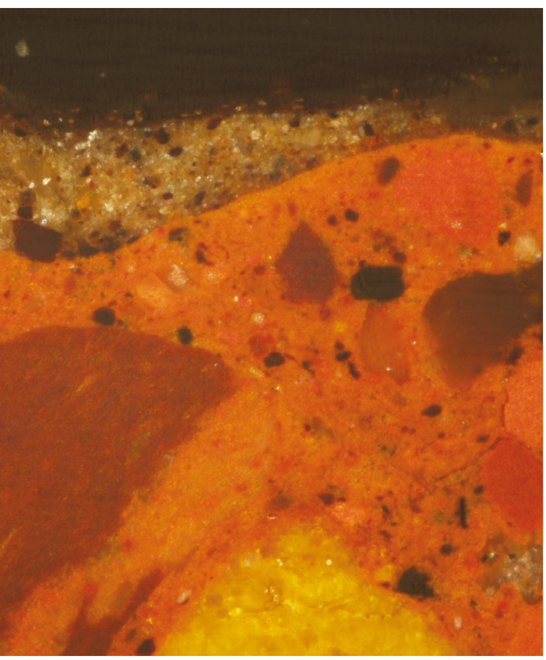
Znanost za Umetnost
Science in Art

Konservatorstvo in restavratorstvo danes
Conservation and Restoration Today



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Institute for the Protection of Cultural Heritage of Slovenia
Center za konservatorstvo
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CIP - Katažni zapis o publikaciji
Narodna in univerzitetna knjižnica, Ljubljana

7.025.3"21"(082)(0.034.2)
7.025.4"20"(082)(0.034.2)

ZNANOST za umetnost : konservatorstvo in restavratorstvo danes : zbornik prispevkov mednarodnega simpozija = Science in art : conservation and restoration today : international symposium proceedings / [znanstvena besedila Marin Berovič ... [et al.] ; glavni urednici Tamara Trček Pečak, Nada Madžarac ; prevodi iz angleščine v slovenščino Breda Misja ... [et al.], prevodi spremnih besedil Tamara Soban]. - Ljubljana : Zavod za varstvo kulturne dediščine, 2013

ISBN 978-961-6902-59-5
1. Vzp. stv. nasl. 2. Berovič, Marin 3. Trček Pečak, Tamara
270068992

Zavod za varstvo
kulturne dediščine Slovenije
Institute for the Protection of
Cultural Heritage of Slovenia
Center za konservatorstvo
Conservation Centre
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Znanstvena besedila | Scientific texts
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Tuji avtorji so znanstvena besedila posredovali v angleščini, slovenska avtorja pa v obeh jezikih.
All scientific texts were written in English; the Slovenian authors also provided their texts in Slovenian.

Prevodi iz angleščine v slovenščino | Translations into Slovenian
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Prevodi spremnih besedil | Translations of introductory texts
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Lektoriranje slovenskih besedil | Slovenian language editing
Vlado Motnikar

Lektoriranje angleških besedil | English language editing
Jo Kirby

Uredniške korekture pred tiskom | Editorial revise before printing
Mateja Neža Sitar

Grafično oblikovanje (2011/2012) | Graphic Design (2011/2012)
Jelena Kauzlarić

Izdal | Published by
Zavod za varstvo kulturne dediščine
Institute for the Protection of Cultural Heritage of Slovenia

Zanj | Publishing Executive
dr. Jelka Pirkovič,
generalna direktorica | Director general

Ljubljana 2013

Mednarodni simpozij | International symposium
Znanost za umetnost
Science in Art

Konservatorstvo in restavratorstvo danes
Conservation and Restoration Today

Narodna galerija, Ljubljana, 16.–17. februar 2005
National Gallery of Slovenia, 16–17 February 2005

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Soorganizatorji | Co-organizers
Restavratorski center ZVKDS; Restoration Center of the Institute for the Protection of Cultural Heritage of Slovenia;
Narodna galerija, Ljubljana; National Gallery of Slovenia;
Moderna galerija, Ljubljana; Museum of Modern Art, Ljubljana.

Za pomoč se zahvaljujemo | Special thanks to
Ivo Nemec, Tanja Pak, Breda Pečak, Polonca Ropret

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MODERNA GALERIJA LJUBLJANA

JO KIRBY

NADA MADŽARAC

TAMARA TRČEK PEČAK

CHRISTOPHER HOLDEN,
ROY PERRY

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Znanost za Umetnost
Science in Art

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Zbornik prispevkov mednarodnega simpozija
International Symposium Proceedings

Simpozij in izid zbornika so omogočili:
The symposium and the publication of the proceedings were supported by the following institutions:

Zahvala
Special thanks

Ministrstvo za kulturo Republike Slovenije
Ministry of Culture of the Republic of Slovenia

ZVKDS, Center za konservatorstvo, Restavratorski center
Restoration Centre, Conservation Centre of the Institute for the Protection of Cultural Heritage of Slovenia

Narodna galerija, Ljubljana
National Gallery of Slovenia

Moderna galerija, Ljubljana
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Akademija za likovno umetnost in oblikovanje, Univerza v Ljubljani
The Academy of Fine Arts and Design of the University of Ljubljana

ADRIA AIRWAYS

LEK, d. d.

JO KIRBY

Narodna galerija, Moderna galerija in Restavratorski center ZVKDS so februarja 2005 skupaj organizirali mednarodni simpozij *Znanost za umetnost – Konservatorstvo in restavratorstvo danes*. Simpozij je sovpadel z razstavo del Hansa Georga Geigerja (Mojstra HGG), umetnika iz sedemnajstega stoletja, v Narodni galeriji v Ljubljani. Nekatere slike so bile zanemarjene in poškodovane, posebno žuželke in vlaga so povzročile strukturno nestabilnost in luščenje barve. Ko so slike prispele v Narodno galerijo, jih je bilo treba najprej konservatorsko obdelati in restavrirati, preden so jih lahko razstavili v sijoči podobi, v kakršni jih občinstvo lahko občuduje vse odtlej.

Pred posegi je bilo treba dela najprej nadvse temeljito pregledati in proučiti. Izkušen restavrator ob pogledu na umetnino vidi veliko več kot povprečen obiskovalec galerije, še več pa lahko ugotovi, če so mu na voljo določeni pripomočki. Stanje in strukturo slik Mojstra HGG so proučili z rentgensko radiografijo, ki je med drugim pokazala spremembe, do katerih je morda prišlo med postopkom slikanja. Za dokumentiranje videza del pred in med posegi ter po njih je bila bistvena fotografija, preiskave z ultravijolično svetlobo pa so pokazale, kako obsežna so bila predhodna restavriranja. Preiskava prečnega prereza zelo majhnega vzorca barve je pokazala strukturo barvne plasti, to je, kako je umetnik izdelal sliko in katere materiale je uporabil.

Vsi ti postopki so dobro znani. Obstajajo pa tudi drugi načini bolj poglobljenega proučevanja struktur, ki bi lahko bili – in tudi že so – koristni za konservatorje in restavratorje, čeprav so težje razumljivi. Kadar so podatki predstavljeni kot spekter, kromatogram ali kvantitativna ocena elementov v barvi z določenega območja, jih lahko nemudoma razbere le tisti, ki je analizo s tovrstno opremo opravil. Kako naj torej restavrator

Predgovor
Foreword

The international symposium *Science In Art – Conservation and Restoration Today*, organised jointly by the Narodna galerija/ National Gallery of Slovenia, the Moderna galerija/ Museum of Modern Art, and the Restavratorski center RS/ Restoration Centre of the Republic of Slovenia in February 2005, coincided with an exhibition of works by the seventeenth-century artist, Hans Georg Geiger (the Master HGG), held in the National Gallery of Slovenia, Ljubljana. Some of the paintings had suffered from neglect; insect damage and damp had taken their toll, causing structural instability and flaking paint. When they arrived in the National Gallery of Slovenia, they required conservation treatment and restoration before they could be put on display in the splendid condition in which the public have been able to admire them, both during the exhibition and subsequently.

Before this could be done, the works had to be examined and studied in depth. The experienced restorer sees a great deal more than the average gallery visitor when looking at a work of art, but even more can be observed when the restorer is assisted by certain aids. Thus, the condition and structure of the Master HGG's paintings were studied by X-radiography; this reveals, for example, changes that may have been made during the painting process. Photography was essential for documenting the appearance of the work before, during and after its treatment; examination by ultraviolet illumination revealed the extent of previous restorations. The examination of a cross-section prepared from a minute sample of the paint revealed its layer structure: that is, how the artist constructed his painting and what materials he used.

These are familiar techniques. There are, however, methods of looking into the structure in greater depth which could be – and are – valuable to the conservator or restorer, but not so easy to understand. Information presented in the form of a izkoristi take podatke ali pa sploh ve, da so na voljo? Številni učinkoviti postopki, ki se pogosto uporabljajo pri preiskavah umetnin – na primer energetska razpršitvena mikroanaliza z rentgenskimi žarki v vrstičnem elektronskem mikroskopu (SEM–EDX) in plinska kromatografija – masna spektroskopija –, niso dostopni vsem muzejem in galerijam. Zato je bistveno, da znajo tako pridobljene podatke pravilno interpretirati in da jih razumejo in uspešno uporabljajo ne le konservatorji in restavratorji, ampak tudi umetnostni zgodovinarji in vsi drugi, ki se ukvarjajo z umetnino, njeno zgodovino, njenim stanjem in razstavljanjem. Dodatna prednost je, če ima konservator-restavrator (ali umetnostni zgodovinar) vse potrebno znanje, da lahko postavlja prava vprašanja.

V tej knjigi so natisnjene razprave s simpozija, ki izpolnjujejo več nalog. Bralcem predstavljajo številne preiskovalne metode, ki se navadno uporabljajo pri iskanju odgovorov, ki (si) jih zastavljajo restavratorji in umetnostni zgodovinarji pa tudi sami znanstveniki o tako raznolikih temah, kot so spremembe barve, škoda, ki nastane zaradi metabolizma gliv, ali kako je Rafael izdelal in narisal predrisbo na svojih slikah. Ponazarjajo konkretne primere iz konservatorske in restavratorske prakse. Prikazujejo praktične primere uporabe elegantnih in učinkovitih metod odstranjevanja površinskih plasti in preslikav z encimi in kronskimi etri. In kar je najpomembneje, pokažejo, da je za varno in učinkovito uporabo teh metod nujno, da jih skrbno spremljamo in nadziramo. Implikacije vsega tega so za konservatorje in restavratorje resne, saj mnogi restavratorji nimajo dostopa do znanstvenikov in opreme, ki so potrebni za izvajanje takega nadzora.

