5 °C)

Two pieces of the glass equipment is recommended because of the risk of cracking.

**Storage:**

Recommended Storage Temperature	-3 to 40°C
Shelf-life, months	36

**ADDITIONAL INFORMATION****Disclaimer****Note:**

The information provided in this Technical Data Sheet (TDS) including the recommendations for use and application of the product are based on our knowledge and experience of the product as at the date of this TDS. The product can have a variety of different applications as well as differing application and working conditions in your environment that are beyond our control. Henkel is, therefore, not liable for the suitability of our product for the production processes and conditions in respect of which you use them, as well as the intended applications and results. We strongly recommend that you carry out your own prior trials to confirm such suitability of our product.

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Reference 0.1