Ultra-thin corrosion protective coatings for galvanised steel

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Objectives

New types of primer systems for galvanised steel were investigated, which are is based on spezial phosphonic acids (PA), which form cross-linked self assembled Monolayers (SAM) or multilayers by a simple dipping process. The procedure to form this primer consists of one or two steps :

- SAM or multilayer formation on galvanised steel with special types of phosphonic acids (PA) can be carried out by a simple dipping process with strongly diluted aqueous PA solutions.
- In some cases (if functionalized head groups are used), a second step to polymerise this head groups was also examined.

Different corrosion tests have been carried out to evaluate the performance (corrosion inhibition) of the new primer systems with and without organic top coats.

Some used synthesised or commercial SAM – molecules (Phosphonic acids)

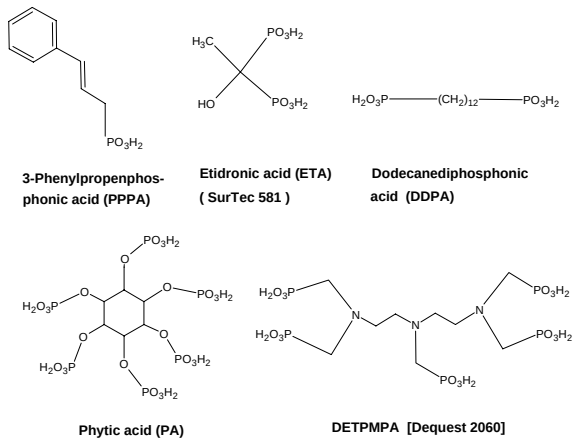

Fig. 1 : ***Structure of some investigated SAM molecules***

Results

- Some special phosphonic acids were used to build up ultrathin layers for the corrosion protection of galvanised steel.
- Contact angle measurements of the galvanised steel electrodes before and after dipping in the phosphonic acid solutions indicated a succuss-ful SAM formation on different zinc surfaces (hot dip galvanised steel as well as electrogalvanised steel, see Fig. 2).
- Examinations of SAM coated galvanised steel sheets showed, that visible acid etching of the zinc surface during the dipping process can be avoided by using adequate conditions (dipping time, temperature, pH – values, additional salts and solvents).
- Different pretreatments of the zinc surfaces (before SAM formation) were investigated including methods for etching / activation in alkaline and acid aqueous solutions and also the usage of conversion layers like the technical important zinc phosphate layers.
- Corrosion tests like salt spray tests or the immersion of galvanised steel sheets with different mono- or multilayers in aerated 1 % NaCl (with or without an organic sealant) indicate, that some of this phosphonic acid layers are able to inhibit the corrosion process significantly, especially the white rust formation (see Fig. 3). In particular, some multilayers, which are formed with multiphosphonic acids like Phytic acid or DETPMPA in the presence of small amouts of spezial salts [$MnSO_4$ or $Cr(NO_3)_3$] induced strong corrosion inhibition effects (reduced white rust formation).
- Several corrosion tests (e.g. salt spray tests and alternating climate tests) with technical lacquerings showed, that also the corrosion creep at defects of the top coat (edge of the sheets, scratches) can be inhibited with some phosphonic acid layers, if the zinc surface had been carefully degreased and adequately pretreated before.

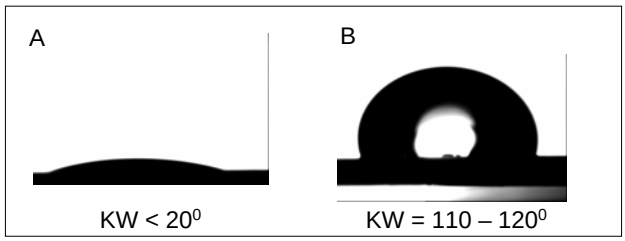

Fig. 2 : ***Contact angle of hot dipped galvanised steel after alkaline and acid pretreatment (A) and with additional dipping in DPS [dodecane-phosphonic acid] solution (B).***

Fig. 3 : ***Electrogalvanised steel sheets (10.5 cm x 19 cm) after 16 h dipping in aerated 1% NaCl. Left : electrogalvanised steel only degreased by a mild alkaline treatment.***
Right : Analog galvanised steel sheet, but with additional acid pretreatment **and coating with PPPA – SAM.**

Conclusion

- Several corrosion tests (galvanised steel sheets) with an without lacquering indicate, that some mono- and multilayers with phosphonic acids are able to improve the corrosion resistance (e.g. inhibition of white rust formation or delamination of lacquerings).
- Further investigations are necessary to optimize the dipping process with phosphonic acids and also to find the best corresponding pretreatment for the galvanised surface in respect to get the most effective corrosion inhibition. Also further basic research is necessary to examine the chemical stucture of the obtained ultrathin layers.

Reference : U. Harm, K.-M. Mangold, W. Fürbeth, Jahrbuch Oberflächentechnik 2010, (Leuze Verlag), **66**, 149.