Udeležba na konferenci je bila številna, zastavljenih je bilo veliko vprašanj in razprave so bile živahne. Vse to je pokazalo – če je bil dokaz sploh potreben –, da se pri proučevanju umetnin in skrbi zanje v vseh institucijah srečujemo z enakimi težavami in si zastavljamo enaka vprašanja. Počaščena sem bila ob vabilu na ta stimulativni in pomembni dogodek in z veseljem sem sodelovala pri razlaganju tega, kako slike nastajajo in se lahko s časom spreminjajo. Najprisrčnejša hvala Tamari Trček Pečak in Nadi Madžarac ter vsem, ki so pomagali pri organizaciji simpozija in na njem predstavili svoje delo. ■

spectrum, a chromatogram, or a quantitative assessment of the elements present in paint from a particular area, is immediately comprehensible only to the analyst working with that equipment. How, then, is the restorer to use this information, or even to know that it is available? Many powerful techniques often used for the examination of works of art – energy dispersive X-ray microanalysis in the scanning electron microscope (SEM–EDX) and gas chromatography coupled with mass spectrometry (GC–MS) are two examples – are not available to every museum and gallery. It is thus essential that the information provided by these techniques is interpreted in such a way that it can be understood and used effectively, not only by conservators and restorers, but also by art historians and all those concerned with the work of art, its history, its condition and its display. This has the added bonus that the restorer (or the art historian) then has sufficient information to be able to ask the right question in the future.

The papers presented at the symposium and published in this book are intended to fulfil several functions. They introduce the reader to a variety of methods of examination commonly used to answer questions posed by restorers and art historians, and by scientists themselves, on topics as varied as colour change, damage caused by fungal metabolites and how Raphael constructed and drew the initial design for his paintings. They illustrate practical examples of conservation and restoration. They demonstrate the use of elegant but powerful methods for the removal of surface coatings and overpaint with enzymes and crown ethers, in practice. Most importantly, they show that the safe and effective use of these methods requires monitoring during the treatment. This has serious implications for conservators and restorers, as many restorers do not have access to the scientist and the equipment for this monitoring to be done.

The high attendance at the conference, the questions raised, the lively discussion, all demonstrated – if any demonstration was needed – that the problems encountered and the questions raised by those studying and caring for works of art are the same in every institution. I was delighted and honoured to be invited to attend this stimulating and important event and to be able to assist in the process of explanation of how paintings are made and how they may change over time. Tamara Trček Pečak and Nada Madžarac and all those who helped to organise the symposium and presented their work deserve our warmest thanks. ■

NADA
MADŽARAC

Mednarodni simpozij z naslovom *Znanost za umetnost, Konservatorstvo in restavratorstvo danes* je potekal februarja 2005 v prostorih Narodne galerije. Zajel je večplastne konservatorsko-restavratorske probleme, s katerimi se soočamo strokovnjaki v muzejih, galerijah ter zavodih in centrih, ki se ukvarjajo s kulturno in še posebej likovno dediščino. To je bila priložnost za neposredno soočanje izkušenj in dosežkov domače in tuje stroke.

Uresničitev mednarodnega simpozija pomeni plod dolgotrajnejših priprav. Zamisel zanj je dozorevala v pogovorih med kolegi, ko smo ocenjevali problematiko v slovenskih muzejih in galerijah. Ugotavljali smo, da so številni problemi pogosto tudi rezultat naše slabe povezanosti.

Tokrat smo se torej zbrali konservatorji–restavratorji, kemiki, umetnostni zgodovinarji, kustosi, dokumentalisti, tehnologi ... Vsak od nas namreč ob svojem ožjem področju posega tudi v širši interdisciplinarni prostor in le soočanje sorodnih spoznanj in izkušenj nas lahko privede do optimalnih rezultatov.

Prvi dan smo predstavili Projekt HGG, ki je bil zaradi manjšega opusa umetnin lahko že od vsega začetka vzorčen primer interdisciplinarnega sodelovanja. Predstavitev je bila nekakšen

Uvod
Introduction

The international symposium *Science In Art – Conservation and Restoration Today* took place in February 2005, at the Narodna galerija in Ljubljana, Slovenia. It presented some of the many and varied issues of conservation and restoration that professionals encounter in art museums, galleries and other institutions and centres involved in preserving cultural heritage, art works in particular. The symposium provided Slovene and foreign experts with an opportunity to exchange experiences and observations directly.

The realisation of this international event was the result of lengthy preparations. The idea evolved slowly from conversations between colleagues about the unfavourable state of affairs in Slovene museums and galleries, which is also, to a certain extent, a consequence of insufficient communication among ourselves.

The symposium brought together conservators-restorers, chemists, art historians, curators, archivists, technologists, and others. In our line of work we all need to be familiar with the broader interdisciplinary sphere, rather than just our own narrow fields of expertise, and it is only by presenting related observations and findings together that we can achieve optimum results.

kolaž krajših prispevkov vseh strokovnjakov, ki so pri tem projektu sodelovali. Prispevki so bili v širši obliki objavljeni že v publikacijah ob sočasni razstavi *Mojster HGG – slikar plastične monumentalnosti*.

Drugi dan je bil namenjen temu, da so se naši strokovnjaki, ki zaradi pomanjkanja sredstev vse težje zaidejo na simpozije v tujino, lahko kar pri nas srečali z vodilnimi strokovnjaki s področja konservatorstva in restavratorstva. Tokrat so se nam pridružili strokovnjaki iz Anglije, Nemčije, Hrvaške in Slovenije: Christopher Holden, Tate Britain, London, Velika Britanija; Rachel Billinge, National gallery, London, Velika Britanija, Jo Kirby Atkinson, National gallery, London, Velika Britanija; Ulrich Weser, Physiologisch-Chemisches Institut der Eberhards-Karls Universitaet, Tuebingen, Nemčija; Denis Vokić, Hrvatski restauratorski zavod, Zagreb, Hrvaška; Marin Berović, Univerza v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo, Slovenija; Radoslav Zoubek in Polona Ropret, ZVKDS, Center za konservatorstvo, Slovenija.

Prispevki drugega dne simpozija predstavljajo za nas pomembno strokovno gradivo, zato smo sklenili, da jih objavimo v publikaciji. Predstavljene so bile najaktualnejše teme (novejše raziskave, IR reflektografija, čiščenje umetnin, vprašanja rekonstruiranja), zadnji dosežki s področja raziskovanja in najnovejše metode v konserviranju in restavriranju umetnin.

Teme, o katerih so tekle besede na simpoziju, nam ne bi smele biti tuje in vsaka od ustanov, ki hrani, proučuje in obnavlja našo kulturno dediščino, bi morala podpirati povezovanje najrazličnejših strokovnih področij.

Nekaj osnovnih misli in napotkov, izrečenih v referatih, bi lahko strnili takole:
1. Preverjanje in uporaba novih materialov v konservatorsko–restavratorski stroki naj bo pretehtano dejanje. To nam je nazorno pokazala dilema pri uporabi encimov. Njihova učinkovitost je namreč na konservatorskem–restavratorskem področju še v fazi preverjanja. Naravoslovne raziskovalne metode bodo v prihodnosti odgovorile na ta vprašanja. Interpretacijo izsledkov bo mogoče pripraviti z dovolj izkušnjami in z zadostnim številom primerjalnih vzorcev.
2. Če želimo izboljšati svoje delovno področje, začnimo spodbujati mlade ljudi, da se bodo lotili eksperimentov. Inovativen posameznik naj si prizadeva tudi za nova spoznanja in za specifičen pristop pri reševanju konservatorskih–

On the first day of the symposium Project HGG was presented; as its body of works is limited, it had served as an exemplary case of interdisciplinary collaboration from the start. The presentation took the form of a “collage” of short papers delivered by all the experts who had participated in the project. The papers had already appeared in extended form in the publication *Mojster HGG – slikar plastične monumentalnosti* (Master HGG – a Painter of Plastic Monumentality), which accompanied the exhibition of the same title.

Day two gave the attending Slovene professionals, who receive less and less funding for attending symposia abroad, a chance to meet the leading foreign experts in the field of conservation and restoration. Joining us this time there were: Christopher Holden, Tate Britain, London, UK; Rachel Billinge, National Gallery, London, UK; Jo Kirby, National Gallery, London, UK; Ulrich Weser, Physiologisch-Chemisches Institut der Eberhards-Karls Universität, Tübingen, Germany; Denis Vokić, Hrvatski restauratorski zavod, Zagreb, Croatia; Marin Berović, Univerza v Ljubljani, Fakulteta za kemijo in kemijsko tehnologijo, Slovenia; Radoslav Zoubek and Polonca Ropret, ZVKDS, Center za konservatorstvo, Slovenia.

The papers delivered on the second day represent crucial study material for us, so we have decided to gather them together in a publication. They deal with such topical issues as the latest research findings; IR reflectography; cleaning works of art; issues related to reconstruction; and the most recent methods used in conserving and restoring works of art.

All professionals working in our field should be acquainted with the topics presented at the symposium, and the institutions involved in preserving, studying, and restoring our cultural heritage should support connections between the various disciplines.

The basic ideas and suggestions delivered in the papers could be summed up as follows:
1. New materials in conservation-restoration work should be thoroughly tested and their use carefully considered, as it is evident from the example of the dilemma concerning the suitability of enzymes. Their effectiveness in conservation-restoration work is still being investigated. Scientific research methods will answer these questions in the future. It will only be possible to interpret the findings with sufficient experience and an adequate number of comparative cases.
2. If we wish our field to improve, we must encourage young colleagues not to shy away from experimentation. It is up to

restavratorskih problemov v različnih muzejskih ustanovah. Bistvena je tudi sposobnost konkretnega razmišljanja in logičnega sklepanja.

Strokovna srečanja, kakršen je bil mednarodni simpozij, prinašajo nova, aplikativna znanja, ki so v širšem evropskem prostoru v konservatorstvu-restavratorstvu že prisotna in uveljavljena. Zato nam je lahko v prihodnosti ena prednostnih nalog tudi ta, da si pridobimo sredstva za tovrstne dobro utemeljene programe.

Pripravili smo dvojezično publikacijo. Z njo smo se želeli približati onim, ki so pri poslušanju morda zajeli celoto, vendar so bili manj osredotočeni na izvirni splet avtorjevih misli in raziskav, pa tudi tistim, ki se simpozija niso mogli udeležiti.

Kolegom in sodelavcem, ki jim bodo referati, zbrani v natisnjeni obliki, namenjeni, želimo odkriti doslej neznane poti, da bodo lahko bolj poglobljeno razmišljali o določeni problematiki, ki ne bo koristna le za posameznika, temveč tudi za stroko. Zagotovo je smiselno taka početja spodbujati in ne zavirati. Le spretno povezovanje domišljije in logike nas bo pripeljalo do optimalnih rešitev.

Spretni poustvarjalci, kar *konservatorji-restavratorji* vsekakor smo, si želimo pri svojem strokovnem delu nenehno napredovati. Z raziskovalnim duhom, prožnostjo, domišljijo in inovativnostjo bi radi spodbujali tudi vse druge, ki se nam pridružujejo v interdisciplinarnem procesu reševanja in končne prezentacije umetnin.

Na tem mestu se zahvaljujemo vsem predavateljem, ki so na simpoziju izvirno predstavili rezultate svojih dolgoletnih raziskav in razkrili vrsto novosti.

Zahvalo dolgujemo vsem tistim, ki so se potrudili, da nam je mednarodni simpozij uspelo realizirati, najprej trem soorganizatorjem: Narodni galeriji, Moderni galeriji in Restavratorskemu centru ZVKDS, ki je nosil večji del finančnega bremena, ter obema sponzorjema: Leku in Adrii-Airways. ■

innovative individuals to arrive at new understandings and to find specific approaches to solving problems of conservation and restoration in different museum institutions. Equally crucial is their ability to think in terms of a concrete problem and draw logical conclusions.

