



УНИВЕРЗИТЕТ ЦРНЕ ГОРЕ
МЕТАЛУРШКО-ТЕХНОЛОШКИ
ФАКУЛТЕТ

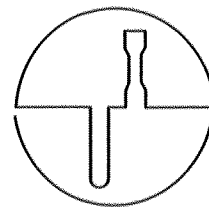
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UNIVERSITY OF MONTENEGRO
FACULTY OF METALLURGY AND
TECHNOLOGY

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ПИБ: 02016702

ПДБ: 30/31-03951-6

Број 2167/1
Подгорица, 16.12.2019

UNIVERZITET CRNE GORE

CENTAR ZA DOKTORSKE STUDIJE
-N/R Prof. dr Predrag Miranović, rukovodilac Centra

Podgorica

PREDMET: Dostava D2 za mr Stojana Božovića

Poštovani,

U prilogu akta dostavljamo predlog odluke o imenovanju Komisije za ocjenu doktorske disertacije: „*Sinergijski efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu*“, kandidata mr Stojana Božovića, sa pretećom dokumentacijom, koji su razmotreni i usvojeni na sjednici Vijeća Metalurško-tehnološkog fakulteta od 16.12.2019. godine.

Srdačan pozdrav,


DEKAN,
Prof. dr Mira Vukčević

Broj 2167
Podgorica, 16.12 2019 god.

Na osnovu člana 64 Statuta Univerziteta Crne Gore („Bilten UCG“ br. 337/2015 i br. 447/2018) i inicijalnog predloga Komisije za doktorske studije Metalurško-tehnološkog fakulteta br. 2137 od 10.12.2019. godine, a u vezi sa čl. 41 Pravila doktorskih studija Univerziteta Crne Gore i t. 3.8 Vodiča za doktorske studije Univerziteta Crne Gore, Vijeće Metalurško-tehnološkog fakulteta u Podgorici, na sjednici održanoj 16.12.2019. godine, utvrdilo je sljedeći -

PREDLOG ODLUKE

- I Kandidat mr Stojan Božović, ispunjava formalne uslove za ocjenu doktorske disertacije: „*Sinergijski efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu*“.
- II Imenuje se *Komisija za ocjenu doktorske disertacije mr Stojana Božovića*, pod navedenim nazivom, u sastavu:
 1. Prof. dr Veselinka Grudić, vanredni profesor, MTF, Podgorica, mentor,
 2. Prof. dr Sanja Martinez, redovni profesor, Fakultet za kemijsko inženjerstvo i tehnologiju, Zagreb, komentor,
 3. Prof. dr Ivana Bošković, vanredni profesor, MTF, Podgorica.
- III Komisija za ocjenu doktorske disertacije je dužna da Vijeću Metalurško-tehnološkog fakulteta u Podgorici, podnese izvještaj koji sadrži ocjenu doktorske disertacije, u roku od 45 dana od dana imenovanja Komisije.

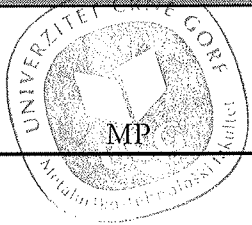
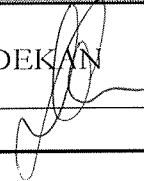
CO:

- Odbor za doktorske studije,
- Sekretar,
- a/a.


Prof. dr Mira Vukčević

ISPUNJENOST USLOVA DOKTORANDA

OPŠTI PODACI O DOKTORANDU			
Titula, ime, ime roditelja, prezime	mr Stojan (Milorad) Božović		
Fakultet	Metalurško-tehnološki fakultet Podgorica		
Studijski program	Hemijska tehnologija		
Broj indeksa	1/16		
NAZIV DOKTORSKE DISERTACIJE			
Na službenom jeziku	„Sinergijski efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu”		
Na engleskom jeziku	„Synergic effect of environmentally acceptable inhibitors on the corrosion of metallic materials in chloride medium”		
Naučna oblast	Elektrohemijska		
MENTOR/MENTORI			
Prvi mentor	dr Veselinka Grudić	Metalurško-tehnološki fakultet Podgorica, Univerzitet Crne Gore, Crna Gora	Fizička hemija
Drugi mentor	dr Sanja Martinez	Fakultet kemijskog inženjerstva i tehnologije, Sveučilište u Zagrebu, Hrvatska	Elektrohemijska
KOMISIJA ZA PREGLED I OCJENU DOKTORSKE DISERTACIJE			
	dr Ivana Bošković	Metalurško-tehnološki fakultet Podgorica, Univerzitet Crne Gore, Crna Gora	Fizička hemija
	dr Veselinka Grudić	Metalurško-tehnološki fakultet Podgorica, Univerzitet Crne Gore, Crna Gora	Fizička hemija
	dr Sanja Martinez	Fakultet kemijskog inženjerstva i tehnologije, Sveučilište u Zagrebu, Hrvatska	Elektrohemijska

Datum značajni za ocjenu doktorske disertacije	
Sjednica Senata na kojoj je data saglasnost na ocjenu teme i kandidata	06.09.2018. godine
Dostavljanja doktorske disertacije organizacionoj jedinici i saglasnost mentora	11.11.2019.godine
Sjednica Vijeća organizacione jedinice na kojoj je dat prijedlog za imenovanje komisija za pregled i ocjenu doktorske disertacije	16.12.2019. godine
ISPUNJENOST USLOVA DOKTORANDA	
U skladu sa članom 38 pravila doktorskih studija kandidat je dio sopstvenih istraživanja vezanih za doktorsku disertaciju publikovao u časopisu sa (SCI/SCIE) liste kao prvi autor.	
Spisak radova doktoranda iz oblasti doktorskih studija koje je publikovao u časopisima sa (upisati odgovarajuću listu)	
Stojan Božović, Sanja Martinez, Veselinka Grudić, A Novel Environmentally Friendly Synergistic Mixture for Steel Corrosion Inhibition in 0,51 M NaCl, Acta Chimica Slovenica, Vol. 66, 2019, pp. 112-122; DOI: 10.17344/acsi.2018.4702; https://acta.chem-soc.si/; ISSN: 1318-0207 (štampana verzija), 1580-3155 (elektronska verzija); SCI Expanded Journal List.	
Obrazloženje mentora o korišćenju doktorske disertacije u publikovanim radovima	
U radu je dokazana mogućnost primjene netoksične i ekološki prihvatljive smješe inhibitora sastavljene od propolisa, tanina, natrijum-benzoata, PEG400 i skroba kao vrlo efikasnog inhibitora korozije čelika u hloridnom rastvoru. Sinergijsko dejstvo pažljivo odabranih komponenata smješe rezultuje stvaranjem vrlo postojanog zaštitnog sloja na površini čelika koji ga štiti od korozije, kao u mirnim, tako i u miješanim rastvorima. Mjerenja izvedena na LPR probi i vrijednosti parametara elektrohemijske impedansne spektroskopije ukazuju da inhibitorom modifikovani sloj korozionih produkata na površini čelika predstavlja barijeru za difuziju kiseonika. Efikasna zaštita čelika inhibitorom modifikovanog sloja korozionih produkata dokazana je FTIR i SEM/EDX analiza ma.	
Datum i ovjera (pečat i potpis odgovorne osobe)	
U Podgorici, 12.12.2019.g.	  DEKAN

Prilog dokumenta sadrži:

1. Potvrdu o predaji doktorske disertacije organizacionoj jedinici
2. Odluku o imenovanju komisije za pregled i ocjenu doktorske disertacije
3. Kopiju rada publikovanog u časopisu sa odgovarajuće liste
4. Biografiju i bibliografiju kandidata
5. Biografiju i bibliografiju članova komisije za pregled i ocjenu doktorske disertacije sa potvrdom o izboru u odgovarajuće akademsko zvanje i potvrdom da barem jedan član komisije nije u radnom odnosu na Univerzitetu Crne Gore



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Broj / Ref: 01/2-1602/2-1
Datum / Date: 09.12. 2019.

UNIVERZITET CRNE GORE
METALURŠKO-TEHNOLOŠKI FAKULTET
N/R DEKANU, PROF. DR MIRI VUKČEVIĆ

Predmet: Evaluacija doktorske disertacije doktoranda Stojana Božovića „Efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu“ korišćenjem softvera *Ithenticate*

Poštovani,

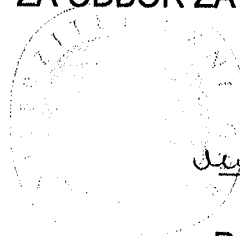
Saglasno članu 9 Odluke o korišćenju softvera za utvrđivanje plagijata na Univerzitetu Crne Gore, Odbor za doktorske studije izvršio je provjeru elektronske verzije doktorske disertacije doktoranda Stojana Božovića pod nazivom „Efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu“ korišćenjem softvera *Ithenticate* dostavljene od strane Metalurško-tehnološkog fakulteta. Nakon izvršene provjere, ustanovljeno je da u pomenutoj elektronskoj verziji doktorske disertacije nema elemenata koji bi se mogli tumačiti kao plagijat, saglasno kriterijumima propisanim članom 8 gore navedene Odluke. U skladu sa navedenim, postupak sticanja doktorske disertacije doktoranda Stojana Božovića može da se nastavi u skladu sa Pravilima doktorskih studija.

U prilogu Vam dostavljamo izvještaj o provjeri predmetne doktorske disertacije generisan od *Ithenticate* softvera.

