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

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Abstract
Investigations on the development of a new primer system for carbon steel have led to some promising intermediate results. Several special phosphonic acids with different head groups (e.g. some thiophene derivatives) and alkyl- or arylspacers have been synthesised. They are able to form stable self-assembled monolayers (SAMs) on passivated steel by dipping the substrates into aqueous phosphonic acid solutions. The SAM formation was validated by current potential curves and also by contact angle measurements, which showed an intensive hydrophobisation of the steel surface, if SAM molecules with non-polar head groups were used. After SAM formation, bi- or terthiophene head groups could be electropolymeriszed in cyclovoltammetric experiments (CV) to form a 2-dimensional conducting polymer layer.
First corrosion experiments with different SAMs on passivated steel showed, that the corrosion resistance of steel surfaces can be improved by an additional SAM layer as a pretreatment for the final organic coating system.

Keywords
coating, primer, self-assembled monolayer, conducting polymer, corrosion protection

Introduction
The investigation of self-assembled monolayers (SAM) on different technical metal surfaces has been one of the most important topics in surface technology in the last few years [1-15]. They are easy and cost-effective to apply as ultrathin organic layers (nanometer range) by a simple dipping or spraying process and can significantly improve different properties of the metal surface (e.g. wettability or corrosion resistance). The formation of SAMs with phosphonic acids or phosphoric acid monoalkylesters on many technical used oxide covered metals (e.g. iron, steel, aluminium, magnesium, zink) is fast (usually about 1 minute at 40-50^0 C) and requires only diluted aqueous solutions of the SAM molecules (typical between 0.1 and 1 mmol). This very low need of usually less or non-toxic chemicals also contributes to the fact, that SAM coatings as intermediate layer between the technical metal and the final lacquering / top coating are often regarded as both cost-effective and environmental-friendly.
This paper gives an overview of the current devolopment of a new primer system for carbon steel, based on the SAM formation with phosphonic acids on passivated steel surfaces.
The effectiveness of the formed SAM to improve the corrosion resistance of metal surfaces like steel depends on different factors. Besides the development of optimal conditions for SAM formation (dipping or spraying process), one important factor is a suitable molecule strucure of the used phosphonic acid to form a stable and densely packed layer with a head group, that strongly bonds to the organic coating.

Another idea to improve the effectiveness in corrosion protection is to polymerize suitable SAM head groups to form a 2-dimensional network, which should additionally stabilize both, the SAM layer itself and the passive layer below on the steel surface. This aim was already achieved in principal in a finished research project of the authors with the use of terthiophene head groups, which could be electropolymerized in CV –experiments [1-4].