Such cross-disciplinary meetings as this international symposium provide knowledge of procedures applied in the field that are new to us, but which elsewhere in Europe are already familiar and well established in conservation-restoration practice. For this reason we should make it a priority to ensure funding for similar conferences also in the future.

This bilingual publication is intended for all those who perhaps formed a general idea of the themes while listening to the presentations of the papers, but would like another opportunity to focus on the authors' original train of thought or specific research, as well as for those who were unable to attend the symposium.

With these proceedings we wish to show our colleagues new ways to think about certain issues, in the hope that this may yield results that will benefit not only individuals, but also our professional field in general. Only a balanced combination of inventiveness and logic can lead to optimum solutions, thus all such efforts should be encouraged and supported.

Conservators-restorers are undoubtedly skilful re-creators, and as such we all wish to improve our skills constantly and enhance our expertise. With an investigative spirit, flexibility, imagination and innovative ability we wish to activate all others involved in the interdisciplinary process of preserving and, ultimately, presenting works of art.

Here I would like to thank all the authors who presented the results of their year-long research projects at the symposium and shared with us their most recent observations. Furthermore, we owe a debt of gratitude to all those who contributed their efforts to the realisation of this international symposium, primarily the three co-organizers: Narodna galerija / the National Gallery, Ljubljana; Moderna galerija / the Museum of Modern Art, Ljubljana; and Restavratorski center ZVKDS / the Restoration Centre of the Institute for the Protection of Cultural Heritage of Slovenia, which bore most of the financial burden, and the two sponsors, the companies Lek and Adria-Airways. ■

TAMARA
TRČEK PEČAK

Konservatorstvo in restavratorstvo je mlada stroka, ki se v zadnjem času razvija vse hitreje. V zadnjih desetletjih je način dela v konservatorsko-restavratorski stroki povsod po svetu doživel velike spremembe. Pojavila se je cela vrsta novih materialov, ki jih uporabljamo pri reševanju umetnin, prišlo je do razvoja nove opreme, tako za konserviranje in restavriranje kot tudi za diagnostiko in dokumentacijo. Vse to je potegnilo za seboj potrebo po novih znanjih, ki jih prejšnje generacije v okvirih naše stroke niso poznale. Obvladati je treba tudi zahtevnejše računalniške programe, delo z opremo, kot sta kamera za infra-rdečo spektroskopijo in mikroskop, obdelavo podatkov ... Prišlo je do potrebe po večji specializaciji, kar poznamo tudi iz drugih strok, pa vendar to pri nas morda predstavlja večjo težavo, zlasti v majhnih oddelkih.

Od srede dvajsetega stoletja se je začela uveljavljati misel, da subjektivno odločanje o tem, kako konservirati in restavrirati nek predmet, ni dovolj. Pojavljati so se začele težnje po bolj objektivnem pristopu, za kar pa so potrebna drugačna znanja. Vse bolj je prišlo do povezovanja z znanstvenimi disciplinami, še posebej s tistimi, ki so lahko pomagale pri ugotavljanju materialne zgradbe vseh delov umetnine.

O povezavi med strokami
Interdisciplinary Connections

Conservation and restoration together form a relatively new field that has recently seen rapid development. In the last decades the work methods in restoration-conservation have undergone major changes worldwide. A whole new range of materials used in preserving works of art has emerged; new technology has been developed, both for conserving and restoring, on the one hand, and diagnosis and documentation, on the other. These new developments entail a need for new knowledge and skills unfamiliar to previous generations of restorers-conservators. We need to be proficient in using advanced computer programs, in handling equipment such as infrared cameras and microscopes, in data processing, and other complex techniques. The need for greater specialisation has also increased, as it has in other fields. But in conservation-restoration this perhaps presents a greater challenge, particularly in small restoration-conservation departments.

The realisation that subjective decisions about how to conserve and restore an object are not enough has prevailed increasingly since the mid-20th century. Aspirations toward a more objective approach arose, also bringing in their wake the need for a different kind of knowledge. This has increasingly led to connections with scientific disciplines, in particular those

Diagnostične preiskave predstavljajo eno najdražjih postavk pri projektu, zato so pri načrtovanju velikokrat omejene na najnujnejše. Pri načrtovanju največkrat mislimo na tisti del preiskav, ki nam odkriva materialno zgradbo izvirnika in s tem lahko pomaga umestiti izbrane umetnine v prostor in čas ali potrditi, morda celo odkriti avtorstvo. To je tisti del preiskav, ki je vezan predvsem na umetnostno-zgodovinski del raziskovanja umetnin in ga ponavadi izvedemo pred konserviranjem in restavriranjem in časovno ni tako omejen.

Manj predvidljiv, a za ohranitev dediščine ključnega pomena, pa je drugi del preiskav. Ta nam pomaga določiti materialno zgradbo kasneje dodanih, nezaželenih materialov in poiskati možnosti in materiale, s katerimi jih lahko brez posledic odstranimo. Prav tako nam lahko rezultati preiskav pomagajo pri določitvi najustreznejših materialov za utrjevanje ali dopolnjevanje ogroženega nosilca ali slikovnih plasti. Ta del preiskav poteka med samim delom, zato je vse bolj nujno imeti strokovnjaka - vsaj za najosnovnejše preiskave – ves čas ob sebi, saj je od rezultatov analiz odvisno nadaljevanje dela. Tak strokovnjak bi moral imeti veliko izkušenj s precej specifično konservatorsko-restavratorsko problematiko, kar pomeni, da bi se moral ukvarjati samo s tem in to dalj časa. Vsak oddelek, ki se želi resno ukvarjati s konseviranjem in restavriranjem umetnin, bi moral imeti vsaj enega takega strokovnjaka.

Dognanja, ki jih lahko prispeva znanost, niso zgrajena na občutkih in osebnih mnenjih, ampak na dejstvih, ki jih je mogoče natančno izmeriti. Meritev in eksperimentov, ki bi jih morali ponavljati v nadzorovanem okolju in ki bi pripeljali do točnih rezultatov, pa pri delu s pravimi predmeti ni vedno tako lahko izpeljati kot v namišljenem laboratoriju. Znanost se zato velikokrat zateče v še bolj poglobljene preiskave in meritve, ki pa jih na koncu konservator-restavrator, ki dela z umetnino niti ne zna več uporabiti. Tu se začnejo težave pri sporazumevanju strokovnjakov iz različnih strok.

Konservatorji-restavratorji si z dolgoletnim praktičnim delom naberejo ogromno izkušenj, ustvarijo si neko svoje znanje, ki temelji na občutku in ni merljivo v znanstvenem smislu, a je izredno dragoceno pri praktičnem delu s predmeti. Strah pred subjektivnim pristopom je utemeljen, zato je sodelovanje z drugimi strokami nujno. Znanstvene discipline lahko s svojimi ugotovitvami pomagajo pri odločitvah, *kaj* je treba storiti – ko pa nastopi vprašanje, *kako*, brez drobnih invencij, ki so branches of science that can help determine the material structure of all parts of a work of art.

Diagnostic tests tend to be the most expensive item on the cost sheet of a given project. As a result, they are limited to only the most essential. In planning a project, we think most frequently of those analyses that reveal the material structure of an original and can consequently help us place a given art work in space and time, or confirm, perhaps even discover, authorship. Such examinations are related primarily to the art-historical part of researching art works; they are usually carried out prior to conservation and restoration and are not subject to time constraints.

The other part of the analyses is less predictable, but crucial for preserving cultural heritage. These concern the determination of the material structure of substances added to an art work later, which are unwanted, and finding ways and means by which they can be removed without adverse consequences. The results of such tests can also help us determine the most appropriate materials for reinforcing or treating endangered supports or paint layers. These tests are carried out during the work process itself, and as the analytical results determine the way in which the work proceeds, it is becoming essential to have an expert present at all times, at least for basic analyses. Such a scientist should have considerable experience with the specific issues of conservation and restoration, which entails that he or she would have to work exclusively in this field, and for an extended period of time. Every department that wishes to do serious conservation-restoration work should, therefore, have at least one scientist working for it.

The observations science can contribute are not based on feelings or personal views, but on facts and data that are precisely measurable. Measurements and experiments that need to be carried out several times in a controlled environment in order to yield accurate results are sometimes harder to carry out with actual objects than in an ideal laboratory situation. For this reason, scientists often resort to ever more exhaustive, detailed analyses and measurements, the results of which the conservator-restorer, who works directly with the art work, no longer knows how to use. This is where communication between experts from different fields begins to break down.

Conservators and restorers acquire an enormous amount of hands-on experience through long years of practical work, accumulating specific knowledge that is based on feeling; this is včasih tudi nenačrtovane, in hitrih odločitev v nepredvidenih situacijah ne gre. Tu pa so še kako dragocene izkušnje.

Iz tega sledi, da je za korektno in uspešno delo nujno sodelovanje različnih strokovnjakov, od katerih vsak prispeva dragocen delež v skupnih prizadevanjih za ohranjevanje dediščine.

V Narodni galeriji smo zato že v letu 2002 začeli s projektom *Znanost za umetnost*. Strokovna srečanja pod tem imenom so bila namenjena prav povezovanju različnih strok, ki se ukvarjajo s proučevanjem in ohranjanjem naše kulturne dediščine.

Srečanje v februarju 2005 je preraslo v mednarodni simpozij. Simpozij je doživel dovolj velik odziv, saj je bilo udeležencev prvi dan okoli 100, drugi dan pa okoli 140. To priča o pomembnosti takih dogodkov pri nas in želji po nenehnem izobraževanju, ki pa jo je zaradi pomanjkanja sredstev največkrat težko uresničiti. V podpiranju takih srečanj s strani Ministrstva za kulturo vidimo dober in finančno ugoden način izobraževanja naših strokovnjakov in razvoja stroke pri nas.

Upamo, da bo gradivo vsakemu prineslo kaj novega znanja, ki bo lahko pomagalo pri odločitvah – *kako*. ■

not measurable in the scientific sense, but it is no less precious in the actual handling of artefacts. The fear of a subjective approach is well founded and collaboration with other fields of expertise is therefore essential. With its ability to produce informative observations, science can help decide *what* needs to be done – but when it comes to *how* it needs to be done, minor, sometimes unplanned interventions and quick decisions in unpredictable situations are indispensable. And here experience proves invaluable.

What follows from the above is that, for the work to be successful and properly done, it is imperative that experts from different fields work together, each contributing an invaluable part to the effort of preserving cultural heritage.

For this reason Narodna galerija / the National Gallery, Ljubljana started the Science in Art project in 2002. Conferences organised under this title are meant to bring together the various disciplines that are involved in studying and preserving our cultural heritage. In February 2005 the conference grew into an international symposium, which was very well received, with 100 people attending on the first day, and 140 on the second.

This testifies to the importance of such events in Slovenia and to the desire for sustained education, which is often difficult to satisfy due to the lack of funding. We welcome the support the Ministry of Culture has given to these conferences as a good and financially favourable way of educating our experts and developing our field in Slovenia.

We hope that the papers in these proceedings will provide everyone with some new knowledge that will help them with their decisions on *how* to do things. ■

Rekonstrukcija spodnje plošče *Velikega stekla – 1965-6* Marcela Duchampa/Richarda Hamiltona

The Reconstruction of the Lower Panel of Marcel Duchamp/ Richard Hamilton's *Large Glass – 1965–6*

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Ključne besede:
propad;
rekonstrukcija;
etika.