Srdačan pozdrav,

ZA ODBOR ZA DOKTORSKE STUDIJE

PREDSJEDNIK



Predrag Miranović

Prof. dr Predrag Miranović

UNIVERZITET CRNE GORE
METALURŠKO-TEHNOLOŠKI FAKULTET

PISMENA SAGLASNOST

Saglasni smo da doktorski rad "**Sinergijski efekat ekološki prihvatljivih inhibitora na koroziiju metalnih materijala u hloridnom medijumu**", kandidata Stojana Božovića krene u dalju proceduru, odnosno da se imenuje Komisija za pregled i ocjenu doktorske disertacije, budući da sadrži sve neophodne elemente propisane za dalju proceduru.

Takođe, napominjemo da je kandidat, u radu **A Novel Environmentally Friendly Synergistic Mixture for Steel Corrosion Inhibition in 0,51 M NaCl**, publikovanom u časopisu **Acta Chimica Slovenica**, Vol. 66, 2019, pp. 112-122; DOI: 10.17344/acsi.2018.4702, a koji se nalazi na **SCI Expanded Journal listi**, koristio rezultate na adekvatan način, odnosno u radu su prezentovani dijelovi doktorske disertacije u skladu sa pravilima doktorskih studija.

S postovanjem,

Podgorica, 11.12.2019.godine



Prof. dr Veselinka Grudić, mentor



Prof. dr Sanja Martinez, komentor

УНИВЕРЗИТЕТ ЦРНЕ ГОРЕ

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Број: 08-1736
Датум, 24. 06. 2015 г.

Ref: _____
Date, _____

Na osnovu člana 72 stav 2 Zakona o visokom obrazovanju (Službeni list Crne Gore br. 44/14) i člana 32 stav 1 tačka 9 Statuta Univerziteta Crne Gore, Senat Univerziteta Crne Gore, na sjednici održanoj 24. juna 2015. godine, donio je

ODLUKU O IZBORU U ZVANJE

Dr VESELINKA GRUDIĆ bira se u akademsko zvanje **vanredni profesor Univerziteta Crne Gore** za predmete: Hemijska termodinamika, Tehnološke operacije II, Elektrohemija, Hemijski izvori struje i Zaštitne prevlake na studijskom programu Hemijska tehnologija na **Metalurško-tehnološkom fakultetu**, na period od pet godina.



REKTOR

Prof. Radmila Vojvodić

BIOGRAFIJA – Prof. dr Veselinka Grudić

Dr Veselinka Grudić je diplomirala je na Metalurško-tehnološkom fakultetu Univerziteta Crne Gore u Podgorici na odsjeku za neorgansku tehnologiju (1990-1995). Završila je postdiplomske studije i stekla doktorsku titulu na Fakultetu za fizičku hemiju Univerziteta u Beogradu. Od 1995. zaposlena je na Metalurško-tehnološkom fakultetu u Podgorici. Dr Veselinka Grudić je vanredni profesor na Metalurško-tehnološkom fakultetu Univerziteta Gore za predmete: Hemijska termodinamika, Tehnološke operacije II, Hemijski izvori struje i Zaštitne prevlake. Njena profesionalna orijentacija je u području elektrokemijske sinteze različitih oksida metala (metode sagorijevanja gela), elektrokemijskog ispitivanja različitih površinskih procesa na granici elektroda / elektrolita, ispitivanje mehanizma i kinetike sorpcionih procesa, kao i zaštita metalnih materijala od korozije primjenom inhibitora. Bila je mentor velikog broja specijalističkih radova, jednog magistarskog rada i trenutno je mentor dvije doktorske disertacije. Ima više od 30 naučnih i konferencijskih radova, od kojih je 15 radova SCI indeksiranih publikacija. Bila je uključena u 7 naučno -istraživačkih i bilateralnih projekata.

SPISAK REFERENCI

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2. V.L. Vukašinović Pešić, V.N. Rajaković-Ognjanović, N.Z. Blagojević, **V.V. Grudić**, B.M. Jovanović, Lj.V. Rajaković, "Enhanced arsenic removal from water by activated red mud based on hydrated iron(III) and titan(IV) oxides", *Chem. Eng. Commun.*, (2012), 199(7): 849-864. ISSN: 0098-6445
3. **V. Grudić**, Đina Perić, Nada Z. Blagojević, Vesna L. Vukašinović-Pešić, Snežana Brašanac, Bojana Mugoša, "Pb(II) and Cu(II) sorption from aqueous solutions using activated red mud – evaluation of kinetic, equilibrium and thermodynamic models", *Pol. J. Environ. Stud.*,(2013), 22(2): 377-385. ISSN: 1230-1485
4. **Grudić Veselinka V.**, Blagojević Nada Z., Vukašinović-Pešić Vesna L., Brašanac Snežana R., "Kinetics of degradation of ascorbic acid by cyclic voltammetry method", *CI&CEQ*, (2015), 21(2): 351-357. ISSN: 1451-9372
5. **V.Grudić**, J.Pješčić-Šćepanović, I.Bošković, "Removal of cadmium (II) from aqueous solution using fermented grape marc as a new adsorbent", *CI&CEQ*,(2015), 21(2): 285 – 293. ISSN 1451- 9372
- 6.**Veselinka V. Grudić**, Snežana Brašanac,Vesna L. Vukašinović- Pešić and Nada Z. Blagojević "Sorption of cadmium from water using neutralized red mud and activated neutralized red mud " *ARPN Journal of Engineering and Applied Sciences* (2013), 8(11): 933 - 943. ISSN: 1819 – 6608
- 7.**Veselinka Grudić**, Ivana Bošković, Željko Jaćimović, Sorption kinetics of Cd(II) ions on fermented grape marc, *Environment Protection Engineering* (2017), 43(4): 243 -252

8. Grudić Veselinka, **Ivana Bošković**, Dragan Radonjić, Željko Jaćimović, Bojana Knežević, The Electrochemical Behavior of Al Alloys in NaCl Solution in the Presence of Pyrazole Derivative, Iranian Journal of Chemistry & Chemical Engineering, Vol 38, Issue 2-Serial Number 93, **2019**, pp. 127-138
9. **Bošković Ivana**, Grudić Veselinka, Ivanović Mileta, Milašević Ivana, Investigation of Reduction and Precipitation Rate of Colloidal Gold Particles Obtained in the Process of Electrical and Electronic Waste Recycling, Iranian Journal of Chemistry & Chemical Engineering, Vol 37, Issue 2-Serial Number 88, March and April **2018**, pp. 133-138
10. Veselinka Grudić, Sanja Martinez, Bojana Knežević and Ivana Bošković, Corrosion inhibition of steel in a sodium chloride solution by natural honey, Materials Testing 61(9), pp. 881-884, **2019**,
11. Veselinka Grudić, Ivana Bošković, Sanja Martinez, Bojana Knežević, CORROSION INHIBITION MILD STEEL IN NaCl SOLUTION IN THE PRESENCE OF PROPOLIS EXTRACT, Macedonian Journal of Chemistry and Chemical Engineering, Vo. 37, No.2, pp. 203-213, (2018), DOI:10.20450/mjce.2018.1513
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13. Stojan Božović, Sanja Martinez, Veselinka Grudić, A Novel Environmentally Friendly Synergistic Mixture for Steel Corrosion Inhibition in 0,51 M NaCl, Acta Chimica Slovenica, Vol. 66, 2019, pp. 112-122; DOI: 10.17344/acsi.2018.4702; <https://acta.chem-soc.si/>; ISSN: 1318-0207 (štampana verzija), 1580-3155 (elektronska verzija); SCI Expanded Journal List.



Sveučilište u Zagrebu

REPUBLIKA HRVATSKA

Na temelju članka 21. i 84. Statuta Sveučilišta u Zagrebu,
sukladno članku 93. Zakona o znanstvenoj djelatnosti i visokom obrazovanju,
na prijedlog Povjerenstva za utvrđivanje kriterija i potvrdu izbora u zvanje,

Senat Sveučilišta u Zagrebu potvrđuje da je

dr. sc. **SANJA MARTINEZ**

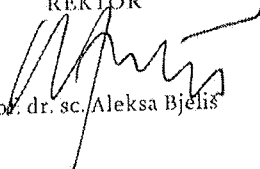
izvanredna profesorica
Fakulteta kemijskog inženjerstva i tehnologije Sveučilišta u Zagrebu
izabrana na vrijeme od pet godina u znanstveno-nastavno zvanje

REDOVITE PROFESORICE

u području tehničkih znanosti,
polje: kemijsko inženjerstvo – analiza, sinteza i vođenje kemijskih procesa
i
polje: temeljne tehničke znanosti - materijali

Klasa: 640-03/12-07/120
Urbroj: 380-021/081-12-2
Zagreb, 18. rujna 2012.