Figure 1 shows schematically this process of SAM formation on passivated steel with subsequent electropolymerisation of thiophene head groups.
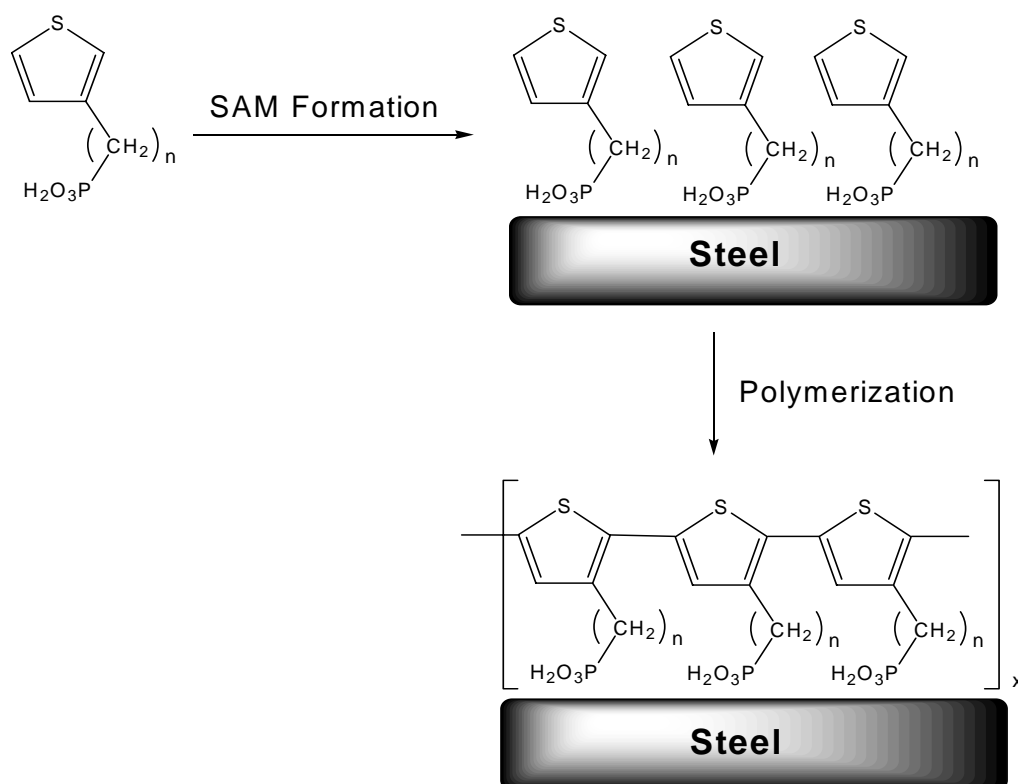

Fig. 1: *SAM formation on passivated steel surfaces with subsequent electropolymerisation of thiophene SAM head groups to form a 2-dimensional network.*

Short anodic polarisations during the used CV cycles led to the initiation and progress of the desired electropolymerisation of the terthiophene head groups to form a 2-dimensional network of connected SAM headgroups. A more detailed description and discussion of the CV experiments has already been given in earlier publications [1-4].

First corrosion tests did not show a significantly improved corrosion resistance after the step of electropolymerisation in comparison with analog SAM covered samples without electropolymerisation. This was probably the consequence of the demanded high anodic potential for the electropolymerisation step (about 1.4 V vs. NHE in propylene carbonate as solvent), which may lead to first damages of the used passive layer on the steel surface.

Later CV experiments to electropolymerise N-pyrrole or aniline SAM head groups under more moderate conditions (lower anodic potential / aqueous solutions) failed to prove a formation of polymeric structures [1, 5].

Another important disadvantage of the electropolymerisation step was the limitation to some special oxide layers for the previous passivation of the steel surface. Only these oxide passive layers have semi-conducting properties which are nessessary for the electropolymerisation of the SAM head groups. The technical more advantageous phosphating procedures to passivate steel surfaces would have been excluded because of the very low electric conductivity of phosphate layers.

This first results led to the conclusion, that the whole procedure to build up the new primer system has to be simplified and improved to become more promising for technical applications. Besides further basic research to optimize the conditions for the SAM formation with different SAM molecules on different passive layers of the steel surfaces, new strategies to simplify the whole process were nessessary. All of them have in common, that they avoid the described disadvantages of the previous process step with the electropolymerisation of SAM head groups. Other preconditions for the new developments were, that the whole process should be cost effective, environment-friendly and easy to apply in different technical areas.

Currently investigated possible replacements of the electropolymerisation procedure are :

I.   The most cost effective way to replace the electropolymerisation step is the simple use of reactive SAM head groups, which will form stable chemical bonds to the lacquer polymers, when the lacquer is cured by heating. In this case, after lacquering the SAM head groups are indirectly connected via the polymer backbone of the lacquering. Although some trials with those SAM layers on simple passivated steel surfaces were already done [1, 6, 7-12], there is a need for further testing these systems, especially in combination with more effective phosphate layers as pretreatment of the steel surface.

II.   The usage of organic oligomeric structures (e.g. oligomers of conducting polymers) with 2 or more alkylphosphonic acid anchor chain groups.