Keywords:
deteriorated;
reconstruct;
ethical.

POVZETEK: **Kadar umetnina zelo propade ali se poškoduje, včasih presodimo, da je potrebno rekonstruirati kak njen del ali narediti novo kopijo ali repliko celote. Pričujoči prispevek opisuje tak primer. Obravnava zgodovino in nastanek dela, vzrok propada, razloge za rekonstrukcijo, postopke rekonstrukcije in etična vprašanja, ki so vzniknila ob tem.**

ABSTRACT: When a work of art has become so badly deteriorated or damaged, occasionally it is considered necessary to reconstruct part of it or make a complete new copy or replica. This paper describes one such case. The history and construction of the work; the cause of the deterioration; the reasons to reconstruct; the reconstruction procedures and the ethical issues raised are covered.

Uvod

Hamiltonova replika slike Marcela Duchampa *Nevesta, ki jo slačijo njeni samski moški*, celo, bolj običajno imenovane *Veliko steklo*, je vključena v zbirko moderne umetnosti Galerije Tate in razstavljena v Tate Modern na Banksidu v Londonu (slika 1). Richard Hamilton jo je prvotno naredil za veliko Duchampovo retrospektivno razstavo, ki jo je organiziral Arts Council of England v Tatu leta 1966. Replika je bila potrebna, ker je bil Duchampov zdrobljeni original v Filadelfiji v ZDA (slika 2) prekrhek za transport. Leta 1984 se je spodnja plošča replike razbila, potem ko je zaradi napake v materialu počila do nepopravljivega stanja. Zato je bila spodnja plošča v celoti rekonstruirana.

Zgodovina in nastanek replike

Hamiltonova replika ni bila mišljena kot kopija, ampak kot rekonstrukcija Duchampovih izvirnih postopkov. Hamilton je zapisal:

Te naloge se ni mogoče lotiti na enak način, kot se delajo kopije slik – tako, da bi se postavilo poleg izvirnika platno in reproducirala poteza za potezo. Tudi po fotografijah ni mogoče zadovoljivo delati, saj se izgubi veliko informacij že na sami ravni izdelave. Odločili smo se za alternativni način, tj. za uporabo podrobne dokumentacije iz "Zelene škatle" [2], da s tem ponovno prehodimo vso pot – da rekonstruiramo postopke, namesto da bi imitirali učinke dejanja. Duchampov odnos do slikarstva se po letu 1912 postopno premakne do točke, kjer je ustvarjalno dejanje lahko le še podelitev statusa umetnine predmetu množične proizvodnje. Ta navidezno izkrivljena propozicija je logično nadaljevanje stališča, ki je Duchampa pripeljalo do tega, da je ločil čutne in manipulativne vidike slikarstva od svojih tedanjih povsem konceptualnih interesov. Tehnika *Stekla* – ročna izdelava in celo metoda načrtovanja – je tako zasnovana, da umetnika obvaruje kakršnega že koli čustvenega odnosa do medija.

Risba je v glavnem geometrijska. Barva je nanešena na ploske površine, ki so zamejene s svinčeno žico. Nobenih prehodov ni, kjer ne bi mogli povsem zvesto slediti Duchampovi izvedbi brez sleherne misli na ponarejanje. Najbolj bistvena odločitev pri rekonstrukciji je bil sklep, da se bomo izognili kopiranju sedanjega videza *Stekla*. Poleg fragmentacije samega stekla je namreč prišlo do izrazite deterioracije.

Introduction

Richard Hamilton's replica of Marcel Duchamp's *The Bride Stripped Bare by her Bachelors*, Even, more commonly referred to as the *Large Glass*, is in the Tate Gallery's collection of Modern Art, on display at Tate Modern, Bankside, London (Figure 1). It was originally made for a major retrospective exhibition of Duchamp's work organised by the Arts Council of England at the Tate in 1966. A replica was necessary as Duchamp's broken original in Philadelphia, USA (Figure 2), was too fragile to travel. In 1984, the lower glass panel of the replica shattered, an inherent fault causing it to crack to an unrestorable state. Consequently this lower panel has been completely reconstructed.

History and Construction of the Replica

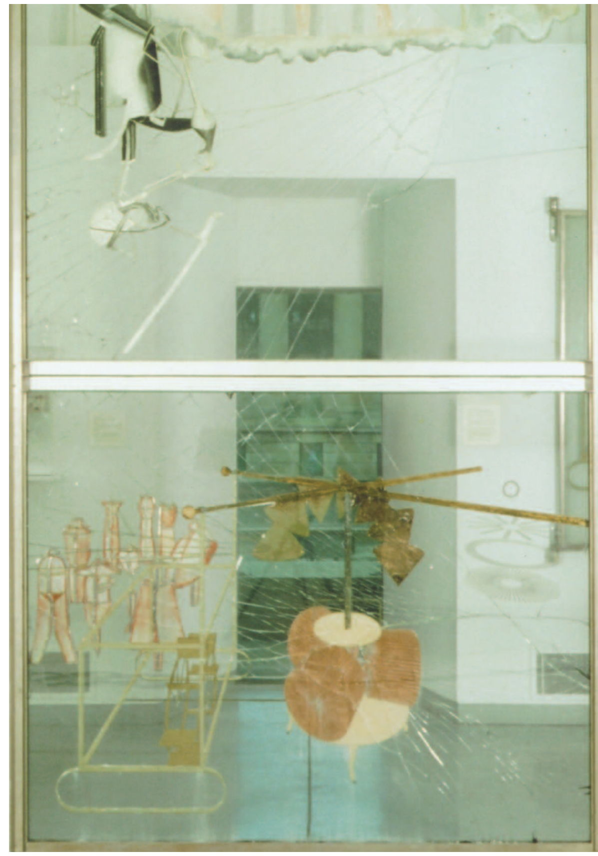
Richard Hamilton's replica was not intended to be a copy, but a reconstruction of Duchamp's original procedures. Hamilton wrote:

It isn't possible to approach this task in the way that copies are made of paintings – to set up a canvas beside the original and reproduce the marks stroke for stroke. To work from photographs isn't satisfactory because much information, even at the straightforward level of fabrication, is lost. The alternative method, that of using the detailed documentation of the 'Green Box' [2] to cover the ground again – to reconstruct procedures rather than imitate the effects of action – was the one adopted. Duchamp's attitude to painting after 1912 moves progressively to a point where the act of creation can be no more than the nomination of a mass-produced object to a status of art. This seemingly perverse proposition is the logical extension of a point of view which caused Duchamp to divorce the sensual and manipulative aspects of painting from his purely conceptual interests of that time. The techniques of the *Glass* – the craftsmanship and even the planning method – are devised to isolate the artist from any emotional relationship with his medium.

Drawing is mainly draughtsmanship of a geometric kind. Paint is applied in flat areas contained by boundary lines of lead wire. There are no passages where the Duchamp hand cannot be followed quite faithfully without the least consciousness of forgery. The most crucial decision in the reconstruction was that of opting to avoid a copy of the present appearance of the *Glass*. Severe deterioration has taken place quite apart from the fragmentation of the glass itself. In its fifty or so years of its life

Slika 1. **Hamiltonova replika *Velikega stekla* Marcela Duchampa, frontalni pogled: *The Bride Stripped Bare by her Bachelors, Even (The Large Glass) [Nevesta, ki jo slačijo njeni samski moški, celo (Veliko steklo*)] (London, Tate Modern, T02011), 1965–6. Olje, svinec, prah in lak na steklu, 277,5 x 175,9 cm, spodnja plošča je rekonstruirana. © Tate, London.**

Figure 1. Richard Hamilton's replica of Marcel Duchamp's *Large Glass*, front view: *The Bride Stripped Bare by her Bachelors, Even (The Large Glass)* (London, Tate Modern, T02011), 1965–6. Oil, lead, dust and varnish on glass, 277.5 × 175.9 cm, lower panel reconstructed.© Tate, London.



Slika 2. **Duchampovo originalno *Veliko steklo*, frontalni pogled: *La Mariée mise à nu par ses célibataires, même – The Bride Stripped Bare by her Bachelors, Even (The Large Glass) [Nevesta, ki jo slačijo njeni samski moški, celo (Veliko steklo)*] (Philadelphia, Philadelphia Museum of Art, 1952-98-1), 1915–23. Olje, lak, svinčena folija, svinčena žica in prah na dveh steklenih ploščah, vstavljenih v aluminijast, lesen in jeklen okvir, 277,5 x 175,9 cm. © Artists Rights Society (ARS), New York / ADAGP, Paris / Estate of Marcel Duchamp and Philadelphia Museum of Art.**

Figure 2. Marcel Duchamp's original *Large Glass*, front view: *La Mariée mise à nu par ses célibataires, même – The Bride Stripped Bare by her Bachelors, Even (The Large Glass*) (Philadelphia, Philadelphia Museum of Art, 1952-98-1), 1915–23. Oil, varnish, lead foil, lead wire and dust in two glass plates mounted with aluminium, wood and steel frames, 277.5 × 175.9 cm. © Artists Rights Society (ARS), New York / ADAGP, Paris / Estate of Marcel Duchamp and Philadelphia Museum of Art.

Delo je v svojih približno petdesetih letih obstoja podleglo drastičnim spremembam. Mi smo se zato trudili obnoviti izhodiščni namen – da bi naredili táko steklo, kot je bilo zasnovano, pri čemer se dopušča možnost sprememb, a sprejema neizogibno dejstvo, da bo ta ponovitev mojstrovine neogibno živela drugačno življenje. Niti poskusili nismo ponoviti najočitnejše značilnost Filadelfijskega *stekla*, ki izhaja iz nesreče, zaradi katere preko njega teče na tisoče razvejanih, svetlečih se razpok. Duchamp se je pri načrtovanju *Velikega stekla* sicer poslužil naključja v treh skrbno nadzorovanih sekvencah. Razbitje je bila nepredvidena katastrofa, zaradi katere pa si ni delal pretiranih skrbi. Ta, nova verzija je izdelana na armiranem steklu – ukrep, ki bo po vsej verjetnosti ohranil videz mladosti modela. K *Filadelfijskemu steklu* smo se občasno zatekli bolj zato, da bi pridobili vpogled v konstrukcijo vsebine, kot pa da bi kopirali upodobitve na površini originala. Obstajajo tudi manjše razlike – odstopanja, ki smo jih sprejeli, da bi pri rekonstrukciji ohranili celovitost, ki bo enakovredna celovitosti izvirnika [1].

Na odprtju retrospektivne razstave v Galeriji Tate je Duchamp na zadnjo stran replike napisal "Richard Hamilton/pour copie conforme/Marcel Duchamp/1966".

Struktura sestoji iz risbe iz svinčene žice, pobarvane z oljnimi barvami in podložene s svinčeno folijo, s prahom, zalitim z mastiksom, in s premazom za zrcala, sestavljena pa je na površini dveh ločenih kaljenih steklenih plošč višine 1369 mm, širine 1700 mm in debeline 6 mm, ki sta vstavljeni druga nad drugo v prosto stoječ aluminijast okvir. Dve podobni stekleni plošči na hrbtni strani fizično varujeta sestavne dele slike.

