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WATERBORNE COATINGS FOR THE PROTECTION OF BRONZE CULTURAL HERITAGE

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Objects of tangible cultural heritage, such as sculptures, are often made of bronze and located outdoors where they are directly exposed to the corrosive effect of precipitation, humidity, sunlight, temperature and airborne contaminants. To protect them organic coatings, varnishes and waxes are used that meet the requirements of the conservation profession. However, in recent decades, legislations were enacted in order to restrict the use of coatings with high content of volatile organic compounds due to their toxicity and negative impact on the environment and human health. For this reason, efforts are being made in all branches of industry to replace solventborne with waterborne coatings, in which the content of organic solvents is reduced and replaced by water. However, waterborne coatings still offer weaker protection than solventborne coatings under similar conditions and there are several approaches to improve their performance.

The aim of this thesis was to investigate the applicability of industrial waterborne coatings for corrosion protection of bare and patinated bronze surfaces and the possibility of enhancement of their corrosion protection efficiency and adhesion by surface pre-treatment with long-chain phosphonic acids.

Sculptures made of bronze are artificially patinated before protective coating application and exposure to the outdoor environment. This artificially formed patina is very reactive, so it was necessary to study its behavior before applying the protection. Artificial sulphide patina was formed on various bronze substrates (CuSn12, CuSn6, RG7) used in the production of bronze sculptures. The corrosion behaviour of the patina was investigated by electrochemical methods, in different corrosive environments: artificial urban and acid rain as well as in NO_2 rich atmosphere, with alternating wet and dry cycles. The morphology and composition of the samples were analyzed using microscopic (SEM) and spectroscopic (FTIR) techniques. It was found that the patina undergoes transformation when exposed to a corrosive medium, increasing

its resistance and corrosion stability. This entire process depended significantly on duration of wet period and corrosivity of medium, while the bronze substrate composition was less important factor.

Since waterborne coatings contain water, which is less volatile than organic solvents, it was necessary to study the influence of temperature and duration of the drying process on coating final properties. In the first step, conducting tests with an industrial coating, containing a corrosion inhibitor, enabled the selection of suitable coating application parameters. Then, additional waterborne coating was selected, which does not contain corrosion inhibitor, and both coatings were applied on differently patinated bronze substrates, as well as on bare bronzes. Although both coatings proved to be effective, the coating containing corrosion inhibitor showed slightly higher level of corrosion protection and was selected for further studies. It is important to emphasize that this coating does not change the visual appearance of the surface either during application or after exposure to a corrosive environment, as required by conservation ethics.

In the next step, the possibility of improvement of waterborne coating corrosion protection and adhesion on bare and patinated bronzes was examined. For this purpose surface pre-treatment with long-chain phosphonic acid was applied. The level of corrosion protection of bare and artificially patinated bronze was tested by electrochemical measurements (polarization measurements and electrochemical impedance spectroscopy) under conditions of simulated acid rain (pH 5) or NO_2 atmosphere. The adhesion of the coating to the metal substrate was tested using the pull-off method. It was found that 12-amino dodecyl phosphonic acid, when applied on bronze by immersion in ethanolic solution, can act as a corrosion inhibitor, as well as a coating adhesion promoter.

The research was extended to two other phosphonic acids that differ in chain length and terminal group. Furthermore, all three acids were applied by the brush method in addition to the immersion, which would be more suitable in the practice of cultural heritage. It has been shown that certain improvements can be achieved with both methods, which are more pronounced on a bare surface than on a patinated surface, which is quite porous and reactive. The arrangement of the phosphonic acid films was analyzed by goniometry and the correlation between phosphonic film crystallinity and its effect on coating properties was observed.

In summary, it has been shown that industrial waterborne acrylic coatings can effectively protect bare and patinated bronzes, even if the level of protection does not reach the level of similar solventborne coatings. It has been shown that pre-treatment with appropriate phosphonic acid can improve the protective properties and adhesion of such coating.

Keywords: adhesion, corrosion protection, long-chain phosphonic acids, patina, self-assembled monolayers, waterborne coating

FAKULTET KEMIJSKOG INŽENJERSTVA I TEHNOLOGIJE
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VODORAZRJEDIVI PREMAZI ZA ZAŠTITU BRONČANE KULTURNE BAŠTINE

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Objekti materijalne kulturne baštine, poput skulptura, često su izrađeni od bronce i nalaze se na otvorenom gdje su izravno izloženi korozivnom djelovanju oborina, vlage, sunčeve svjetlosti, temperature i zagađivača iz zraka. Za njihovu zaštitu koriste se organski premazi, lakovi i voskovi koji zadovoljavaju zahtjeve konzervatorske struke. Posljednjih desetljeća doneseni su zakoni kojima se ograničila uporaba premaza s visokim udjelom hlapivih organskih spojeva zbog njihove toksičnosti i negativnog utjecaja na okoliš i zdravlje ljudi. Zbog toga se u svim granama industrije premazi na bazi otapala nastoje zamijeniti premazima na bazi vode u kojima je sadržaj organskih otapala smanjen i zamijenjen vodom. Međutim, premazi na bazi vode i dalje pružaju slabiju zaštitu od premaza na bazi otapala pod sličnim uvjetima te postoji nekoliko pristupa za poboljšanje njihove učinkovitosti.