According to these new strategies to develop a technically advantageous primer system for passivated steel, some first results are presented now in this paper.

Recent Results and Discussion
The recent results in the development of the new primer system can be divided into three main topics.

I.   Synthesis of further phosphonic acids with different head groups and molecular structures.

II.   Characterisation of the SAM formation on passivated steel surfaces

III.   Some first results of corrosion testing

I. Synthesised SAM molecules

Some of the phosphonic acids synthesised were already known from literature and others were new compounds.
They are to be used for later SAM formation studies on different passive layers on steel surfaces with subsequent corrosion testing with and without final lacquering.

The Figures 2 – 4 give an overview of the most important phosphonic acids, which were synthesized so far for the development of the new primer system on steel surfaces.

Figure 2 shows some earlier synthesised phosphonic acids, which were investigated after SAM formation on passivated steel. With those phosphonic acids, the new primer system should have been realised according to the process, which was described in the introduction and illustrated in Fig. 1.
However only SAMs with a terthiophene head groups (TTHPA) could until now be electropolymerised under conditions, which were not favorable for a technical application.
So, other more simplified and technically favorable methods to optimize corrosion inhibition effects of SAMs are now investigated. These new strategies required new types of phosphonic acids. One new type are phosphonic acids with polar / reactive head groups. Examples of those synthesised molecules are shown in Figure 3 . The idea of this most simple and cost-effective method is, that the reactive SAM head groups were connected together, when a final suitable organic coating (binder) is hard cured by heating or other techniques. This could spare the expensive process step of electropolymerisation as shown in Figure 1.
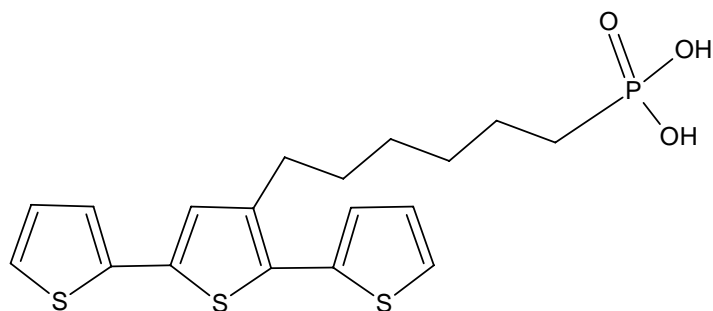
Terthiophenehexane phosphonic acid (TTHPA)
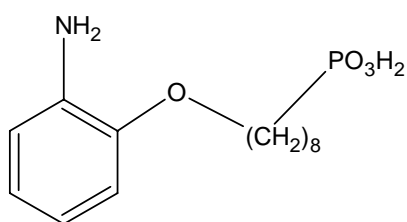
2-Aminophenoxy- octyl-

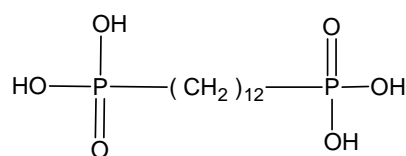**phosphonic acid (APOPA)**
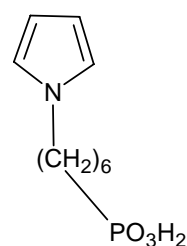
N-pyrrole-hexanephosphonic acid (PHPA)

Fig. 2 : *Earlier synthesised phosphonic acids with head groups of monomers from conducting polymers (terthiophene, aniline and N-pyrrole head group). An electropolymerisation of head groups via CV experiments on passivated steel could until now only be achieved with the terthiophene head group (TTHPA) in organic electrolytes like propylene carbonate.*