O *Velikem steklu* je bilo napisanih veliko knjig in člankov (izbor najdete v Bibliografiji); Duchamp je za bistveni pri razumevanje tega dela štel svoji "Zeleno škatlo" in "Belo škatlo" [2]. Ronald Alley je v katalogu, ki ga je Galerija Tate izdala leta 1981, napisal:

Vsak poskus, da bi te zapiske povzeli v nekaj besedah, bi predstavljal grobo zavajanje; lahko rečemo le, da je *Steklo* vodoravno razdeljeno na dva dela, z ženskim delom (Domeno neveste) zgoraj in moškim delom (Aparaturo samcev) spodaj, in da sestavlja diagram ironičnega, izredno kompleksnega stroja za ljubljenje, pri katerem moški in ženski stroj komunicirata le preko dveh obtočnih sistemov brez stične točke. Poleg tega nekateri vidijo v njem reference na alkimijo, na karte tarot, na krščanski simbolizem, pa tudi razmišljanje o perspektivi in četrti dimenziji [3].

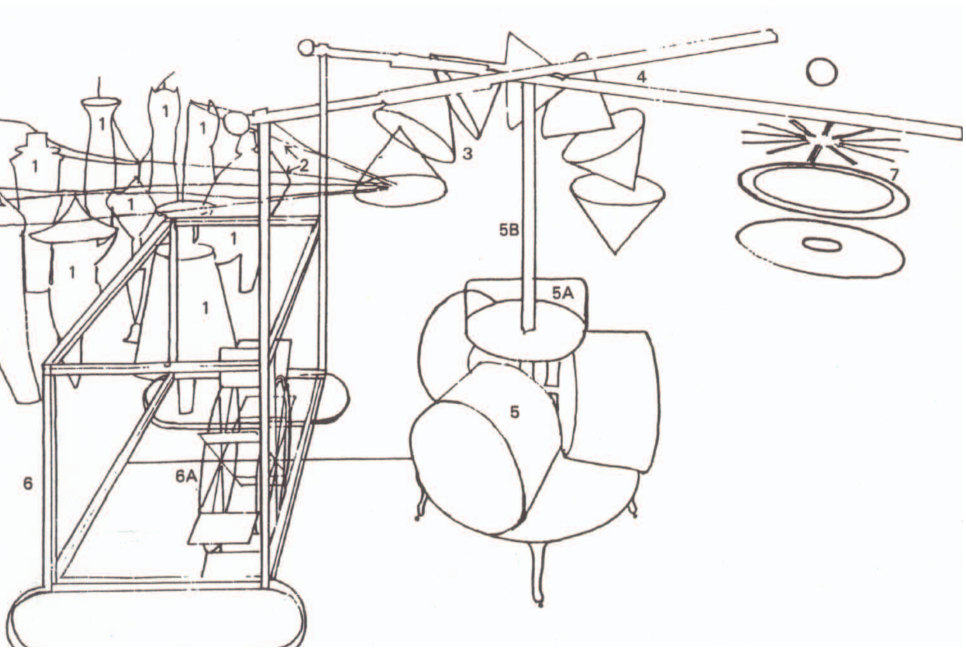
it has succumbed to drastic changes. Our efforts have been directed at a recapitulation of intention – to make the glass as it was conceived, allowing for the possibility of change but accepting the inevitability of a different life for this echo of a masterpiece. The most obvious feature of the Philadelphia *Glass*, caused by the accident which ran sparkling fractures in a thousand rivulets across it, we have not attempted to repeat. Duchamp did use chance in three closely controlled sequences in his planning of the '*Large Glass*'. The breaking was an unpredicted calamity which caused, however, little distress in its victim. This new version is made on armour plated glass – a provision likely to preserve the appearances of its model's youth. References were made to the Philadelphia *Glass* more to gain knowledge of the construction of subject matter than to copy delineations on the surface of the original. There are slight differences – deviations accepted to maintain the integrity in the reconstruction equalling that of the original [1].

At the opening of the Tate Gallery retrospective exhibition, Duchamp inscribed the reverse of the replica, 'Richard Hamilton/pour copie conforme/Marcel Duchamp/1966'.

The structure consists of a lead wire drawing coloured with oil paint, backed with lead foil, dirt-infused mastic and mirroring, assembled on the surface of two separate toughened glass panels, height 1369 mm, width 1700 mm, thickness 6 mm, and fitted one above the other in a free-standing aluminium framework. Two similar plain glass panels at the reverse provide physical protection for the design components.

The *Large Glass* has been the subject of many books and articles (see bibliography for a selection of these) and Duchamp considered his 'Green' and 'White' Boxes [2] of crucial importance to the understanding of it. Ronald Alley wrote in the 1981 Tate Gallery catalogue:

Any attempt to summarise this commentary in a few words would be grossly misleading, but what can be said is that the *Glass* is divided horizontally into two parts, with the female section (the Bride's Domain) at the top and the male section (the Bachelor's Apparatus) below, and that it constitutes a diagram of an ironic love-making machine of extraordinary complexity in which the male and female machines communicate only by means of two circulatory systems, and without any point of contact. In addition some have seen in it references to alchemy, the Tarot cards, Christian symbolism, and also a preoccupation with perspective and the fourth dimension [3].



Slika 3. **Replika *Velikega stekla* Richarda Hamiltona; spodnja steklena plošča ("Aparatura samcev"): glavne komponente podobe. 1. Polmoški kalupi; 2. Kapilarne cevke; 3. Filtri; 4. Škarje; 5. Mlinček za čokolado; (5A Kravata, 5B Bajonet); 6. "Sani" (6A Mlinsko kolo); 7. Okulistove priče.**

Figure 3. Richard Hamilton's replica of the *Large Glass*; lower glass panel ('Bachelor Apparatus'): the main design components. 1. Malic Moulds; 2. Capillary Tubes; 3. Sieves; 4. Scissors; 5. Chocolate Grinder; (5A Necktie, 5B Bayonet); 6. Glider (6A Waterwheel); 7. Oculist Witnesses.

Počenje spodnje plošče

19. junija 1984 ob pol dveh zjutraj je varnostnik na nočnem obhodu slišal nenavaden zvok iz Galerije 36. Prižgal je luči, in ko se je nato vrnil, da bi zadevo raziskal, je spodnja steklena plošča podobe *Velikega stekla* (slika 3) pred njegovimi očmi počila. Čeprav je steklo prekrivalo nešteto razpokanin, je ostalo v veliki meri nedotaknjeno; izgubilo se je le nekaj sto koscev iz središča okvare, kjer se je steklo izbočilo navzven.

Ko so zjutraj steklo podrobno pregledali, se je izkazalo, da se je razpočilo na kakih 200.000 koscev, približno na 5 do 13 koscev na cm^2 (standard za kaljeno steklo je 60 na 6 cm^2). Jedro okvare je bilo področje poleg desnega kolesa "Mlinčka za čokolado" (slika 4), edinega dela slike, ki je odpadel, čeprav se je izbočilo in razplastilo tudi več drugih področij. Odtod se je žarkasto širilo navzven več nizov linearnih razpok, ki so sicer sledile glavnim razpokam, so pa povzročile tudi zdrs sosednjih delcev in s tem prekinile neprekinjeno površino stekla. Te razpoke so se verjetno pojavile pri tem, ko se je steklo izbočilo, okvir iz aluminija pa mu je omejeval širjenje. Ekspandirano steklo je bilo tesno stisnjeno v okvir, saj je zapolnilo ves dodatni prostor za raztezanje, vključno s 5-milimetrsko vrzeljo med zgornjim robom in vodoravno stekleno prečko.

The Breaking of the Lower Panel

At 1.30 am on the 19th of June1984 a security guard, making his night patrol, heard a strange noise coming from Gallery 36. Having turned on the lights, he returned to investigate and saw the lower image-bearing glass (Figure 3) of the *Large Glass* shattering before his eyes. Although the glass was covered with a myriad of cracks it remained largely intact, losing only a few hundred pieces from the centre of the failure point as it bellied outwards.

When examined in the morning the glass was found to have cracked into approximately 200,000 pieces, about 5–13 per cm^2 (the standard for toughened glass is 60 per 6 cm^2). The failure emanated from an area next to the right wheel of the 'Chocolate Grinder' (Figure 4), the only part of the image to have fallen away, although many other areas had buckled and delaminated. Radiating from this area were a series of linear cracks, following the paths of the general cracks but involving slippage of adjacent pieces, so breaking the continuity of the surface plane of the glass. These had probably developed as the glass bowed outwards, its expansion restrained by the aluminium framework. The expanded glass was jammed tightly into the framework having filled all the allowance made for expansion, including the 5 mm gap between the top edge and the horizontal glass beam.

Slika 4. Detajl razbitega stekla in "Mlinčka za čokolado".

Figure 4. Detail showing the shattered glass and the 'Chocolate Grinder'.

Reševanje

Za katastrofalno okvaro spodnje plošče ni bilo videti nobenega neposrednega vzroka, stanje pa je bilo vidno in slišno nestabilno (slišati je bilo občasno nežno pokljanje), zato je bila prva skrb rešiti ploščo, če je le mogoče, in ohraniti podobe iz svinca, ali pa si zagotoviti vsaj model za rekonstrukcijo. Steklo bi lahko vsak trenutek padlo na tla v drobcih, ki jih ne bi bilo več mogoče sestaviti, saj za razliko od lepljenega stekla kaljeno steklo ni sestavljeno iz več plasti stekla z vmesno plastjo veziva, ki bi ga držalo skupaj.

Kot prvi ukrep smo poskrbeli za to, da so galerijo povsem zaprli za javnost in gibanje okoli stekla omejili na zgolj najnujnejše, s čimer smo zmanjšali možnost, da steklo popolnoma razpade. Reže v tleh pred umetnino smo prekrili s polietilensko plastiko in le-to prilepili na tla, da ne bi steklo v primeru popolnega sesutja popadalo v jašek.

Razpočenemu steklu se je bilo mogoče približate le s prednje strani. Zadnja stran, na kateri je izdelana podoba, je bila zaščitena z drugo stekleno ploščo, vpeto v okvir; presodili smo, da jo je preveč tvegano poskusiti odstraniti. V naglici izvedeni poskusi na razbitih steklenih ploščah so pokazali, da bi lahko kaka zunanja obloga ohranila razpokano ploščo dovolj celo, da bi nato lahko namestili kako bolj togo podporo, na kateri bi jo bilo mogoče odstraniti. Zdaj je bil problem najti primerno oblogo, ki bi jo bilo mogoče nanesti preprosto in s čim manjšim pritiskom. Za ta namen

The Rescue

No immediate cause of the catastrophic failure of the lower panel was apparent and as the condition was visibly and audibly unstable (an occasional faint cracking could be heard), the first concern was to rescue the sheet if at all possible and to save the lead images, or to provide a model for its reconstruction. It could have fallen to the floor in irretrievable fragments at any time as, unlike laminated glass, toughened glass is not a laminar construction with adhesive interlayers which might hold it together.

The first procedure was to ensure that the Gallery was sealed from general access and that there was only essential movement around the glass to reduce the chance of its complete disintegration. The open floor grille in front of it was covered with polythene sheeting taped to the floor to stop the glass falling into it in the event of its total collapse.