REKTOR


Prof. dr. sc. Aleksa Bjeliš

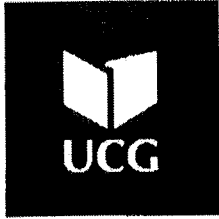
BIOGRAFIJA – Prof. dr Sanja Martinez

Dr. sc. Sanja Martinez rođena je 23. prosinca 1968. u Zagrebu, gdje je završila osnovnu i srednju školu. Diplomirala je na Prirodoslovno-matematičkom fakultetu Sveučilišta u Zagrebu, smjer inženjerska fizika. Doktorirala je 26. svibnja 2000. Od travnja 1994. zaposlena je na Fakultetu kemijskog inženjerstva i tehnologije, momentalno kao redoviti profesor u trajnom zvanju. Prof. dr. sc. Sanja Martinez znanstveno se bavi izuzetno širokim spektrom elektrokemijskih i elektrokemijsko-inženjerskih tema. U području elektrokemijskog i korozijskog inženjerstva treba istaknuti njezin doprinos istraživanjima sustava katodne zaštite, modeliranja raspodjele struja i potencijala u tim sustavima te istraživanjima korozije u protočnim sustavima pod različitim hidrodinamičkim uvjetima rada. Također izučava zaštitu metalnih konstrukcija od korozije uporabom premaza, kao i pojavu katodne delaminacije. Posebno velik znanstveni doprinos daje u području zaštite čeličnih materijala od korozije pomoću prirodnih, ekološki prihvatljivih inhibitora. U periodu od 1994. do 2017. aktivno je sudjelovala u realizaciji četiri znanstvena projekta MZOŠ-a, pri čemu je bila voditelj dvaju projekata. Od 2014. do 2017. bila je suradnik na projektu NANOSENS HRZZ-a. Sudjelovala je na jednom europskom istraživačkom IPA projektu, a trenutno je lokalni koordinator jednog CEEPUS projekta. Prof. dr. sc. Sanja Martinez objavila je jedno poglavlje u znanstvenoj knjizi, 35 znanstvenih radova u časopisima citiranima u tercijarnim publikacijama, 8 znanstvenih radova u časopisima citiranima u sekundarnim publikacijama, 19 radova u zbornicima radova s međunarodnih skupova te 9 radova u zbornicima s domaćih skupova. Prof. dr. sc. Sanja Martinez predavala je vrlo velik broj kolegija na svim razinama visokog obrazovanja (preddiplomska, diplomatska i poslijediplomska nastava). Po izboru u zvanje docenta 2003. predavanja održava najprije na kolegijima Elektrokemijska korozija materijala i Tehnike zaštite od korozije, a kasnije i na kolegijima: Metalni materijali, korozija i zaštita, Konstrukcijski materijali i zaštita, Elektrokemijsko i korozijsko inženjerstvo (50 %), Elektrokemija (50 % – 100 %), Korozijska stabilnost materijala i Elektrokemija bioloških procesa i biomolekula (33 %). U poslijediplomskoj nastavi sudjelovala je u predavanjima i izvođenju vježbi u okviru nekoliko kolegija: Korozija materijala i računalno modeliranje u koroziji (izborni kolegij), Odabrana poglavlja elektrokemije (temeljni kolegij na specijalističkom poslijediplomskom studiju Korozija i zaštita) te izbornih kolegija Tehnike zaštite od korozije i Katodna zaštita. Od 2014. na doktorskom studiju Kemijsko inženjerstvo i primijenjena kemija predaje predmet Novi izazovi u korozijskoj problematici (50 %), a od 2016. predmet Eko-prihvatljivi inhibitori korozije na III. Ciklusu Doktorskog studija iz Primijenjene kemije Sveučilišta u Tuzli (33 %).

Bila je mentor 21 diplomskog i 20 završnih radova, 1 specijalističkog rada te izravni voditelj 3 diplomatska rada. Bila je mentor 4 i komentor 1 doktorskog rada, a trenutno je mentor 5 doktorskih radova. Posebno treba istaknuti da je koautorica jednog sveučilišnog udžbenika te jednog digitalnog udžbenika, jednog recenziranog i jednog nerecenziranog nastavnog teksta te koautorica Rječnika strukovnog nazivlja iz područja korozije i zaštite materijala.

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07.10.2016

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Broj 1992

Podgorica, 07.10. 2016. god.

Na osnovu člana 72 stav 2 Zakona o visokom obrazovanju („Službeni list Crne Gore“ br. 44/14, 47/15, 40/16) i člana 32 stav 1 tačka 9 Statuta Univerziteta Crne Gore, Senat Univerziteta Crne Gore na sjednici održanoj 27. oktobra 2016. godine, donio je

ODLUKU O IZBORU U ZVANJE

Dr Ivana Bošković bira se u akademsko zvanje **vanredna profesorica Univerziteta Crne Gore** za predmete **Fizička hemija I** i **Fizička hemija II** na osnovnom akademskom studijskom programu **Hemijska tehnologija**, **Fizička hemija** na osnovnom akademskom studijskom programu **Farmacija** na Medicinskom fakultetu, **Fizička hemija sa elektrohemijom** na osnovnom akademskom studijskom programu **Metalurgija**; **Prahovi i keramika** na postdiplomskom specijalističkom akademskom studijskom programu **Hemijska tehnologija**, **neorgansko usmjerenje** i **Kataliza** na postdiplomskom specijalističkom akademskom studijskom programu **Hemijska tehnologija** na Metalurško-tehnološkom fakultetu, na period od pet godina.



REKTOR

[Signature]
Prof. Radmila Vojvodić

Dr Ivana Bošković je diplomirala je na Metalurško-tehnološkom fakultetu Univerziteta Crne Gore u Podgorici na odsjeku za neorgansku tehnologiju (1990-1995). Završila je postdiplomske studije i stekla doktorsku titulu na Fakultetu za fizičku hemiju Univerziteta u Beogradu. Od 1995. zaposlena je na Metalurško-tehnološkom fakultetu u Podgorici. Sada je vanredna profesorica i član je Hemijskog društva Crne Gore. Njena naučno-istraživačka oblast je usmjerena na fizičku hemiju materijala i zaštitu životne sredine. Objavila je 20 radova u međunarodnim naučnim časopisima, 3 rada u domaćim časopisima i ima oko 50 saopštenja na međunarodnim konferencijama. Recenzentica je časopisa Chemical and Biochemical Engineering Journal i Iranian Journal for Chemistry and Chemical Engineering

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UNIVERZITETE CRNE GORE
METALURŠKO-TEHNOLOŠKI FAKULTET
KOMISIJI ZA DOKTORSKE STUDIJE

Predmet: Zahtjev za ocjenu doktorske disertacije

Molim Vas da imenujete komisiju za ocjenu doktorske disertacije: „**Sinergijski efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu**“.

Podgorica,
11.11.2019. godine

Kandidat:
mr Stojan Božović
Božović Stojan

Izjava o autorstvu

Potpisani **Božović Stojan**
Broj indeksa/upisa 1/16

Izjavljujem

da je doktorska disertacija pod naslovom

„Sinergijski efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu.”

- rezultat sopstvenog istraživačkog rada,
- da predložena disertacija ni u cjelini ni u djelovima nije bila predložena za dobijanje bilo koje diplome prema studijskim programima drugih ustanova visokog obrazovanja,
- da su rezultati korektno navedeni, i
- da nijesam povrijedio autorska i druga prava intelektualne svojine koja pripadaju trećim licima.

U Nikšiću, 12.12.2019.

Potpis doktoranda

Božović Stojan

Božović Stojan



UNIVERZITET CRNE GORE
METALURŠKO-TEHNOLOŠKI FAKULTET
HEMIJSKA TEHNOLOGIJA

Broj dosijea: 1/2016

Na osnovu člana 165 Zakona o opštem upravnom postupku ("Službeni list RCG" br. 60/03) i službene evidencije, a po zahtjevu Božović Milorad Stojan, izdaje se

POTVRDA O STUDIRANJU

Student **Božović Milorad Stojan**, rođen **11-10-1990** godine u mjestu **Nikšić**, opština **Nikšić**, Republika **Crna Gora**, upisan je studijske **2016/2017** godine, u **I** godinu studija, kao student koji se **samofinansira** na **akademske doktorske studije**, studijski program **HEMIJSKA TEHNOLOGIJA**, koji realizuje **METALURŠKO-TEHNOLOŠKI FAKULTET** - Podgorica Univerziteta Crne Gore u trajanju od **3 (tri)** godine sa obimom **180 ECTS** kredita.

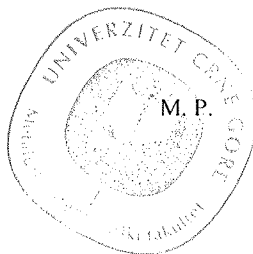
Studijske **2019/2020** godine prijavio je *da sluša* **2** predmeta sa **60.00** (šezdeset) ECTS kredita.

Po prvi put iz **III (treće)** godine, prijavio je *da sluša* **2** predmeta sa **60.00** (šezdeset) ECTS kredita, što iznosi **100.00%** od ukupnog broja ECTS kredita u **III** godinu.

Saglasno Statutu Univerziteta Crne Gore, **Božović Milorad Stojan** je po prvi put prijavio *da sluša* **više od 2/3**, odnosno **66,67%** (šezdesetšest 67/100 %), od ukupnog broja ECTS kredita sa **III** godine i studijske **2019/2020** ima status **redovnog studenta** koji se **samofinansira**.

Uvjerenje se izdaje na osnovu službene evidencije, a u svrhu ostvarivanja prava na: (dječji dodatak, porodičnu penziju, invalidski dodatak, zdravstvenu legitimaciju, povlašćenu vožnju za gradski saobraćaj, studentski dom, studentski kredit, stipendiju, regulisanje vojne obaveze i slično).