Figure 3 shows some more recently synthesised molecules with polar / reactive head groups, which are currently used as SAM layers in corrosion tests with and without further lacquering. The molecules DDPA and EADPA in Fig. 3 were already synthesised and tested as SAM molecules on metal surfaces for corrosion inhibition in different research projects in the last years. They had shown a good performance in corrosion inhibition on some metals like aluminium and magnesium [6, 11-12]. Some first corrosion tests on passivated steel have also indicated possible improvements in corrosion inhibition by this kind of SAM molecules [1] (see also Fig. 7).
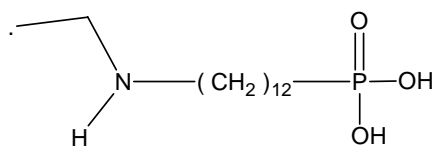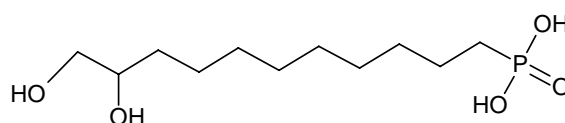
N-Ethylaminododecane -
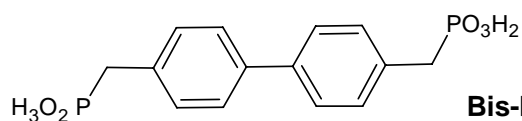
phosphonic acid (EADPA)

Dodecanediphosphonic acid (DDPA)
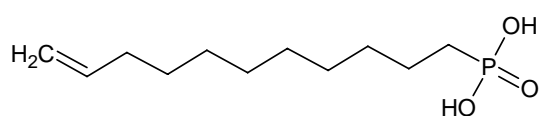
Undecenyl phosphonic acid (UDPA)

10,11-Dihydroxyundecyl -

phosphonic acid (DHUPA)

Bis-benzylphosphonic acid (BBPA)

Fig. 3 : *Some synthesized phosphonic acids with alkyl- or arylspacer and polar / reactive head groups, which are currently used for SAM formation on passivated steel.*

Another new idea to replace the electropolymerisation step is the use of already partially polymerised structures (so called oligomers) as SAM molecules. These molecules consist of an oligomeric backbone structure (e.g. oligomers from conducting polymers like Oligothiophenes) with several alkylphosphonic acid anchor groups. They could already form partially connected SAM structures only by simple SAM formation on the passivated metal surface without further treatment. Until now, two main types of those molecules were new synthesised and first corrosion tests with those SAM molecules have already begun.

Figure 4 shows the molecular structures of the two types of oligomer phosphonic acids, which were recently synthesised and are currently used in corrosion tests on passivated steel. With those molecules, a partial network of connected SAM head group structures already exists after SAM formation. This could lead to a significant simplification of the whole process and could therefore be promising for different technical applications.
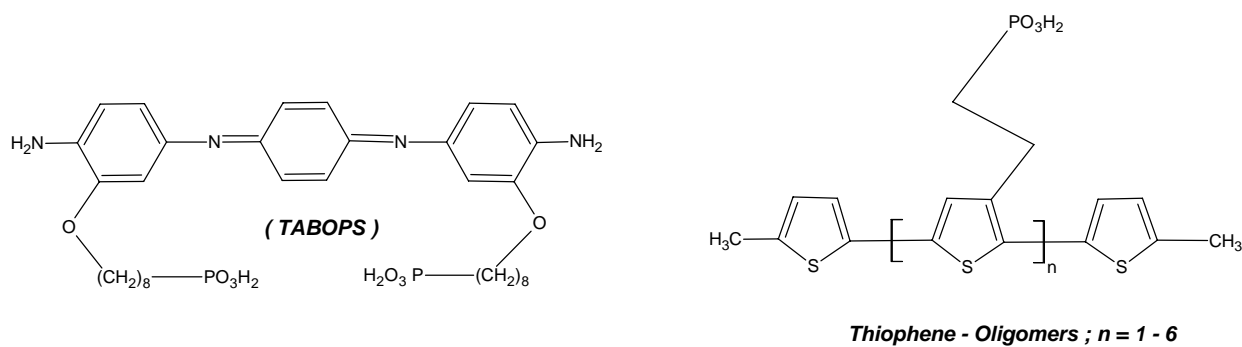
Fig. 4 : *Recently synthesized SAM molecules with a oligomeric backbone structure (oligo-aniline or oligothiophene), which are now used in current corrosion tests after SAM formation on passivated steel.*

Characterisation of the SAM formation on passivated steel surfaces

The two most important methods to evaluate the successful SAM formation after dipping or a spraying process until now are contact angle measurements with small water drops and some electrochemical investigations.