The shattered glass was only accessible from the front. The back, on which the image is formed, was protected by another sheet of glass held in the framework and considered too risky to remove. Hasty tests on broken sheets of glass showed that a facing could hold the shattered sheet sufficiently intact to allow the subsequent attachment of a more rigid support upon which it could be removed. The problem was to find a suitable facing that could be applied easily with minimum pressure. Transpaseal® (a self adhesive clear plastic film used as a protective cover for books and similar items)

smo uporabili Transpaseal® (samolepilno prozorno plastično folijo, ki se uporablja za zaščitne ovitke za knjige in podobno). Za lahko in preprosto nastavljivo togo podporo smo pripravili dve plošči 25-milimetrskega ekspandiranega polistirena (stiropora), obloženega z dvostransko lepilnim papirjem, občutljivim na pritisk (kakršen se uporablja za hrbtno stran fotografij).

Transpaseal® smo nanesli na prednjo stran stekla v majhnih, prekrivajočih se kosih: pustili smo jih prosto pasti na površino in jih potem nežno zgladili z mehkimi čopiči za razpraševanje. Folijo smo nanesli v dveh plasteh; kosi druge plasti so bili večji.

Naslednji dan smo nežno odstranili zaščitno hrbtno steklo, kar nam je omogočilo nanesti Transpaseal® na površino stekla, ki nosi podobo. Pri tem Transpaseal® ni nikjer prekril svinca, ki izrisuje podobe. Medtem ko smo delali, je temperatura v galeriji narasla na 30° C in vidno premikanje stekla je nakazovalo, da se bo zdaj zdaj sesulo. Zato smo se odločili, da ga odstranimo brez nadaljnjega odlašanja. Med odstranjevanjem aluminijastih profilov in spojk, ki so jih držale vpete v glavni okvir, smo steklo podprli z rokami. Obenem smo odstranili zaščitno plast na samolepilnem papirju, ki je bil že prilepljen na plošči iz stiropora. S tem smo podporni plošči pripravili, da ju prislonimo na prednjo stran stekla, ki sta jo zdaj prekrivali dve plasti folije Transpaseal®. Najprej smo pritrdili glavno ploščo iz stiropora, ki je prekrivala vse steklo s sliko. Ploščo smo podprli s prednje strani, na zadnjo stran pa smo nežno pritisnili z rokami: s tem se je vzpostavila dovolj močna vez. Plošča je bila dovolj prožna, da se je prilagodila konveksni obliki, ki jo je bilo privzelo steklo. Potem smo sprostili vmesno stekleno prečko iz nosilnih profilov in jo previdno izvlekli. Zdaj je bil dostop do gornjega dela stekla prost in pritrdili smo lahko še zgornji trak stiropora. Preden smo steklo lahko odstranili, je bilo treba še odbiti oba zgornja vogala, da je šlo steklo lahko mimo blokov, ki nosita zgornji stekleni plošči; le-ti sta med reševanjem ostali na svojem mestu.

Podprto steklo smo potem obrnili vodoravno in ga položili na debelo vezano ploščo, da smo ga lahko prenesli v konservatorski - restavratorski oddelek. To nam je uspelo brez dodatnih izgub, steklo pa se je tudi takoj precej zravnalo.

Vzrok okvare

Ko je bilo reševanje zaključeno, smo se lahko posvetili razmišljanju o vzroku okvare in o tem, kako bi škodo popravili. Za katastrofo se ni ponudila nobe-

was used for this purpose. Two sheets of 25 mm-thick expanded polystyrene sheeting faced with double-sided pressure-sensitive adhesive tissue (used for mounting photographs) were prepared to form a lightweight, easily applied rigid support.

The Transpaseal® was applied to the face of the glass in small overlapping pieces, allowed to float onto the surface before being delicately brushed down with soft dusting brushes. Two layers of the film were applied to the front, the second layer being of larger pieces than the first.

The next day, the protective backing glass was gently removed, allowing application of Transpaseal® to the image-bearing face of the glass. This was done without the Transpaseal® covering any of the lead forming the images. While work was going on, the temperature in the Gallery rose to about 30 °C and the visible movement of the glass indicated its imminent collapse. It was therefore decided to remove it immediately. The glass was supported manually while the aluminium channelling and clips holding it into the main frame were removed. Meanwhile, the release sheets covering the adhesive tissue applied to the expanded polystyrene panels were removed, in preparation for the application of these supporting panels to the front face of the glass, now covered with two layers of Transpaseal®. The main polystyrene panel was applied first, covering all the image-bearing glass. An adequate bond was achieved by applying gentle hand pressure from the back while the panel was supported at the front. The panel was sufficiently flexible to follow the convex form assumed by the glass. The central glass beam was then released from its retaining blocks and eased out. The top of the glass now being accessible, the upper strip of the polystyrene was applied. To remove the glass it was then necessary to chip away both top corners to allow it to pass the blocks supporting the top sheets of glass, which remained in position throughout the rescue.

The supported glass was then lowered into a horizontal position and placed on a substantial plywood panel so that it could be transferred to the Conservation Department. This was achieved without further loss and the glass immediately assumed a relatively flat plane.

Cause of the Failure

The rescue completed, thoughts could be turned to the cause of the failure and how to repair the damage. No convincing explanation for the catastrophe was apparent until the manufacturers of the glass, Pilkington Glass Ltd, were consulted. On seeing the shattered

na prepričljiva razlaga, dokler se nismo posvetovali z izdelovalci stekla, Pilkington Glass Ltd. Tehnični predstavnik podjetja je ob pogledu na razpočeno ploščo brez omahovanja zatrdil, da je vzrok "spontana sprostitev napetosti", ki jo je povzročila prisotnost mikrodelcev nečistoč nikljevega sulfida, ki so prišli v steklo v postopku izdelave. Natančni mehanizem tega pojava ni znan, saj je delež tovrstnih okvar, ki sicer niso nepoznane, premajhen, da bi se splačalo pojav obsežno raziskovati. Vendar pa so take okvare zaradi vsebnosti nečistoč dovolj resno jemali, da so od leta 1965 kaljeno steklo, ki se uporablja za ograje, po postopku kaljenja (pri katerem gre tudi za segrevanje, ki mu sledi hitro hlajenje) ponovno segreli do točke, pri kateri bi morebitne prisotne nečistoče povzročile takojšno okvaro plošče namesto poznejše pri uporabi.

Mehanizem razpoka celotne plošče po začetni okvari, ki jo je verjetno povzročila majhna razpoka skozi površino, je znan. Pri postopku kaljenja stekla nastane plošča, pri kateri sta površini pod tlačno napetostjo, notranjost pa pod natezno napetostjo. Energija notranje napetosti se sprosti že, če še tako majhna razpoka predre površino, in hitro privede do popolnega zdrobljenja plošče, kot pri tipičnem razbitju vetrobranskega stekla.

Skrb vzbujajoče pri tem je, da ne poznamo metode, s katero bi zaznali prisotnost nečistoč, ki bi utegnile povzročiti tovrstne okvare, in tako ostaja usoda drugih treh steklenih plošč *Velikega stekla* negotova.

Rekonstrukcija

Problemu rekonstrukcije smo se skrbno posvetili konservatorji, restavratorji in kustosi ter se o tem posvetovali z Richardom Hamiltonom. Duchamp se je sicer sprijaznil s tem, da se je (navadno) steklo originala zdrobilo, in ga je popravil za razstavitev, v našem primeru pa je šlo za okvaro povsem druge vrste, ki je izključevala možnost, da bi steklo še kdaj postavili na ogled, posebno še glede na to, da zgornja plošča ni bila prizadeta. Na začetku smo upali, da bomo podobe lahko prenesli na novo stekleno ploščo (z izjemo zrcalnih "Okulistovih prič" in tistih delov "Filtrov", ki so iz smole in prahu). Vendar smo se potem odločili, da je edino pravilno ploščo rekonstruirati povsem na novo. Odločilno pri tem je bilo, kot prvo, da bi od vseh elementov lahko prenesli zgolj svinčeno žico, ki bi jo v postopku morali ponovno napeljati. Ne bi pa bilo mogoče prenesti elementov prevleke za zrcala, smol in barve, zaradi česar bi bil velik delež rekonstrukcije iz novih materialov. Kot drugo, delni prenos podobe bi nepopravljivo razdelil poškodovani izvirnik, če pa bi ga

sheet, their technical representative was in no doubt that the cause was 'spontaneous stress relief' bought about by the presence of micro-particle impurities of nickel sulphide introduced into the glass during its manufacture. The precise mechanism of this phenomenon is not known because, although such failures were not unfamiliar, their proportion was too small to justify extensive research into it. However, such inclusion faults have been regarded sufficiently seriously that, since 1965, toughened glass for use as balustrades has been reheated after the toughening process (which involves heating followed by rapid cooling), to the point where any impurities present would result in the failure of he sheet immediately, rather than later when in service.

The mechanism by which the whole sheet cracked, following the initial failure probably caused by a minute crack penetrating through the surface, is well known. The process of toughening glass produces a sheet in which the two surfaces are in compression while the interior is in tension. The energy of the interior tension is released by the smallest of cracks penetrating the surface, quickly causing complete cracking of the sheet like the typical car windscreen failure.

Disconcertingly, there is no method of detecting the presence of inclusions liable to cause such failure so that the fate of the other three sheets comprising the *Large Glass* remains uncertain.

The Reconstruction

The problem of reconstruction was given careful consideration by conservators and curators in consultation with Richard Hamilton. Although Duchamp had accepted the shattering of the original glass (annealed glass) and repaired it for display, the failure in this instance was of a very different order, rendering the glass irretrievable in a displayable form, especially as the upper glass was unaffected. Initially it was hoped to transfer the images (apart from the mirrored 'Oculist Witnesses' and resin-plus-dust parts of the 'Sieves') onto a new sheet of glass. However, it was decided that a completely new reconstruction of the sheet was the correct action. The main factors leading to this decision were, firstly, that the only element which could be transferred was the lead wire, which would have to be reworked during the process. The mirroring, resin and paint elements could not be transferred; thus a substantial proportion of the reconstruction would be of new material. Secondly, partial transfer of the image would disperse the damaged original irretrievably, whereas retaining it intact would leave it as an interesting archival relic, to which reference could

pustili pri miru, bi ostal kot zanimiva arhivska relikvija in bi ga lahko uporabili za referenco med rekonstrukcijo v prihodnje.

Strinjali smo se, da za ponovno izdelavo podobe uporabimo iste materiale in tehnike kot Hamilton. Na razpolago smo imeli njegove delovne risbe, ki so na posameznih listih za vsak sestavni del. Edina izjema so "Filtri"; ta list se je namreč izgubil.

Prva tehnična odločitev je bila izbira primernega tipa stekla. Čeprav je bila naša začetna reakcija, da se bomo kaljenemu steklu – in s tem možni ponovni katastrofi – izognili, smo se na koncu vendarle odločili zanj (v upanju, da je zaradi izboljšav v tehnologiji proizvodnje zdaj varnejše) ob upoštevanju nasveta, ki so ga Hamiltonu dali leta 1965 pri Pilkingtonu, češ da je to steklo najtrpežnejše. Alternativi, tj. navadno ali laminirano steklo, nista nudili bistvene prednosti pred kaljenim steklom. Čeprav bi se navadno steklo bolj ujemalo z Duchampovim originalom, pa se ne bi skladalo s Hamiltonovo repliko in bi zahtevalo za zaščito kaljeno steklo na obeh straneh.