Broj:
Podgorica, 10.12.2019 godine



301
SEKRETAR,

BIOGRAFIJA – Stojan Božović

Stojan Božović je rođen 11.10.1990. u Nikšiću, gdje je završio osnovnu školu i gimnaziju „Stojan Cerović”- prirodno-matematički smjer. Osnovne studije na Metalurško-tehnološkom fakultetu u Podgorici upisao je akademske 2009/2010. godine na smjeru Hemijska tehnologija i iste završio 2012. godine. Specijalističke studije na istom fakultetu upisao je akademske 2012/2013. godine na Organskom usmjerenju i iste završio 2013. godine. Specijalistički rad na temu „Ispitivanje kinetike degradacije vitamina C metodom ciklične voltametrije” je radio pod mentorstvom dr. Veselinke Grudić. Pripravnički staž preko Programa Stručnog Osposobljavanja je odradio u P.Z.U. Apoteka “Lijek” Podgorica u periodu od 15.01. 2014. godine do 15.10.2014. godine. Master studije na Tehnološko-metalurškom fakultetu Univerziteta u Beogradu upisao je studijske 2014/2015. godine na smjeru Hemijsko inženjerstvo i iste završio 2015. godine. Master rad na temu „Određivanje sile istiskivanja tablete iz blister pakovanja Al/Al i PVC/Al” je radio pod mentorstvom dr. Milorada Zrilića. Doktorske studije na Metalurško-tehnološkom fakultetu u Podgorici upisao je studijske 2016/2017. godine na smjeru Hemijska tehnologija, oblast Elektrohemijska-Korozija. Kao student doktorskih studija učestvovao je na razmjeni studenata na Fakultetu kemijskog inženjerstva i tehnologije, Sveučilišta u Zagrebu preko CEEPUS programa u ukupnom trajanju od 10 mjeseci. Ima objavljen naučni rad u časopisu sa SCI liste kao prvi autor, kao i više radova na kojima je bio autor i koautor na međunarodnim naučnim konferencijama.

Govori engleski i ruski jezik i služi se njemačkim jezikom.

SPISAK REFERENCI:

Stojan Božović, Sanja Martnez, Veselinka Grudić, A Novel Environmentally Friendly Synergistic Mixture for Steel Corrosion Inhibition in 0,51 M NaCl, Acta Chim. Slov., **2019**, 66, 112-122.

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Tena Gvozdanović, Stojan Božović, Sanja Martinez, Inhibicija korozije konstrukcijskog čelika u neutralnom kloridnom mediju smjesom netoksičnih korozijskih inhibitora, International Conference, 17th Ružička days, “Today science- tomorrow industry”, Book of Abstracts, Osijek, 2018.

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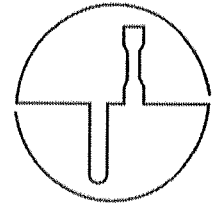
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Број 1975

Подгорица, 13. 11. 2019.

Na osnovu člana 33. Zakona o upravnom postupku („Sl. list CG“ br. 56/14) i na lični zahtjev studenta Metalurško-tehnološkog fakulteta u Podgorici, a u vezi sa t. 3.8. Vodiča za doktorske studije Univerziteta Crne Gore i na osnovu službene evidencije Fakulteta, izdaje se sljedeća-

P O T V R D A

Mr Stojan Božović, student doktorskih studija Metalurško-tehnološkog fakulteta u Podgorici, studijski program *Hemijska tehnologija*, dostavio je ovom Fakultetu doktorsku disertaciju pod nazivom *“Sinergijski efekat ekološki prihvatljivih inhibitora na koroziju metalnih materijala u hloridnom medijumu”*, dana 12.11.2019. godine, na dalji postupak.

SEKRETAR,
Seka Sekularac-Petrović
Seka Sekularac-Petrović

Scientific paper

A Novel Environmentally Friendly Synergistic Mixture for Steel Corrosion Inhibition in 0.51 M NaCl

Stojan Božović,^{1,*} Sanja Martinez² and Veselinka Grudić¹¹ University of Montenegro, Faculty of Metallurgy and Technology, Cetinjski put, 81000 Podgorica, Montenegro² University of Zagreb, Faculty of Chemical Engineering and Technology, Department of Electrochemistry, ReCorr Laboratory, Savska cesta 16, HR-1000 Zagreb, Croatia* Corresponding author: E-mail: stojan.bozovic90@yahoo.com,

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Abstract

The ubiquitous use of plain and low-alloy steels in neutral, chloride bearing environments presents an everyday challenge for corrosion protection professionals. This paper explores the possibility of developing a non-toxic and environmentally friendly synergistic inhibitor mixture made of propolis, tannin, sodium benzoate, PEG400 and starch that could be applied into the solution to induce the formation of a persistent protective layer on steel. Components of the mixture were chosen based on the references giving their characteristics relevant to their possible action in the solution and/or at the surface of the steel. The efficiency of the protective layer formed under the influence of the inhibitor mixture, and then measured by the LPR probe in the inhibitor-free solution, was the lowest under quiescent conditions (75%) and the highest (95%) under flow conditions. Both, LPR and EIS data indicate that the inhibitor modified layer presents a barrier for diffusion of oxygen that acts as a primary corrosion reaction depolarizer in the investigated neutral chloride solution. The demonstrated persistence of the inhibitor modified layer is of primary interest as it gives possibility batch application.

Keywords: Synergistic inhibitor mixture; steel; corrosion inhibition

1. Introduction

Steel is the most widely used metallic material thanks to its good mechanical properties and low price. However, when it comes into contact with aerated neutral electrolyte, especially in the presence of chloride ions, steel is subject to rapid corrosion degradation.

Neutral saline aqueous environments of various origins are frequently simulated in laboratory by the use of 0.35–0.85 M NaCl solutions.¹ Corrosion rates recorded on plain steel by polarization and weight loss techniques are fairly consistent and range between 0.1 and 0.5 mm per year.^{2,3} These rates are generally not acceptable and protective measures have to be applied. Due to the inherent characteristics of corroding systems (e.g. complex geometry or need for good thermal conductance) corrosion inhibitors frequently stand out as the most practical or the only solution. Unfortunately, protection of steel in neutral chloride media is challenging from theoretical and practical viewpoint. It can readily be observed that considerably more literature is found on inhibition of steel corrosion in acidic

media than in neutral media and that the inhibitor effectiveness is generally higher. From the theoretical aspect, the reason is that in near-neutral, neutral and alkaline media, inhibitor action is complicated by formation of iron oxides and hydroxides at the surface of metal.⁴

In acidic media, bare iron (or steel) surface is positively charged and behaves as a soft Lewis acid, hence, soft Lewis base compounds with heteroatoms O, N, S, P and/or π electrons in their structure, are good inhibitor candidates due to the possibility of soft acid-soft base adsorption bond formation.^{5,6} On the other hand, when oxide is present, surface acidity and basicity depends on oxide's isoelectric point, which e.g. for Fe_2O_3 , equals pH 8.6.⁷ Below this pH it may be assumed that the surface oxide is protonated, positively charged and acting as a hard Lewis acid. Hard Lewis bases would therefore be good inhibitor candidates capable of hard acid-hard base adsorptive bond formation.

In the present study, tannin, sodium benzoate, propolis, starch and polyethylene glycol (PEG400) were chosen as components of the investigated inhibitor mixture. When

such a mixture rich in OH groups is used for inhibiting corrosion, in near neutral and neutral pH, part of the OH groups will be deprotonated forming anions that have electronegativity practically equal to their ionization potential, and therefore act as almost pure electron donors or hard Lewis bases.⁵ Adsorptive hard acid-hard base bond which is of predominantly ionic character would therefore be possible between compounds of the mixture and the oxidized steel surface. Additionally, metal cations in high oxidation state, such as ferric ions dissolved from the steel surface into the electrolyte, are hard Lewis bases, so that formation of protective deposits of hardly soluble complexes and/or chelates of ferric ions with anionic organic ligands is possible.⁸

Components of the inhibitor mixture investigated in the present study were chosen after careful consideration of their environmental friendliness and previously published characteristics relevant to corrosion inhibition. E.g., ethanolic propolis extract applied to mild steel forms a very effective anticorrosion coating in neutral and near neutral aqueous 3.5% w/v NaCl solution.⁹ Propolis was also proven to be effective on copper in neutral chloride solution,¹⁰ but copper is more favourable for adsorption of organic compounds under such conditions.¹ Adsorption of effective propolis layer on steel from the solution is probably hindered by its insufficient concentration due to the limited solubility of propolis in water. Dispersion of propolis in neutral chloride medium produces a yellowish emulsion.⁹ Based on literature data, PEG is used as an alternative solvent for non-ethanolic propolis extraction,¹¹ and when used together with propolis, could beneficially influence propolis dispersibility in a water solution.¹² Furthermore, it has been shown that a compact layer, with barrier effect for the diffusion of oxygen in 0.1 NaCl solution, has been deposited on mild steel from the solutions containing 1000, 2500 and 5000 g ppm of PEG after 30 min of immersion time, showing that PEG itself can act as a corrosion inhibitor.¹³ Formation of the protective ferric “tannate film” deposited from solution of tannin is also possible, and it was shown to begin at pH = 3, but relevant efficiencies are attained only at concentrations ~1000 ppm.¹⁴ Recent investigation of low carbon steel inhibition by 1–5% tannic acid solution in 3.5% NaCl shows that efficiencies up to 51% can be obtained.¹⁵ Concentrations of the same order are needed for efficient steel corrosion inhibition in chloride media by starch¹⁶ and sodium benzoate.¹⁷ In the present study, minimal quantities of individual components that would be effective, based on the above literature references, were chosen for the inhibitor mixture composition.

In general, extra costs are incurred in neutral chloride media because the enhancement of inhibitor effectiveness is frequently attained through the increase in concentration up to a few thousands of ppm.¹⁸ The most explored strategy for lowering inhibitor concentration, while retaining good efficiency is application of synergistic inhibiting mixtures.^{1,18–22} In the present case, different chemical nature of components of the mixture used was

expected to yield a combination of mechanisms of action, which is usually argued to be the basis for synergism.²³

Propolis was chosen as a starting component of the mixture. It is generally accepted that propolis is composed of approximately 50% resin (polyphenolic fraction), 30% wax, 10% essential oils, 5% pollen and 5% other organic and inorganic compounds.⁹ Main propolis phenolic esters and flavonoids are of amphiphilic nature,²⁴ and are expected not only to inhibit corrosion but also to increase the hydrophobicity of steel or corrosion products due to adsorption with the hydrophilic part of the molecule oriented to the surface and the hydrophobic part oriented towards the liquid phase.²⁵ Chestnut tannin extract⁶ was chosen as a second component in order to increase the water-soluble inhibiting fraction of the mixture. Since polyphenols are weak organic acids known to decrease pH of neutral solutions,¹⁴ along with the inhibitive effect of the tannate layer, iron dissolution enhancing effect may be expected.¹⁵ Increased release of iron ions from steel, on the other hand, is favourable for ferric tannate formation. Hence, sodium benzoate¹⁷ has been added to the mixture for controlled iron release, until the protective surface layer is fully formed.