Contact angle measurements were often made with different passivation methods for the steel surface and with different SAM molecules during the last years. These measurements are a very fast and simple method to investigate and to confirm the SAM formation. The typical contact angles for passivated steel surfaces are in the range of $10 – 60^0$ and after SAM formation with non polar phosphonic acids (e.g. dodecane phosphonic acid) the contact angle increases to values in the range $100 – 150^0$, depending on the roughness of the surface. The typical conditions for these experiments were dipping the passivated steel substrates for about 1 minute at 45^0 C in a 10^{-3} M aqueous solution of the used phosphonic acid. The high contact angle values of $100 – 150^0$ indicate a strong hydrophobisation, which is caused by the alkylgroups of the SAM layers on the surface.

A more detailed description of these experiments and the achieved results have already been published in the last years [1-5].

The second important method to investigate the formed SAM layers are some electrochemical measurements like current density-curves or electrochemical impedance (EIS). In most cases current density curves in aqueous solutions with an anodic polarisation of the steel working electrodes were used starting from the free corrosion potential up to the potential, where transpassive iron dissolution occurs.

When a dense SAM layer is formed, usually a significant decrease of the anodic current in the passive area can be observed. This can be explained by a decreased iron dissolution of SAM coated steel surfaces. The additional SAM layer acts as a barrier layer for iron ions to move from the steel surface to the aqeous solution.

Results of such electrochemical measurements have been published elsewere in detail
 [1-5]. Therefore in this paper only some recent current density curves with a series of new SAM layers on passivated steel [5] are described.

Rotating disk electrodes (A= 0.36 cm^2) of passivated carbon steel (St 37) were used as working electrodes (rotating speed was 500 U / min.) in a cell with a platinum counterelectrode and a Ag / AgCl reference electrode. As electrolyte 0.1 M Na$_2$HPO$_4$ was used.
Passivation of the steel surface was done by dipping into 10% HNO$_3$ for 4 Minutes at 35^0 C in an ultrasonic bath [1-4].
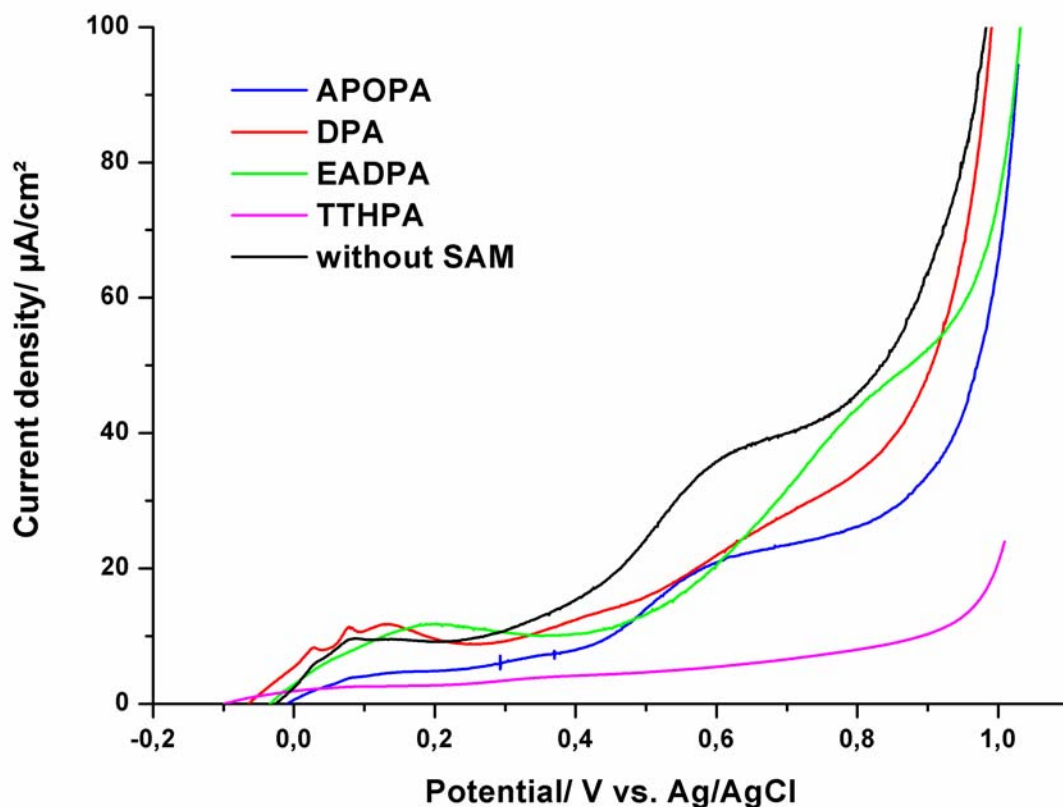