Cilj ovog doktorskog rada bio je istražiti primjenjivost industrijskih vodorazrjedivih premaza u svrhe korozijske zaštite čistih i patiniranih brončanih površina te mogućnost unaprjeđenja učinkovitosti njihove zaštite i adhezije površinskom predobradom dugolančanim fosfonskim kiselinama.

Skulpture izrađene od bronce umjetno se patiniraju prije nanošenja zaštitnog premaza i izlaganja vanjskom okolišu. Ova umjetno stvorena patina je vrlo reaktivna te je bilo potrebno proučiti njeno ponašanje prije nanošenja zaštite. Umjetna sulfidna patina formirana je na različitim brončanim podlogama (CuSn12, CuSn6, RG7) koje se koriste u izradi brončanih skulptura. Korozivno ponašanje patine istraženo je elektrokemijskim metodama u različitim korozivnim okolišima: umjetna urbana i kisela kiša, kao i u atmosferi bogatoj NO_2 s izmjeničnim vlažnim i suhim ciklusima. Morfologija i sastav uzoraka analizirani su mikroskopskom (SEM) i spektroskopskom (FTIR) tehnikom. Utvrđeno je da se patina transformira kada je izložena korozivnom mediju gdje dolazi do porasta njene otpornosti i korozijske stabilnosti. Cijeli ovaj

proces značajno je ovisio o trajanju vlažnog razdoblja i korozivnosti medija dok je sastav brončane podloge bio manje bitan faktor.

Budući da vodorazrjedivi premazi sadrže vodu, koja je manje hlapiva od organskih otapala, bilo je potrebno istražiti utjecaj temperature i trajanja procesa sušenja na konačna svojstva premaza. U prvom koraku provođenje testova s industrijskim premazom, koji sadrži inhibitor korozije, omogućilo je odabir odgovarajućih parametara nanošenja premaza. Zatim je odabran dodatni vodorazrjedivi premaz koji ne sadrži inhibitor korozije te su oba premaza nanesena na različito patinirane brončane podloge kao i na gole bronce. Iako su se oba premaza pokazala učinkovitima, premaz koji je sadržavao inhibitor korozije pokazao je nešto višu razinu korozijske zaštite te je odabran za daljnja istraživanja. Važno je naglasiti da ovaj premaz ne mijenja vizualni izgled površine niti tijekom nanošenja niti nakon izlaganja korozivnoj okolini što je u skladu s konzervatorskom etikom.

U sljedećem koraku ispitana je mogućnost poboljšanja korozijske zaštite i adhezije vodorazrjedivog premaza na čistoj i patiniranoj bronci. U tu svrhu primijenjena je predobrada površine dugolančanom fosfonskom kiselinom. Razina antikorozivne zaštite čiste i umjetno patinirane bronce ispitana je elektrokemijskim mjerenjima (polarizacijska mjerenja i elektrokemijska impedancijska spektroskopija) u uvjetima simulirane kisele kiše (pH 5) ili atmosfere NO_2. Adhezija premaza na metalnu podlogu ispitana je pull-off testom. Utvrđeno je da 12-aminododecilfosfonska kiselina, kada se nanese na broncu uranjanjem u etanolnu otopinu, može djelovati kao inhibitor korozije te kao promotor adhezije premaza.

Istraživanje je prošireno na dvije druge fosfonske kiseline koje se razlikuju po duljini lanca i terminalnoj skupini. Nadalje, sve tri kiseline su uz metodu uranjanja nanesene i metodom kista koja bi bila prikladnija u praksi za kulturnu baštinu. Pokazalo se da se objema metodama mogu postići određena poboljšanja koja su izraženija na čistoj nego na patiniranoj površini budući da je ona dosta porozna i reaktivna. Uređenost filmova fosfonske kiseline analizirana je goniometrijom te je proučavana korelacija između kristalnosti filma fosfonske kiseline i njezinog učinka na svojstva premaza.

U konačnici, pokazalo se da industrijski, vodorazrjedivi akrilni premazi mogu učinkovito zaštititi čistu i patiniranu broncu čak i ako razina zaštite ne doseže razinu zaštite sličnih organski

premaza. Pokazalo se da prethodna obrada odgovarajućom fosfonskom kiselinom može poboljšati zaštitna svojstva i adheziju takvog premaza.

Ključne riječi: adhezija, korozijska zaštita, dugolančane fosfonske kiseline, patina, samoorganizirajući monoslojevi, vodorazrjedivi premaz