The last two components added to the mixture were polymeric substances, PEG and starch. Besides with the intention of increasing propolis solubility, PEG was added alongside with starch, with the intention of strengthening surface layer through interaction with tannin. Tannins have an abundance of hydroxyl groups in close proximity capable of strong and specific interaction with carbohydrate polymers via hydrogen bonding and hydrophobic interactions.²⁶ When phenolic components and PEG and starch are mixed, the hydroxyl groups of phenolic chemicals can interact with PEG oxygens²⁷ and side chains of starch amylopectin,²⁸ respectively.

In this paper we extend the synergistic approach by hypothesising that a carefully chosen mixture of non-toxic and environmentally benign inhibitive compounds could modify the rust layer on steel. This layer would form in neutral chloride solutions, as to produce a persistent film which would lower corrosion rate considerably. The inherent advantage of the novel mixture would be environmental friendliness as well as the retention and resiliency of the inhibitor modified rust layer even in the inhibitor free solution. High concentration requirement would be counteracted by a long inhibitor free period, following batch application, during which the protective surface film would ensure acceptable corrosion rates.

2. Experimental

2.1. Solutions

Tests were performed on 0.51 M NaCl, obtained by dissolving analytical grade NaCl (Lachner, p.a.) in redistilled water.

Natural propolis (Naturwaren-niederrhein, GmbH, Propolis Pulver) was used at a concentration of 100 ppm in 0.51 M NaCl. 100 mg of propolis was first dissolved in 5 ml of 70% ethanol before preparing 1 dm³ of solution. Chestnut Tannin (Tanin Sevnica) and sodium benzoate (AGZ, food additive) were both used at a concentration of 2000 ppm.

PEG400 (Sigma Aldrich) and corn starch (Sigma Aldrich) were used in concentrations of 200 and 400 ppm, respectively.

The inhibitive mixture of 2000 ppm of tannin (T), 2000 ppm of benzoate (B) and 100 ppm of propolis (P), 200 ppm of PEG400 (PEG) and 400 ppm of starch (S) in 0.51 M NaCl is in further text denoted by abbreviation T+B+P+PEG+S, and the other combinations of single components are denoted accordingly.

All the measurements were done in aerated solutions under ambient conditions.

2. 2. LPR Probe

The measurements of corrosion rate were performed on the LPR (Linear Polarization Resistance) probe manufactured by RCSL with the data collector MS1500L. The corrosion rate was determined by software of the MS1500L instrument.

Corrosion monitoring LPR pins made of C1010 steel had composition declared by the producer (Metal Samples) as: C (0.02–0.08), Mn (0.3–0.6), P (0–0.04), S (0.05) and Fe (bal.).

LPR electrodes were, prior to immersion, treated mechanically by abrasive paper of grit 240, followed by degreasing with ethanol in an ultrasound bath and rinsing in redistilled water. Measurements were made by immersion of the electrodes in the solution of 0.51 M NaCl, as well as in solutions with the chosen concentrations of inhibitors. A protective layer at the electrode surface was formed for 24 h in quiescent solutions. In one experiment, the layer was deposited from the inhibited solution mixed at 80m RPM, in order to rate the influence of solution mixing on layer formation and its protective properties. In the non-inhibited solutions, the rust layer was formed, while in the inhibited solutions, the rust layer modified by the action of corrosion inhibitors was obtained. The layer formed without inhibitor is in the rest of the text referred to as the "rust layer", and the layer formed under the influence of the inhibitors in 0.5 M NaCl or the layer-forming solution, is in the rest of the text referred to as the "inhibitor-modified rust layer". The corrosion rate was measured after the probe was transferred into a fresh 0.51 M NaCl solution and left to stand for 24 h. The LPR measurement was then performed in a quiescent solution as well as in a solution stirred by magnetic stirrer at 90 to 150 RPM. Long-term measurements with the layer formed in the most effective inhibitor mixture as well as the pure rust layer were performed continuously for 10 days. In this way, the persistence

of the protective layer is tested by LPR probe, which was previously found to be particularly suitable technique for that laboratory testing of inhibitor persistence.²⁹

2. 3. Electrochemical Impedance Spectroscopy (EIS)

For EIS, the PalmSens3 device with PC Trace 5.3 software has been used. A cylindrical steel sample made of API X52 5L steel embedded in epoxy resin and having circular cross section exposed to the electrolyte, was used as a working electrode.

Typical chemical composition of commercial grade API 5L used is C (0.26 max.), MN (1.40 max.), Si (0.4 max.), P (0.03 max.), S (0.03 max), Fe (bal.).³⁰

A saturated calomel electrode was used as reference electrode and a graphite electrode was used as an auxiliary electrode. The working electrode surface was 0.2826 cm². Prior to electrochemical testing, the surface of the working electrode was mechanically treated by abrasive paper of various grits, namely: 240, 600 and 800. Subsequently, the surface was degreased in an ultrasonic bath with ethanol and washed with redistilled water.

EIS measurements were performed in quiescent solution, at the open circuit potential, at frequencies from 10 kHz to 1 mHz, with the amplitude of 10 mV. The electrodes on which a protective layer (of rust or inhibitor-modified rust) has been forming for 24 h, as in the experiment with LPR probe, were left to freely corrode for another 24 h in a fresh 0.51 M NaCl solution, in order to simulate a situation 24 h after batch inhibitor treatment. Additionally, EIS measurement has been done in the inhibited solution prior to transfer into the fresh NaCl in order to compare inhibitive effect in inhibitor bearing and inhibitor free solutions.

2. 4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded using a PerkinElmer spectrometer Spectrum One. Spectra were obtained in the range from 400 to 4000 cm⁻¹, each spectrum being an average of ten scans with a resolution of 4 cm⁻¹. Coupons used as substrate were made of previously mentioned API X52 5L material and were cut to size 30 × 40 × 3 mm, polished with abrasive paper of grit 240, 600 and 800 and degreased before exposure to inhibitor mixture solution. Inhibitor-modified rust layer has been formed for 24 hours, identically as for the EIS measurements, and then the coupons were left in 0.51 M NaCl for 10 days. 350 mg of KBr was rubbed onto the surface of steel coupons after ending the experiment and drying of the coupons. Samples bearing KBr were then hydraulically pressed into a 13 mm stainless steel die and the resulting pellets further subjected to FTIR measurement. Preparation of pellets was in conformance with the standard ASTM E1252:2007.

2. 5. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) Analysis

SEM and EDX analysis was recorded using Tescan Vega III, SBU EasyProbe scanning electron microscope with 15 kV accelerating voltage of the electron beam at various magnifications. Measurements were done on surface of the coupons prior to FTIR experiments.

3. Results and Discussion

Cathodic reaction takes place on iron or steel through two possible processes. At lower pH values of the solution, hydrogen evolution is controlled by the rate of charge transfer reaction, and at higher pH of the solution, oxygen reduction is controlled by the rate of oxygen diffusion. Lorbeer and Lorentz,³¹ state pH of 4.2 as critical, above which the dominant cathodic process is oxygen reduction and anodic iron dissolution is inhibited by time-dependent formation of a three-dimensional porous oxide layer on the electrode surface. In the present study, the pH of uninhibited solution was 6, while the pH of inhibited solutions was between 4.6 and 4.7 so the primary conjugate cathodic reaction of metal dissolution was reduction of oxygen. This reaction is known to be under diffusion control and satisfactory degree of corrosion inhibition requires dense blocking of the surface.²³ Oxygen reduction generates OH^- ions which react with the dissolved Fe^{2+} ions yielding $\text{Fe}(\text{OH})_2$ that is considered to be a precursor of other rust forming compounds.¹⁶ Formation of particular rust component depends on pH, temperature and oxygen content. The rust layer partially protects metal surface from dissolution.² It has been found that increasing the immersion time of iron and steel in the solution enables thickening of the corrosion product layer resulting in the decrease of the corrosion rate. The decrease of the weight loss has been observed for carbon steel during the first 10 days of immersion in 3.5% NaCl, followed by a period of 20 days in which the weight lost remained low, while in the following 30 days the weight loss became more noticeable and higher.³ This observation indicates that dissolution of rust itself also occurs under the attack of chloride ions. The experiments in the present study were focused on modification of the rust layer by the inhibitors in order to obtain a persistent protective layer that lowers the corrosion rate to acceptable values.