Fig. 5 : *Current density curves with rotating disc electrodes of passivated carbon steel (St 37) in 0.1 M Na$_2$HPO$_4$. The sweep rate was 1 mV s^{-1} .*

Typical conditions for SAM formation on passivated steel with the new synthesised phosphonic acids were described in the introduction and former publications [1-4]. The structures of the used phosphonic acids as SAM molecules are given in Figures 2 – 4 .
In the case case of carbon steel passivated in 10% HNO$_3$, the SAM with terthiophene head groups (TTHPA) showed the most effective inhibition of the iron dissolution while all SAM coated surfaces showed a decreased iron dissolution in comparison to only passivated steel electrodes.
All these results of the current density curves indicate, that an additional SAM layer could increase the corrosion resistance of passivated steel surfaces by reducing the anodic iron dissolution.

First results with SAM coated steel substrates in corrosion tests

Some first corrosion tests with a small number of SAM coated steel substrates were already made during the last few years with and without a final lacquering. These tests indicated, that the corrosion protection properties of some high-class passive layers on carbon steel surfaces (e.g. the described passivation with 10% HNO_3 or some technical phosphate layers) could be improved by an additional SAM [1]. Currently a more comprehensive program with different corrosion tests has started. This includes some more simple laboratory short tests like dipping passivated steel plates in an aerated 1% NaCl solution for some hours and compare optically the amount of the formed rust. This method is described now in this paper with first results for carbon steel substates, which were passivated in 10% HNO_3 .
Furthermore some significant industrial corrosion tests like salt spray tests or tests with stan-dardised pretreated steel plates in climate change chambers (after final lacquering) have quite recently started with different industry partners. These results are to be published later. In the near future some salt-spray tests with standardised passivated steel plates and measurements on the adhesion of different lacquerings should be carried out.

So in this paper only the first results of some more simple laboratory tests by dipping the steel substrates without lacquering in aerated 1% NaCl solution will be discussed.

Experimental setup
Carbon steel substrates (St 37 plates with 1.5 cm x 2 cm / thickness 4 mm / grinded with SiC-paper of 500 and 800 grid / degreased with acetone) were passivated as described above with 10 % HNO_3 and then coated with different additional SAM layers.

