Novel protective coatings for steel based on a combination of self-assembled monolayers and conducting polymers

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Objectives

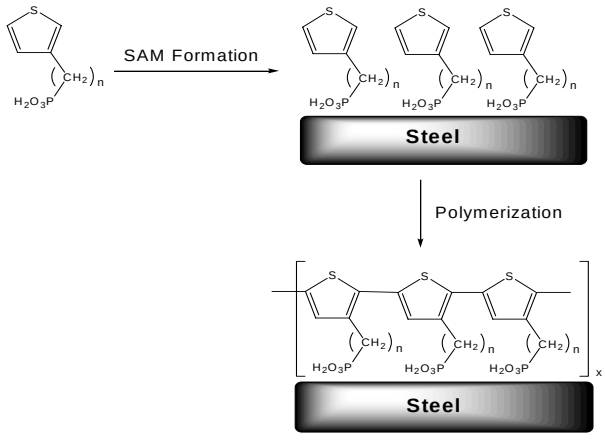
A new primer system for carbon steel has been developed, which is based on a combination of self-assembled Monolayers (SAM) and conducting polymers.
The procedure for this primer mainly consists of two or three steps.

First a practical way for the SAM formation of special taylored derivated phosphonic acids on passivated carbon steel was developed.

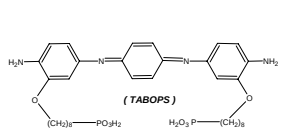
In a second step, methods to electropolymerise the head groups with monomers of conducting polymers were examined. Currently some cost-saving alternatives to the electropolymerisation step are under development.
Several characterisation methods of the formed SAM layers were tested and different corrosion tests with and without lacquering were used to examine the effectiveness in corrosion protection of different SAM layers.

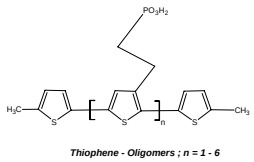
A main advantage of the new primer system consists in the very low need of chemicals by using a strongly diluted aqueous solution of the monomer phosphonic acids. This will lower costs and avoid environmental pollution.

Steps to build up the new primer system (simplified) :

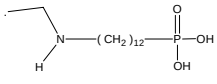


Some synthesised SAM - molecules

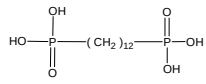




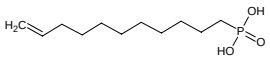
Thiophene - Oligomers ; n = 1 - 6



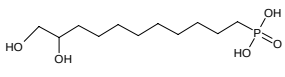
N-Ethylaminododecane - phosphonic acid (EADPA)



Dodecanediphosphonic acid (DDPA)



Undecenyl phosphonic acid (UDPA)



10,11-Dihydroxyundecyl - phosphonic acid (DHUPA)

Experimental Results

- Contact angle measurements of the electodes before and after dipping in the phosphonic acid solutions indicated the successful SAM formation (see below).
- The anodic current density curves (in 0.1 M Na_2HPO_4) of passivated steel electrodes before and after SAM formation showed a significant inhibition of the iron dissolution caused by different SAMs.
- Electropolymerisation of terthiophene head groups after SAM formation could be observed in CV experiments in propylene carbonate.
- Optical Investigations and REM images of the electrode surface before and after SAM formation were used to investigate the etching of the passivated steel surface by the dipping process (acidic solutions).
- Corrosion tests indicate the effectiveness of SAM's to increase corrosion inhibition of passive / phosphate layers on carbon steel with and without lacquering as top cover.

TTHPA-SAM on passivated low carbon steel

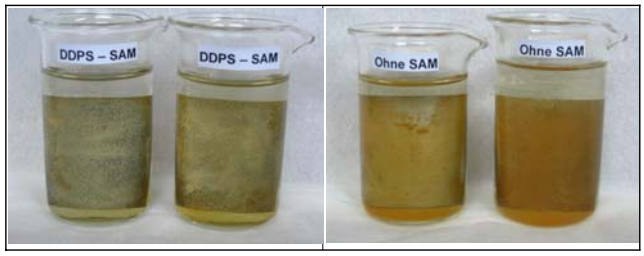
KW = 107.5⁰ / 105.8⁰

DPA - SAM on passivated low carbon steel

KW = 146.6.0⁰ / 146.7⁰

Contact angle of low carbon steel (St 37) after phosphating (SurTec 608) and SAM – formation (dipping process) with DPA or TTHPA

Fast corrosion test : Zinc phosphated carbon steel with (left) and without (right) DDPA – SAM after 17 h immersion in 1 % NaCl



Conclusions

- The SAM – formation on passivated steel surfaces is easy and cost-saving by a simple dipping or spraying process with diluted aqueous solutions of the phosphonic acids.
- The electropolymerisation of terthiophene – head groups (TTHPA) could be achieved by cyclovoltammographic experiments in propylene carbonate. This method is to expensive for technical applications and has further disadvantages. So more suitable alternatives are under development, including SAMs with reactive head groups and SAMs with oligomeric structures.
- First corrosion tests with passivated / phosphated low carbon steel panels indicate an improved corrosion resistance caused by additional SAM – layers.
- Further optimisation of the current procedures are necessary for the successful technical application of the new primer sytem.