3. 1. Measurements at the LPR Probe

Figure 1 a) shows LPR corrosion rates on electrodes with the rust layer or with the inhibitor-modified rust layer formed under the influence of various inhibitors and inhibitors mixtures. The rates were measured after 24 h in layer-forming solutions, 24 h after transfer to quiescent

0.51 M NaCl solution and in the same solution at the magnetic stirrer rate of 150 rpm. Except for tannin, single components show <30% inhibitive action both in the inhibitor solutions and quiescent 0.51 M NaCl with a formed layer. As expected,¹⁵ the solution of tannin as a chelating agent significantly increases corrosion rate of steel to 1.6 mmpy, but at the same time forms the most protective modified rust layer suppressing the corrosion rate in 0.51 M NaCl to 0.06 mmpy. Addition of benzoate to tannin solution decreases the corrosion rate to 0.11 mmpy but at the same time hinders the formation of protective tannin modified rust layer, increasing the corrosion rate in 0.51 M NaCl to 0.2 mmpy. Further addition of propolis and PEG decreased the corrosion rates in quiescent 0.51 M NaCl, while the addition of starch decreased the corrosion rate in quiescent and mixed 0.51 M NaCl. For the final inhibitor mixture, all corrosion rates were below 0.1 mmpy.

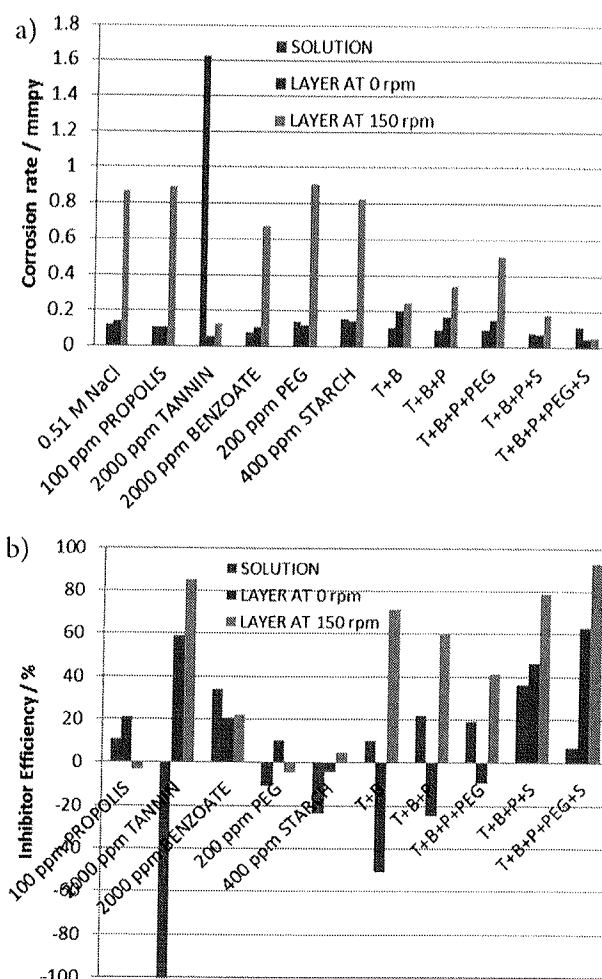


Figure 1. a) corrosion rates and b) the appending inhibitor efficiencies obtained from the LPR measurements after 24h in the layer-forming solution and after subsequent 24h in 0.51 NaCl at 0 and 150 rpm.

Measurements for each system, has been done in triplicate and the expanded measurement uncertainty

equal to $U = (0,051 \times \text{corrosion rate} + 0,005) \text{ mmpy}$ has been calculated from these data.³²

The efficiency of the inhibitor containing solution, or the inhibitor-modified rust surface layer can be calculated by the equation:

$$IE / \% = \frac{CR_0 - CR}{CR_0} \quad (1)$$

where CR_0 denotes corrosion rate for the system without inhibitor or with only the rust layer and CR denotes corrosion rate for the system with the inhibitor or the inhibitor-modified rust layer.

In parallel to the corrosion rates, the inhibitor/layer efficiencies are presented in Figure 1 b). Tannin shows a highly negative efficiency of -1200% when present in the solution, while at the same time forming a protective modified rust layer that shows the efficiency of $\approx 60\%$ in quiescent and $\approx 84\%$ in mixed 0.51 M NaCl . Benzoate counteracts the facilitation of iron dissolution by tannin but decreases the efficiency of the inhibitor-modified layer below the efficiency of the pure rust layer. Addition of propolis, PEG and starch, gradually “repairs” the layer, at the same time still successfully counteracting the iron dissolution by tannin. Although interpretation is complicated by the mixed mechanism of action of various components, by comparison of single inhibitor component action with their mixed effect, it is revealed that starch acts in synergy with T+B+P mixture in the layer-forming solution as well as in quiescent and mixed 0.51 M NaCl . Starch also shows synergy with T+B+P+PEG mixture in quiescent and mixed 0.51 M NaCl .

Figure 2. shows LPR inhibitor efficiencies with the inhibitor-modified rust layer formed under the influence of T+B+P+PEG+S inhibitor mixture, measured in quiescent 0.51 M NaCl solution and in the same solution mixed

at various magnetic stirrer rotation rates. Identical measurements were repeated for 10 days in order to assess inhibitor-modified rust layer persistence.

The increase in the inhibitor efficiency is observed with the increase in magnetic stirrer rotation rate. The increase is most remarkable between the quiescent system and the system with the lowest mixing rate of 80 RPM . This observation may be explained by the increase of oxygen transport to the electrode by stirring causing higher increase in corrosion rate^{33,34} for rust covered electrodes than for the inhibitor-modified rust covered electrodes. However, the inhibitor efficiency levels off with further increase in the electrolyte mixing rate. It is reasonable to assume that as the oxygen supply through mixing completely counteracts the diffusional influence the efficiency becomes almost constant with stirring rate.

The data also show gradual loss of efficiency with time. After 10 days of immersion, with the inhibitor-modified rust layer, the efficiency at 150 rpm is $\approx 70\%$ and the corrosion rate is still below 0.2 mmpy as opposed to inhibitor free system in which the corrosion rate at 150 rpm roughly equals 0.875 mmpy . The concept of improving corrosion resistance of steel by the formation of a surface layer that efficiently blocks corrosive components from surrounding medium, is self-explanatory, and has also previously been proposed in for steel corrosion in hot tap-water.^{35,36}

The brown-orange colour of rust in the system without inhibitor indicates that its main component is lepidocrocite ($\gamma\text{-FeOOH}$).³⁷ On the inhibitor protected electrode, a dark violet layer is visible, proving formation of ferric tannate.¹⁴ Significantly smaller amount of corrosion products is observed in the solution with electrodes having inhibitor-modified rust layer indicating better protection offered by that layer compared to the protection provided by the pure rust layer.

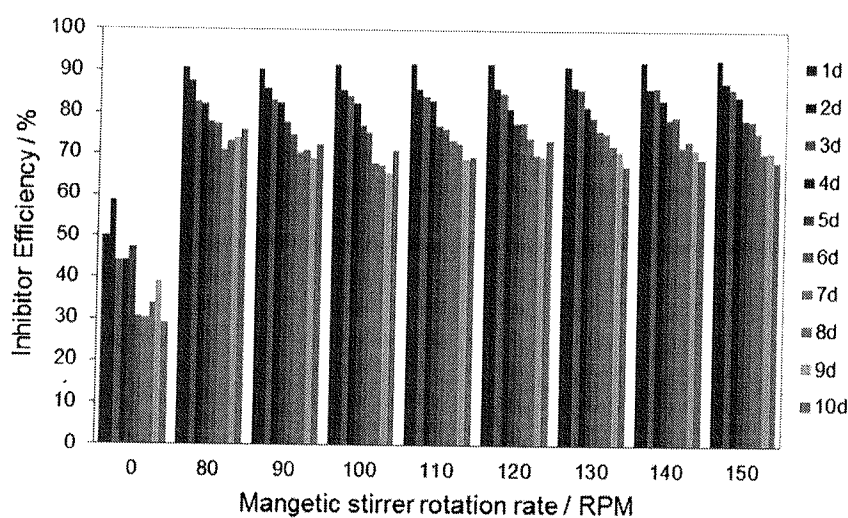


Figure 2. LPR inhibitor efficiencies with the inhibitor-modified rust layer formed under the influence of T+B+P+PEG+S inhibitor mixture, measured in quiescent 0.51 M NaCl solution and in the same solution mixed at various magnetic stirrer rotation rates

3. 2. Electrochemical Impedance Spectroscopy (EIS)

Figure 3 shows the EIS results for the electrodes with layers formed without and with T+B+P+PEG+S inhibitor

mixture. To compare protective effect of the presence of the inhibitors in solution, the measurement was also done in the layer-forming solution immediately before transfer of the electrode with the formed protective layer into fresh 0.51 M NaCl solution. Figure 4 shows the equivalent cir-