Potem ko smo popokano ploščo odstranili iz okvirja, smo jo podrobno pregledali in stanje zabeležili tako, da smo fotografsko dokumentirali odkrito zadnjo stran in čez papir prerisali risbo iz svinčene žice v vseh podrobnostih. Namen tega je bil, da natanko zabeležimo deformacije, kar nam bo v pomoč pri restavriranju, in da si olajšamo začetno konservatorsko - restavratorsko seznanjanje z delom. Kjer je bilo to mogoče, smo skozi svinčeno folijo prerisali žice z uporabo črnega Letraline®, samolepilnega traku na krep papirju, ki se uporablja pri grafiki za pravilno ukrivljene linije, na prozorno folijo Melinex® debeline 175 µm, napeto na lesen okvir in položeno preko stekla, tako da se je stikala z njegovo površino.

Za pregled prednje strani stekla je bilo treba ploščo obrniti. To smo varno izvedli tako, da smo ploščo stisnili med dve vezani plošči. Predhodno smo na ploskve med liki pritrdili papir enake debeline kot sestavine podobe in preko vsega pregrnili debelo polsteno odejo, da bi preprečili poškodbe. Potem ko smo steklo obrnili, smo odstranili ploščo stiropora, ki smo jo pritrdili na prednjo stran stekla med odstranjevanjem iz okvirja.

Rekonstrukcija plošče se je začela z zbiranjem materialov. Pri Pilkington Glass Ltd. smo naročili novo ploščo kaljenega stekla ter kupili več manjših debelih steklenih plošč za poskusne kose. Večino potrebnih materialov je bilo moč kupiti povsod, nekaj težav je bilo le z iskanjem dobavitelja svinčene folije (debeline 100 µm) ter svinčene žice. Potrebovali smo žico treh premerov: 0,5 mm, 0,6 mm in 1 mm.

Potem smo zbrali Hamiltonove risbe ter si po-

be made during the reconstruction of the image and in the future.

It was agreed to remake the image using the same materials and techniques as those employed by Hamilton. His working drawings, consisting of a separate sheet for each component, were available, except that for the 'Sieves', which had been lost.

The first technical decision was to select a suitable type of glass. Although the initial reaction was to avoid toughened glass, and thus a possible repetition of the catastrophe, it was eventually decided to use it (hoping that, with improved production techniques, it would be safer), having regard to the advice given to Hamilton by Pilkingtons in 1965 that the glass was the most durable. Alternatives such as annealed or laminated glasses offered no significant advantages over toughened glass. The annealed glass, although more consistent with Duchamp's original, would have been inconsistent with Hamilton's replica, and would have required toughened glass on either side to protect it.

Following the removal of the shattered panel from the frame, a full examination was made and the condition recorded by full photographic documentation of the exposed reverse side and a detailed tracing of the lead wire drawing. The tracing was made as a means of recording the distortions in detail, to act as an aid for restoration and to help with the initial familiarisation of the restorers with the work. Where possible, the wires were traced through the lead foil using 1 mm-wide black Letraline®, a self-adhesive tape with a crêpe paper base, used for graphic artwork involving accurate and controllable curved lines, on 175 µm-thick transparent Melinex® film stretched on a wooden loom, laid over the glass so that it was in contact with its surface.

To examine the front of the glass, it was necessary to turn the sheet over. This was safely achieved by sandwiching it between two sheets of plywood. Card of the same thickness as the design components was first attached in the areas between the shapes, with a thick felt blanket on top to prevent damage. After turning, the expanded polystyrene panel attached to front of the glass for its removal from the frame was removed.

Work on reconstructing the panel began with the assembly of the materials. A new, toughened glass panel was ordered from Pilkington Glass Ltd and smaller plate glass panels purchased for trial pieces. Most of the materials required were commonly available, but some problems were encountered in finding a supplier of thin foil (100 µm thick), and lead wire. Three different diameters of lead wire were required: 0.5 mm, 0.6 mm and 1 mm.

Hamilton's drawings were then assembled, using Duchamp's measurements from the 'Green Box' to help with their correct alignment. A way of reproducing the

magali z Duchampovimi meritvami iz "Zelene škatle" za njihovo pravilno postavitev. Nato smo se posvetili vprašanju, kako bi reproducirali manjkajočo risbo "Filtrov". Najprej smo mislili, da reprodukcija "Filtrov" s hrbtne strani v Hamiltonovi razpravi ustreza manjkajoči risbi. Fotografsko smo jo povečali in jo prerisali, da bi jo primerjali z risbo na steklu. Zaradi bistvenih odstopanj v obrisu cele risbe je bila nesprejemljiva kot nadomestek. Multipel "Filtrov" v lasti Hamiltona se je prav tako preveč razlikoval, da bi ga lahko uporabili. Na koncu smo naredili risbo tako, da smo povečali detajl s fotografskega negativa stekla, posnetega pred poškodbo. Razmerje povečave smo določili tako, da smo vključili "kravato" (zgornji del "Mlinčka za čokolado" tik pod "Filtri"). To smo uskladili z ustrezno obstoječo Hamiltonovo risbo.

"Okulistove priče"

Prva podoba, ki smo jo rekonstruirali na novem steklu, je bila zrcalna "Okulistove priče", ki smo jo naredili tako, da smo steklo posrebrili, nanj s sitotiskom natisnili podobo z zaščitno metalno barvo (sestavljeno iz 1 dela super fine srebrne paste in 3 delov kovinskega oljno-smolnega topila za barvo) in odvečno "srebrilo" sprali z razredčeno kislino (slika 5). To tehniko je uporabil tudi Hamilton, raje da bi kot Duchamp odvečno "srebrilo" okoli likov odstranil z napornim praskanjem. Imeli smo Hamiltonov izvirni fotografski negativ podobe v naravni velikosti, nismo pa imeli sita za sitotisk. Na

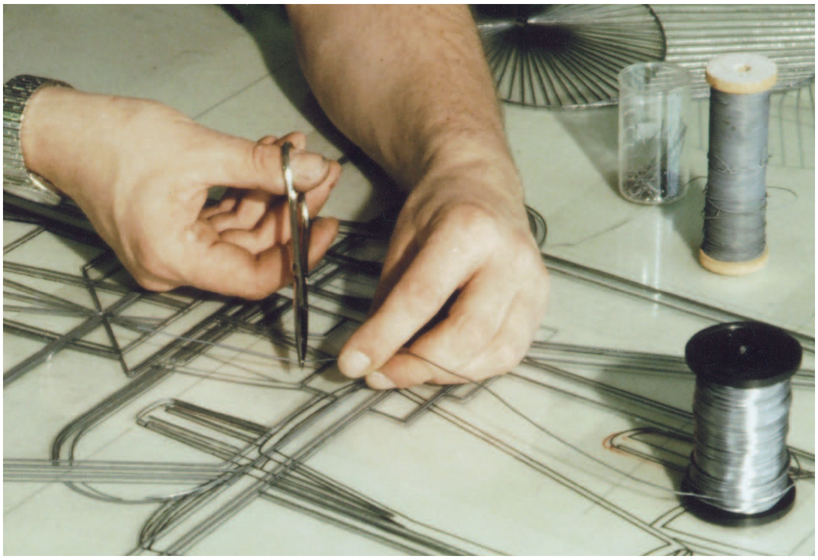
missing drawing of the 'Sieves' was now considered. In the pamphlet produced by Hamilton, a reverse view reproduction of the 'Sieves' was thought to be that of the missing drawing. It was enlarged photographically and a tracing was made for comparison with the drawing on the glass. Due to a significant discrepancy in the outline of the whole drawing it was unacceptable as a replacement. A multiple of the 'Sieves' owned by Hamilton was also too different to be used. Eventually a drawing was produced by the enlargement of a detail from the photographic negative of the glass, taken before the damage occurred. The scale of this enlargement was made accurate by including the 'necktie' element (the top part of 'Chocolate Grinder' immediately below the 'Sieves'). This was matched with Hamilton's extant drawing for it.

"Oculist Witnesses"

The first image to be reconstructed on the new glass was the mirrored 'Oculist Witnesses', formed by silvering the glass, silk-screening the image onto it in a protective metallic ink (consisting of 1 part silver paste super-fine to 3 parts metallic oleoresinous ink medium) and washing away the excess silvering with dilute acid (Figure 5). This was the technique used by Hamilton, in preference to Duchamp's laborious scraping away excess silvering from around the shapes. We had Hamilton's original full-scale photographic negative of the image, but not the silk screen. Using the negative, a screen was made by a commercial specialist using fine, mono-

Slika 5. Rekonstruiranje "Okulistovih prič": sitotisk podobe s metalno barvo.

Figure 5. Reconstructing the 'Oculist Witnesses': silk-screening the image with metallic ink.



Slika 6. Rekonstruiranje risbe iz svinčene žice.
Figure 6. Reconstructing the lead wire drawing.

osnovi negativa je industrijski strokovnjak izdelal sito iz tanke monofilamentne poliestrske tkanine. Tehniko smo izvežbali s številnimi testiranji na steklenih ploščah. Postopek izdelave dokončne podobe je bil sledeč:

1. Sito smo položili na steklo preko risbe, da smo ugotovili pravo lego zanj.

2. Na steklo smo ob robove okvirja sita pritrdili lesene letve, zato da je stalo med tiskanjem v pravi legi.

3. Odstranili smo steklo in predel, ki ga je bilo treba posrebriti, temeljito očistili s Schweigovo formulo št. 23 (zmes za belilno/amoniakovo pasto) ter ga do čistega sprali z deionizirano vodo [4].

4. Površino smo senzibilizirali z raztopino za cinjenje, tj. 0,5 g klorida, ki vsebuje kositer, (kositrovega[II] klorida), raztopljenega v 1000 ml vode. To smo zlili na steklo in po nekaj minutah sprali z vodo.

5. Za premaz za zrcala smo uporabili kemikalije z zaščitenim imenom. Schweigovo formulo št. 36 (raztopino srebrovega nitrata) in št. 37 (natrijev hidroksid plus raztopino amoniaka) smo razredčili z deionizirano vodo v razmerju 1:10 in zmešali skupaj za raztopino za srebrenje. Schweigovo formulo št. 38 (raztopino dekstroze) smo razredčili z deionizirano vodo v razmerju 1:21, da smo pripravili enako količino redukcijske raztopine. 500 ml vsake raztopine je zadoščalo za zrcalno prevleko enega kvadratnega metra. Enako količino obeh raztopin smo odmerili v dve identični brizgalni pištoli in ju hkrati razpršili po pokončno postavljeni stekleni plošči. Raztopini sta se ob stiku zmešali na površini stekla. Razdaljo pršenja, zračni pritisk in trajanje pršenja smo določili s poskusi. Na srebrnem pre-

filament polyester fabric. Numerous tests were made on glass panels to perfect the technique. The process of producing the final image was as follows:

1. The screen was positioned on the glass over the drawing to locate its correct position.

2. Wooden battens were attached to the glass against the edges of the screen's frame so that it could be held in the correct position for printing.

3. The glass was removed and the area to be silvered was thoroughly cleaned with Schweig Formula No.23 (a whiting/ammonia paste mixture) and rinsed clean with de-ionised water [4].

4. The surface was sensitised with a tinning solution consisting of 0.5 g stannous chloride (tin[II] chloride) dissolved in 1000 ml water. This was poured onto the glass and after a few minutes rinsed off with water.