Fig. 6 shows pictures from typical carbon steel samples with and without passivation.
The left sample showes the etched surface after the passivation in 10% HNO_3 in comparison to the only grinded and degreased steel surface on the right side.
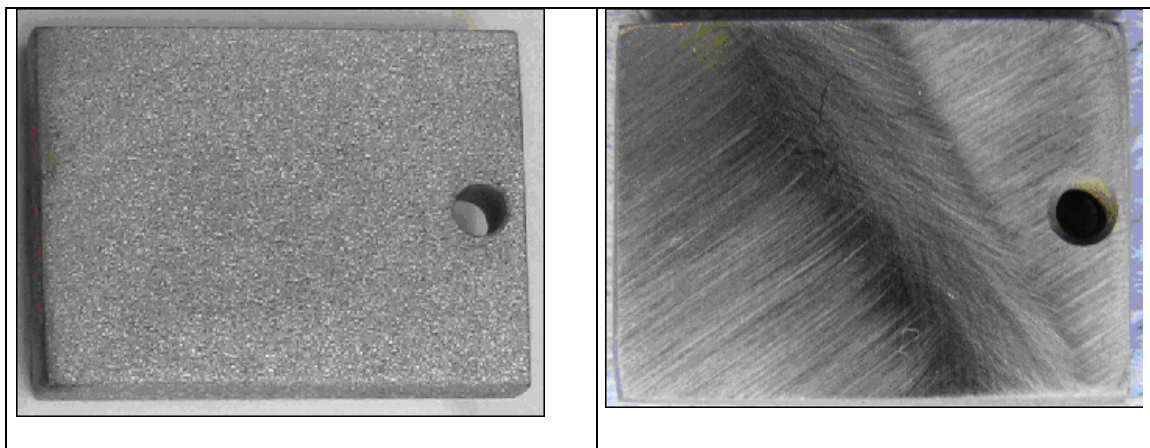

Fig. 6 :   *Typical surface appearance of the used carbon steel samples with (left sample) and without(right sample) passivation in 10% HNO_3 .The right sample of carbon steel (St 37) was only be grinded and degreased with acetone .*

After storing the SAM coated carbon steel plates for at least 1 day in a dry and dust free at-mosphere to allow SAM molecules to come to a better orientation, the substrates were then dipped for some hours in an aerated 1 % NaCl solution, buffered with 10^{-3} M acetic acid and 10^{-2} M sodium acetate to pH 5.6 . Normally the visable rust formation (brown coulored spots) started already after 2 – 4 hours of dipping and was clearly noticable after 6 – 8 hours dipping, when the tests could normally be stopped by removing the steel plates from the NaCl solution. Then the different coated steel substrates could be optically compared in respect to the different amount of brown rust, which was formed on the steel surfaces.