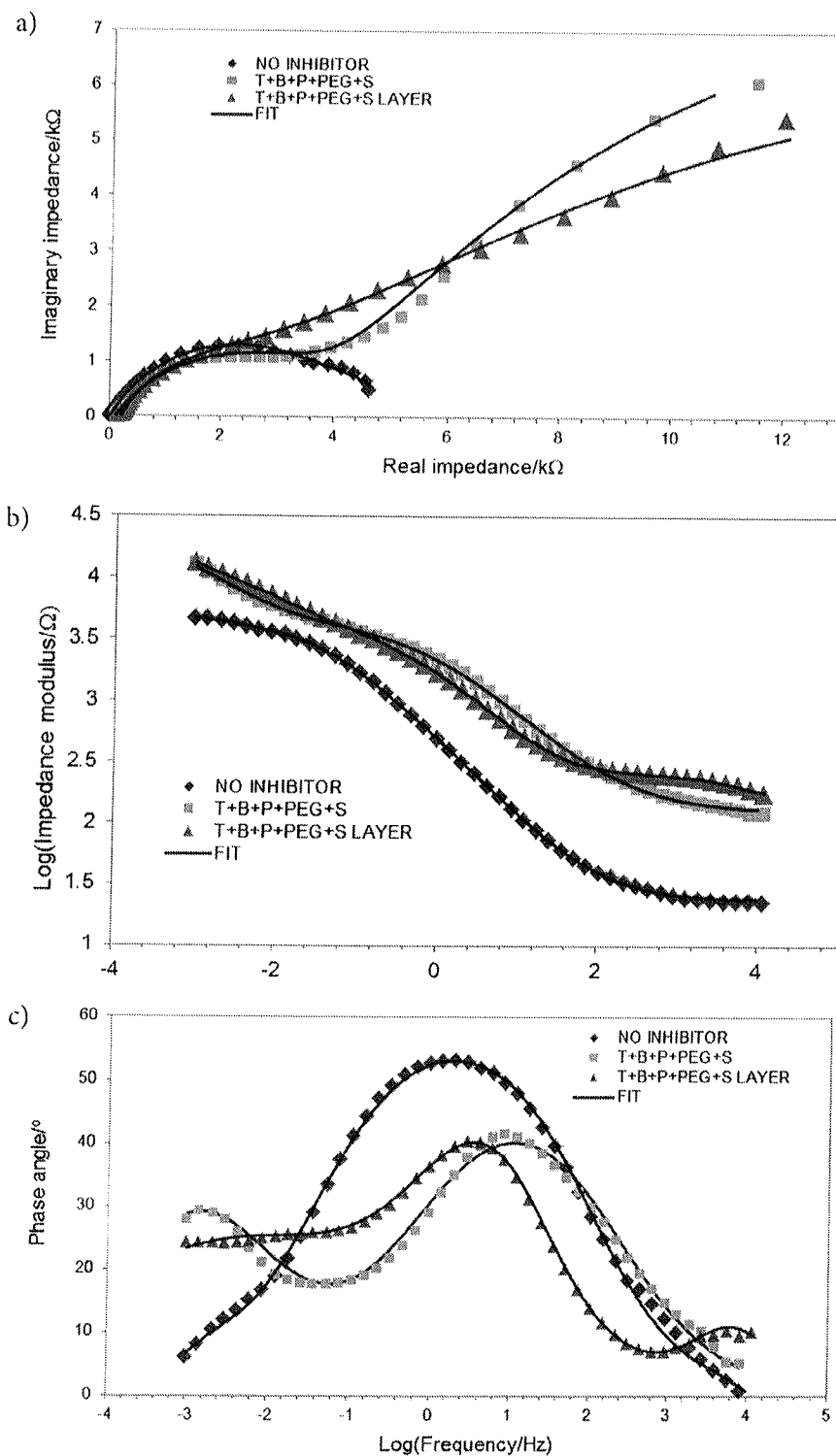
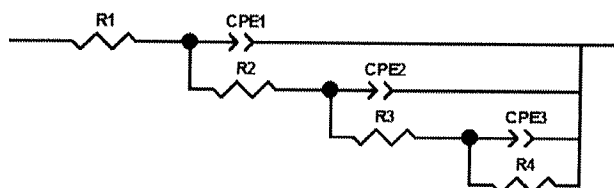


Figure 3. a) Nyquist and b) and c) Bode EIS results on steel electrode after 24 h of immersion in 0.51 M NaCl, in the layer-forming T+B+P+PEG+S solution after 24 h of immersion and after further 24 h of immersion in 0.51 M NaCl with the inhibitor-modified rust layer at the steel surface.

Table 1. Results of EIS data fitting to the equivalent circuit shown in Figure 4.

	R1	C2/ μ F	n1	R2/ Ω	C2/ μ F	n2	R3/ Ω	C3/mF	n3	R4/ Ω	IE _{AVG} /%
NO INHIBITOR	23.5 ± 2.1	–	–	–	951.7 ± 47.5	0.66 ± 0.04	4526 ± 227	145.51 ± 6.59	1 ± 0.00	514 ± 27	–
T+B+P+PEG+S SOLUTION	126.6 ± 2.3	–	–	–	60.9 ± 3.0	0.61 ± 0.04	4197 ± 211	20.57 ± 0.80	0.632 ± 0.03	26333 ± 1358	83.5
T+B+P+PEG+S LAYER	160 ± 5.6	0.345 ± 0.07	0.89 ± 0.05	91.6 ± 7.3	79.6 ± 4.6	0.74 ± 0.05	2268 ± 135	27.69 ± 0.19	0.407 ± 0.03	39370 ± 2134	87.9

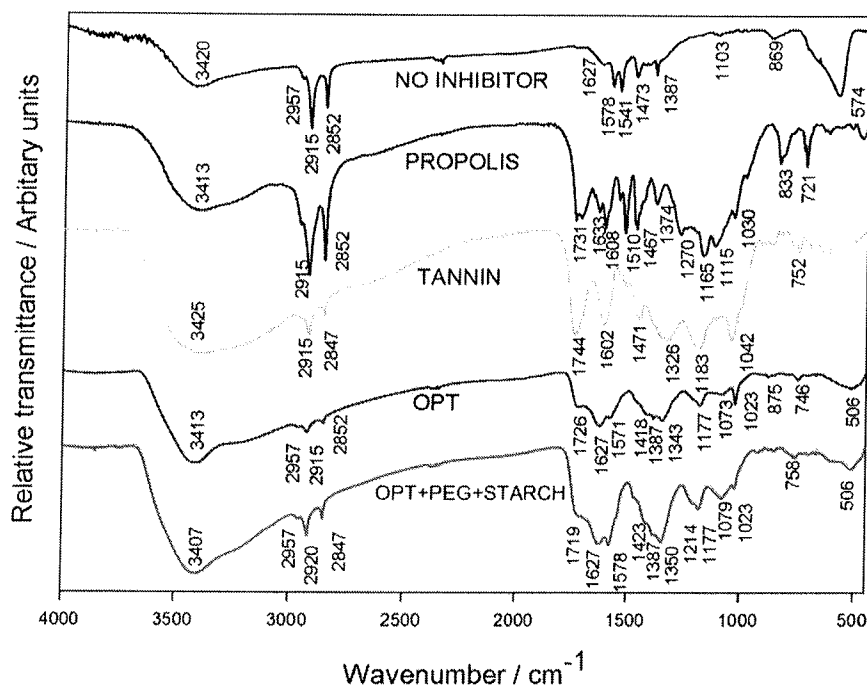
**Figure 4.** Equivalent circuit used for modelling the EIS data.

circuit used for modelling the EIS data. Table 1 shows EIS fitting results. Two parallel nested RC circuits were used to model the EIS spectrum of the electrode with the rust layer and EIS spectrum of the electrode in the inhibitor solution. Three parallel nested RC circuits were used to model the EIS spectrum of the electrode with an inhibitor-modified rust layer.

The efficiency of the rust and inhibitor-modified rust layer can be calculated by the equation:

$$IE/\% = \frac{R - R_0}{R} \quad (2)$$

where R denotes $R_2 + R_3 + R_4$ from Table 1, calculated for the system without inhibitor (R), and system with the inhibitor or the inhibitor-modified rust layer (R_0). High efficiency is obtained irrespective of the inhibitor presence or absence in the solution. High frequency resistance R_1 of the unprotected electrode is probably due to the solution resistance while the R_1 of the protected electrodes may be interpreted as a sum of the solution resistance and resistance due to the partial barrier properties introduced by the surface layers.³⁸ The R_1 resistance is disregarded in the effectiveness calculation due to its value being insignificantly small with respect to the inhibitor-modified rust layer resistance. The inhibitor-modified rust layer protected electrode shows the decrease of n_2 parameter close to

**Figure 5.** FTIR spectra of propolis and tannin and of the layers formed on X52 5L steel electrodes in pure 0.51 M NaCl, T+B+P and T+B+P+PEG+S solution.

0.5, as well as the typical shape of Nyquist plots³⁹ that indicate that the inhibitor-modified rust layer presents a barrier for oxygen diffusion, as previously concluded from LPR measurements.

3. 3. Fourier Infrared Spectroscopy (FTIR)

Figure 5 shows FTIR spectra of propolis and tannin and of the layers formed on steel electrodes in uninhibited, T+B+P and T+B+P+PEG+S solutions. Spectrum of the rust layer from the uninhibited solution indicates a mixture of FeCl₃ (spectrum ID = 8ns2iWUHtq7,⁴⁰), Fe₃O₄ (spectrum ID = 8ns2iWUHtq7,⁴¹) and Fe₂O₃ (Spectrum ID = AVGW5xAY59X,⁴²). In particular, the band at 574 cm⁻¹ corresponds to the Fe-O vibrations of magnetite,⁴³ the bands around 750 and 870 cm⁻¹ show presence of goethite and the bands at 1023 and 1177 cm⁻¹ indicate presence of lepidocrocite. Fingerprint region of FTIR spectra between 400 and 1800 cm⁻¹ of tannin, propolis and T+B+P layer, is similar between the three samples and is also similar to the reference tannin spectrum (Spectrum ID = KPLVhGlArJg,⁴⁴). Dark purple coloration of the electrode surface layer that fully develops over the period of 24 hours, confirms presence of tannin in the form of ferric tannate.¹³ In particular, the band at 1326 cm⁻¹ in tannin spectrum is characteristic of bending vibration of O-C in a phenolic hydroxyl group.⁴⁵ The interaction between ferric ions and the phenolic hydroxyl group shifts the O-C bond stretching vibration to higher wavenumbers, in the present case from to 1343 and 1350 cm⁻¹ in T+B+P and T+B+P+PEG+S layers, respectively. The tannin band at 1744 cm⁻¹ that corresponds to C=O stretching of the polyphenol shifts to shorter wavenumbers,⁴⁵ i.e. 1726 cm⁻¹ in the case of T+B+P layer and to 1719 cm⁻¹ in the case of T+B+P+PEG+S layer. The peaks at 1417 cm⁻¹ and 1423 cm⁻¹, in T+B+P and T+B+P+PEG+S layers, respectively, can be ascribed to the adsorption peak of a polyphenol C=O vibration.⁴⁶

The most remarkable difference in FTIR spectra of rust and inhibitor-modified rust layers is the loss of intensity and shift of magnetite peak at 574 cm⁻¹ of the rust layer to 506 cm⁻¹ in the case of the inhibitor-modified rust layer, probably due to the conversion process to ferric tannate.⁴⁵ FTIR spectra show a dominant role of flavonoid species, present both in tannin and propolis, on the formation of the inhibitor-modified rust layer.