The main result of these experiments was, that most SAM layers could slightly inhibit the rust formation in comparison to the analog passivated steel plates without SAM. More effective were SAMs with 1,12-dodecane diphosphonic acid (DDPA, structure see Fig. 3), which sho-wed clearly the most significant corrosion inhibition from all SAM coatings, which were tested (see Fig. 7).
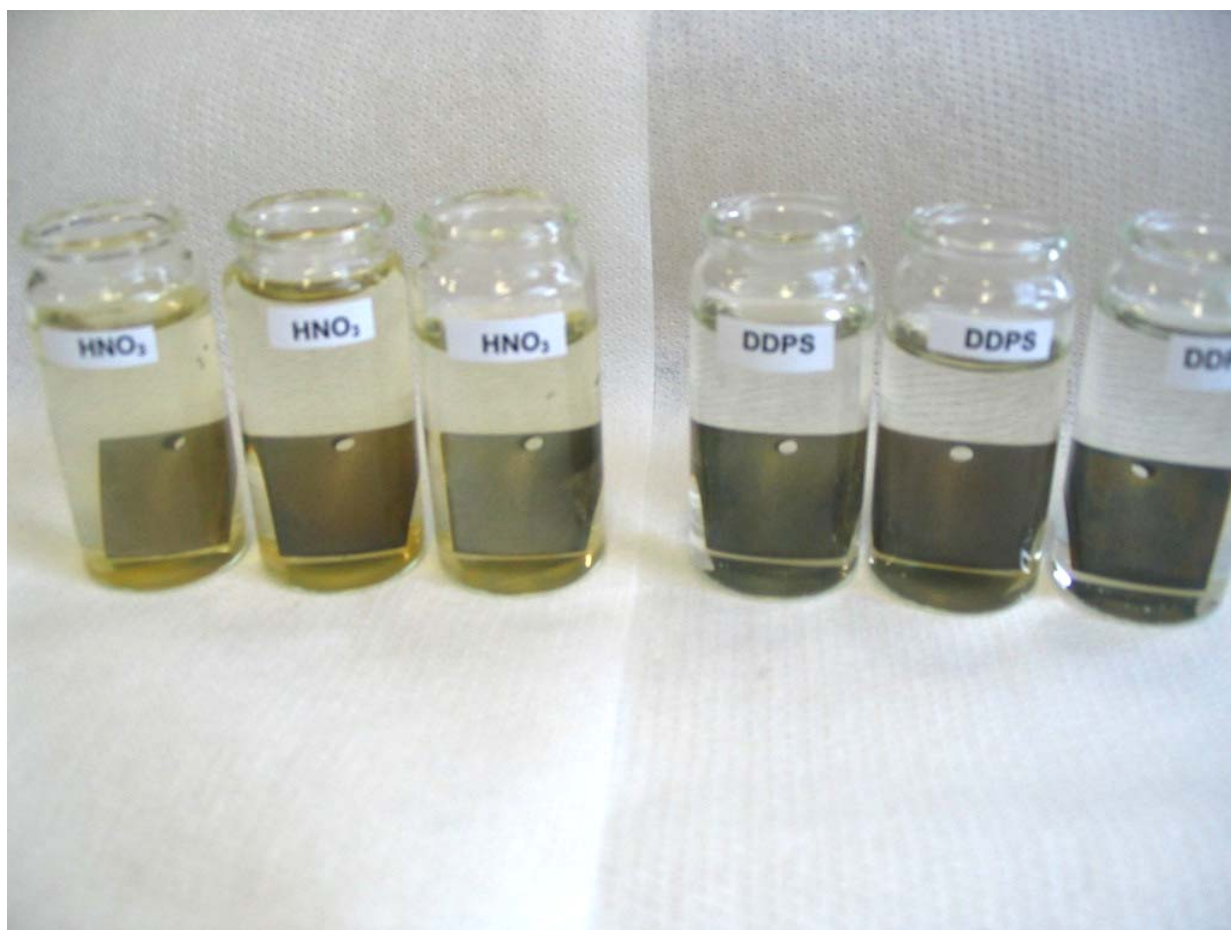

Fig. 7 : *A series of passivated (10 % HNO₃) carbon steel plates (St 37) after 7 h dipping in aerated 1 % NaCl solution. The 3 samples on the left side were the reference with only passivated carbon steel (without SAM), and the 3 samples on the right side were coated with an additional DDPA – SAM (molecule structure see Fig. 3).*

Conclusions

The results shown in this paper are some first steps to simplify and improve the original planned process shown in Fig. 1 to build up a new primer system for steel surfaces.

First some new phosphonic acids were synthesised to enable a simplified process without the expensive and technical disadvantageous step of electropolymerisation. This included new molecules with polar / reactive head groups as well as some first oligomeric phosphonic acids (see Fig. 2-4). Then the successful SAM formation with these new phosphonic acids on different passive layers of carbon steel was investigated and characterised by contact angle measurements and electrochemical experiments.

Finally some first results from corrosion experiments indicate, that the corrosion inhibition performance of some high-quality passive layers on carbon steel (including several technically advantageous phosphating procedures) can be significantly improved by some optimised additional SAM layers.

Outlook

In the future some more optimised oligomeric phosphonic acids should be tested as SAM layers as well as SAMs with head groups, that can easily be polymerised to a 2-dimensional network (compare Fig. 1) via classical polymerisation steps. This could be for example polyaddition reactions initiated by only a short and moderate heating of the samples or radical polymerisations via UV radiation or the influence of catalytical amounts of radical builders.

Acknowledgement

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