3. 4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis

Before the electron microscope scanning, the loosely held part of the layer has been blown off in the nitrogen gas stream so that only the firmly held parts of the layer remained. Figures 6 a), c) and e) show the surface of metal with the rust layer and Figures 6 b) and d) and f) with the inhibitor-modified rust layer from T+B+P+PEG+S solution.

EDX results for measurement positions #1 to #9 are shown in Table 2.

Oxygen and carbon in the rust layer, found in excess with respect to the substrate, probably originate from surface oxides and carbonates that may form in neutral solutions in contact with the air.⁴⁷ Fine grained structure observed in both cases is also probably due to surface oxides and carbonates. The inhibitor-modified rust layer is significantly denser and uniform in micrograph shown in Figure 6 b) than the rust layer shown in Figure 6 a). Corrosion defects in the form of shallow pits are visible only in the case of the rust layer. The morphology of the tannate layer is close to the one recently reported for tannic acid on Q235 carbon steel in 3.5% NaCl.¹⁵ Similarly, due to inhibitor presence, the carbon content of the layer is much higher in the inhibitor-modified rust layer at locations #2, #4, #5 and #8 (16–25 %wt) than in the rust layer at locations #1, #3 and #7 (<6 %wt). Low carbon content is also observed at the location of the crack in the inhibitor layer protruding to the metal surface at position #6, and in the area of the damaged layer where the substrate is clearly visible at position #9.

4. Conclusion

Rust layer obtained by exposing steel surface to 0.51 M NaCl solution containing a mixture of non-toxic, environmentally friendly compounds (propolis, tannin, benzoate, PEG400 and starch) has shown better protective characteristics than the rust layer formed in the inhibitor free solution. From LPR probe measurements in quiescent and mixed solution and from the values of EIS parameters in quiescent solution, it may be concluded that the inhibitor-modified rust layer primarily presents a barrier for oxygen diffusion. A synergy effect has been demonstrated for

Table 2. EDX elemental analysis results in %wt for measurement positions in Figure 6.

Element	#1	#2	#3	#4	#5	#6	#7	#8	#9
Fe	68.7	46.9	57.4	40.6	40.4	66.5	79.0	41.7	66.5
O	25.9	31.7	34.8	29.1	33.2	26.2	19.2	27.8	26.2
C	4.2	16.5	4.6	25.9	21.4	5.6	1.8	25.7	5.6
Na	1.2	3.6	3.2	3.9	3.1	1.7	–	4.8	1.7
Cl	–	1.3	–	0.5	1.8	–	–	–	–

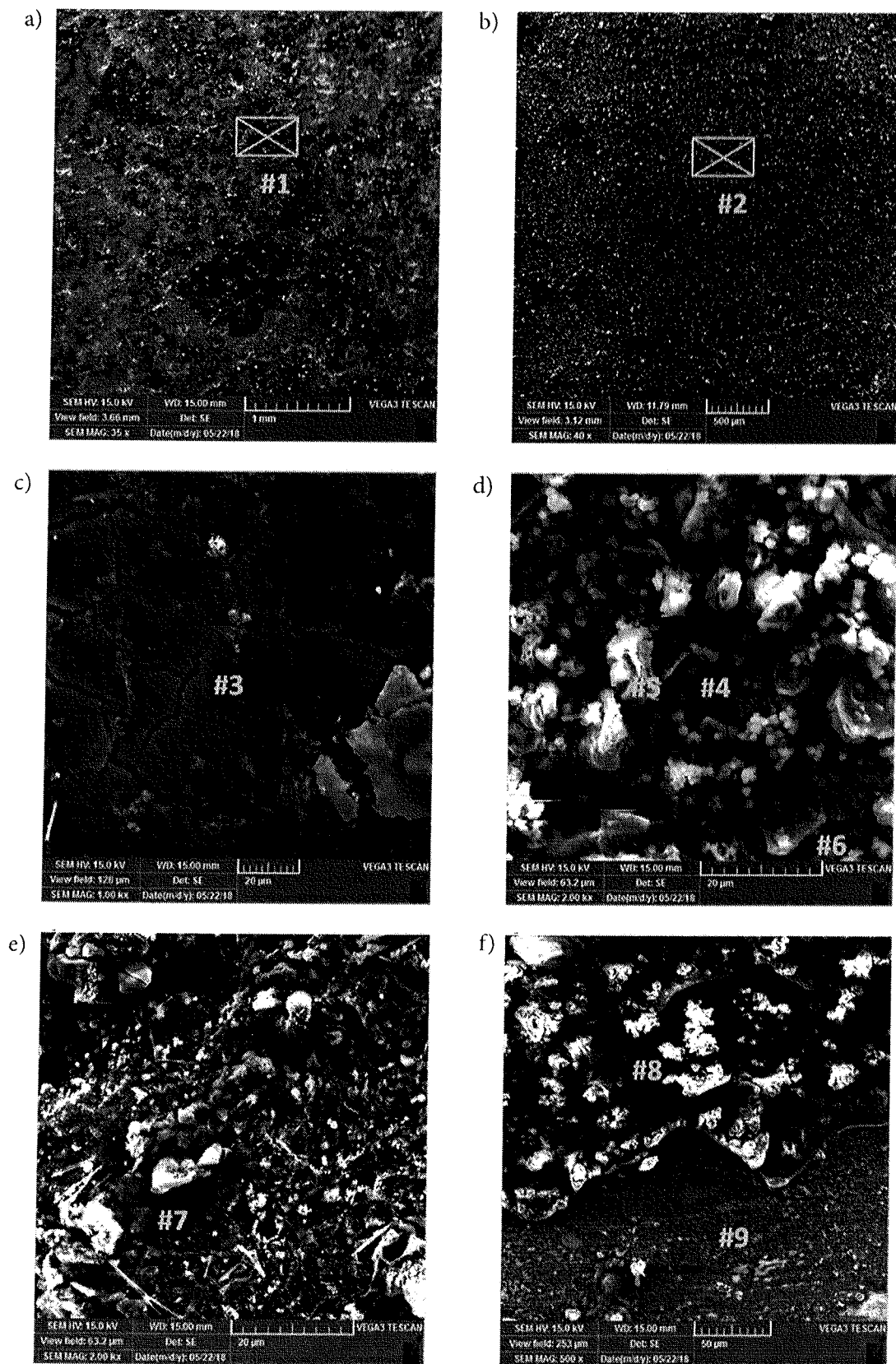


Figure 6. Surface of metal with the rust layer a) magnified 35 \times , c) magnified 1000 \times and e) magnified 2000 \times , and with the inhibitor-modified rust layer from T+B+P+PEG+S solution, b) magnified 40 \times , d) magnified 2000 \times and f) magnified 500 \times .

starch as the mixture component, from LPR data. The inhibitor-modified rust layer shows persistence in a mixed solution. The efficiency of inhibitor-modified rust layer measured by LPR after 24 h of exposure to 0.51 M NaCl is the lowest in quiescent solution 75% and the highest, equalling 95% in mixed solution. Visual observation and FTIR data confirm the formation of ferric tannate in the inhibitor-modified rust layer while the SEM/EDX data show increased carbon content of the inhibitor-modified rust layer having a fine grain structure that is more uniform and denser than the one of the rust layer.

The persistence of the inhibitor-modified rust layer is of great technological interest as it allows batch application, increases flow corrosion resistance and offers prolonged protection at acceptable corrosion rates. The suggested concept of attaining these beneficial effects through rust modification by inhibitors of various action mechanisms is not fully exploited in scientific reports and is worthy of further investigation.

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Povzetek

Vseprisotna uporaba navadnih in nizko legiranih jekel v nevtralnih okoljih s kloridnimi anioni predstavlja vsakodnevni izziv strokovnjakom za zaščito pred korozijo. V prispevku preučujemo možnosti razvoja netoksične in okolju prijazne sinergijske mešanice inhibitorjev iz propolisa, tanina, natrijevega benzoata, PEG400 in škroba, ki jih lahko uporabimo v raztopini, z namenom nanosa trajnega zaščitnega sloja na jeklu. Sestavine zmesi so bile izbrane na podlagi njihovih lastnosti, ki so pomembne za njihovo možno delovanje v raztopini in/ali na površini jekla. Učinkovitost zaščitne plasti, ki je nastala pod vplivom zmesi inhibitorja in nato izmerjena z meritvami linearne polarizacijske upornosti (LPR) v raztopini brez inhibitorja, je bila najnižja v primeru konstantnih pogojev (75 %) in najvišja (95 %) pri pretočnih pogojih. Podatki LPR in elektrokemijske impedančne spektroskopije (EIS) kažejo, da modificirana plast inhibitorja predstavlja bariero za difuzijo kisika, ki deluje kot depolarizator primarne korozijske reakcije v preučevani nevtralni raztopini klorida. Dokazana obstojnost inhibitorško modificiranega sloja ima velik pomen, saj omogoča uporabo tudi v industrijskem merilu.