5. Proprietary chemicals were used for the mirroring. Schweig formula No. 36 (silver nitrate solution) and No. 37 (sodium hydroxide plus ammonia solution) were each diluted with de-ionised water, 1:10 by volume, and mixed together to provide the silvering solution. Schweig formula No.38 (dextrose solution) was diluted with de-ionised water, 1:21 by volume, to provide an equal quantity of reducing solution. 500 ml of each solution was sufficient to mirror one square metre. Equal quantities of solutions were measured into two identical spray guns and sprayed simultaneously onto the vertical glass panel. The solutions mixed on contact at the glass surface. The spray distance, air pressure and the period of spraying were determined by experiment. The silver coating developed a dark film within seconds, achieving an opaque layer in less than one minute. The silvered surface was

mazu je v nekaj sekundah nastala temna plast, ki se je v manj kot minuti razvila v neprozorno plast. Posrebreno površino smo sprali z deionizirano vodo in jo pustili, da se posuši.

6. Podobo smo preko sita odtisnili z zaščitno kovinsko barvo na površino.

7. Ko se je barva posušila, smo višek "srebrila" okoli podobe odstranili z zelo razredčeno raztopino dušikove kisline, čemur je sledilo še zadnje spiranje z vodo. Potem smo steklo ponovno namestili preko risb in preverili, če je lega podobe pravilna.

2 Risba iz svinčene žice

Potem ko smo dokončali in zaščitili "Okulistove priče", smo se lotili svinčene žične risbe (slika 6). Za začetek smo naredili poskusne plošče, da smo se navadili ravnanja z žico in da smo izbrali primerno gostoto mastiks laka v terpentinu, s katerim so bile žice prilepljene na steklo. Ker je svinec zelo mehak material, ga je preprosto oblikovati, vendar se tudi zelo hitro deformira. Vsak koščček žice smo odrezali malce daljši, kot je bilo potrebno, in ga povaljali med dvema lepenkama, da je bil popolnoma raven in enakomerno debel. Potem smo en konec držali pri miru, žico previdno oblikovali, da je sledila risbi, in jo prirezali na pravo dolžino. Oblikovano žico smo prilepili na površino stekla z gostim lakom iz mastiksa, ki smo ga s čopičem nanesli po vrhu žice, da je stekel ob njenih straneh dol in na steklo. Ker se mastiks suši počasi, smo imeli še nekaj časa, da popravimo manjša odstopanja in ne-

rinsed with de-ionised water and left to dry.

6. The image was screen-printed onto the surface with the protective metal ink.

7. After the ink had dried, the excess silvering around the image was removed with a very dilute solution of nitric acid, followed by a final rinse with water. The glass was then replaced over the drawings and the position of the image checked for alignment.

2 The Lead Wire Drawing

The ‘Oculist Witnesses’ complete and protected, work began on the lead wire drawing (Figure 6). Initial test panels were made in order to get used to manipulating the wire, and to select the correct consistency of the varnish of mastic resin in turpentine used to adhere the wires to the glass. Lead, being a very soft material, is easy to shape, but it is also easily distorted. After each piece of wire had been cut slightly longer than that required for each line, it was rolled between two pieces of card to make it perfectly straight and even. One end was then held in position, the wire carefully shaped to follow the drawing, and cut to the exact length. After shaping, it was adhered to the glass surface with thick mastic varnish, applied with a brush along the top of the wire and allowed to run down the side of the wire and onto the glass. The slow drying of the mastic enabled small distortions and slight inaccuracies in the positions of the wires to be corrected for some time. It was found that, in some places, the drawing was not sufficiently detailed to see exactly how the wires should be aligned and joined. Examina-

Slika 7. Rekonstruiranje "Filtrov".
Figure 7. Reconstructing the ‘Sieves’.

pravilne lege žice. Pokazalo se je, da risba ponekod ni bila dovolj podrobna, da bi se natančno videlo, kako naj bodo žice speljane in združene.

Mikroskopske preiskave razbitega stekla so dale podrobnejše podatke. Prav tako se je pod mikroskopom pokazalo, da so bile nekatere od linij ali pa celih likov malce spremenjene glede na izvirne risbe. Risba "Bajoneta" v sklopu "Mlinčka za čokolado" je imela tudi štiri z ravnilom narisane črte s črno barvo. Odvečno posušeno smolo iz mastiksa smo odstranili z vatnimi tamponi, namočenimi v aceton.

3 Barvanje "Filtrov"

Potem ko smo končali črtni obris, smo kot prvo ploskev pobarvali "Filtre" (foto 7). Pri originalu je Duchamp pustil, da se je prah nabiral na plosko položenem steklu tri do štiri mesece; temu postopku je rekel "pridelovanje prahu". V "Zeleni škatli" omenja ščetkanje ali brisanje prahu, tako da nastane "nekakšna barva (prozoren pastel)". To je vidno na fotografiji Mana Raya, ki je tudi v "Zeleni škatli". Prah je potem zalil – "hermetično zaprl" – z mastiksom. Prah na Duchampovem steklu je videti fin in drobnozrnat; mastiks je gost, sega skoraj do vrha žice in je zdaj močno porumenel, razpokan in se lušči. V Hamiltonovi repliki je prah (za katerega pravijo, da naj bi bil izpod Hamiltonove postelje) zrnat in vlaknat ter vsebuje dobršen delež živalske dlake. Medtem ko tonska gradacija barve "Filtrov" v glavnem zvesto sledi Duchampovi verziji, je razporeditev umazanije in smole veliko manj enakomerna, saj sta vlaknasta umazanija in smola sprijeti v kar znatne grudice. Te najdemo v glavnem v temnejših filtrih. Zaradi vlaken kepice vsebujejo precejšnjo količino smole, kar tvori grobo in neravno površino.

Metodo barvanja "Filtrov" smo določili s serijo manjših testov in z modelom v naravni velikosti. Prave vrste prah (iz gospodinjskega sesalnika za prah) smo presejali, da smo dobili fino drobnozrnato umazanijo za osnovno nianso, za posnemanje vlaknatih grudic pa smo skrbno izbrali primerne sprijemke. Izkazalo se je za nepraktično, da bi za verno reproduciranje glavnega prehajanja tonov med "Filtri" in mestnega variiranja v gostoti umazanije in smole najprej nanesli prah in ga potem zalili s smolo, kot je navajal Duchamp v "Zeleni škatli", saj je raztopina smole prah preprosto odplavila. Precej razredčena raztopina smole je bila namreč potrebna, da je nastala dovolj groba površinska struktura.

Na koncu smo uporabili sledečo metodo: raztopino laka smo nanašali z majhno kapalko in jo s čopičem razmazali, da je prekrivala celotno površino posameznega filtra. Izbrali smo primerne sprijemke

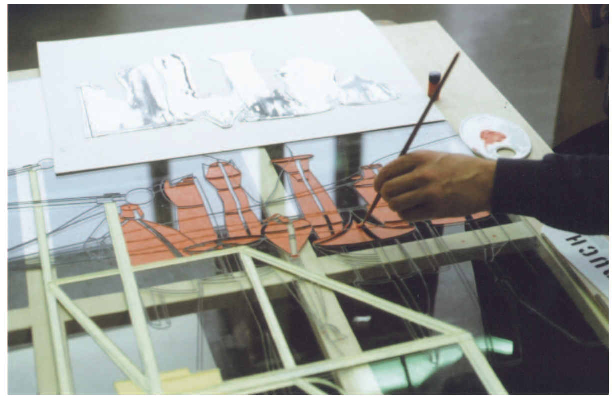
tion of the shattered glass with a microscope helped to supply more detailed information. This examination also revealed that some of the lines, or complete shapes, had been slightly changed from the original drawings. The drawing of the 'Bayonet' section of the 'Chocolate Grinder' also included four ruled, black ink lines. The excess dried mastic resin was removed with cotton wool swabs wetted with acetone.

3 Colouring the "Sieves"

The linear design completed, the first area to be coloured was the 'Sieves' (Figure 7). In making the original, Duchamp allowed dust to collect, with the glass laid flat, for 3 to 4 months; a process he called 'dust raising'. In the 'Green Box', he refers to brushing or wiping the dust so that it forms 'a kind of colour (transparent pastel)'. This is evident in the Man Ray photograph included in the 'Green Box'. The dust was then sealed – 'closed up hermetically' – with mastic. The dust on Duchamp's glass appears fine and particulate; the mastic is thick, almost to the top of the wire, and now severely yellowed, cracked and flaking. In Hamilton's replica, the dust (which is reputed to have come from beneath his bed) is both particulate and fibrous, and contains a considerable proportion of animal hair. While the general tonal gradation of the 'Sieves' follows Duchamp's version quite closely, the distribution of the dirt and resin is far less uniform, the fibrous dirt and resin forming quite large clumps. These are predominately in the darker sieves. Being fibrous, the clumps hold a considerable amount of resin, and give a rough and broken surface.

The method of colouring the 'Sieves' was first established in a series of small tests and a full scale-mock-up. The correct type of dust (obtained from a household vacuum cleaner), could be sieved to provide the fine particulate dirt which gave the general shading. The fibrous clumps could be imitated by carefully selecting appropriate masses. To reproduce accurately the overall tonal gradation across the 'Sieves' and the local variations in the density of the dirt and resin, it was found impractical to apply the dust first and then seal it with the resin, as Duchamp had indicated in the 'Green Box': the resin solution simply washed away the dust. A fairly dilute solution of resin was found to be necessary to produce the rough surface conformation.

The method finally used was as follows: the varnish solution was applied with a small dropper and brushed out to cover the area of each sieve. Appropriate clumps of fibrous material were selected and placed on the wet varnish; these could be manipulated quite easily to produce the correct shapes. The positions of the clumps were established from available photographs vlaknatega materiala in jih položili na moker lak; brez težav jih je bilo mogoče premikati, dokler niso nastale primerne oblike. Položaj grudic smo določili s pomočjo dostopnih fotografij Hamiltonovega stekla in ga narisali v naravni velikosti na polo prozorne folije Melinex, ki smo jo položili pod model v naravni velikosti. Ko so vlaknate grudice vpile lak z okoliške površine, smo ga s kapalko dodajali tako dolgo, dokler nismo dobili približno enakomerno debele plasti. Postopek smo ponavljali, dokler nismo namestili vseh večjih gostih skupkov. Potem smo na moker lak presejali preko filtra drobnozrnat prah za tonsko gradacijo; začeli smo s svetlejšimi filtri in vsakič dokončali po en filter. S to metodo smo izvedli barvanje "Filtrov" skoraj od začetka do konca v enem mahu. Pustili smo, da se je lak delno posušil, in potem naredili še zadnje popravke z razredčenim lakom in rahlim posipom drobnega prahu.



Slika 8. Rekonstruiranje "Polmoških kalupov": barvanje z minijem.

Figure 8. Reconstructing the 'Malic Moulds': painting the red lead paint.

4 Nanašanje oljne barve in podloge iz svinčene folije

Po premoru, med katerim so se "Filtri" posušili, smo steklo dvignili v navpičen položaj in do konca očistili odvečno smolo. Na tej stopnji smo tudi primerja-li vse žice z risbami in jih popravili, preden smo začeli s slikanjem. "Polmoški kalupi" so edina površina, ki je pobarvana z nemešano barvo, z minijem; vse druge površine so pobarvane z mešanicami, za katere ne obstajajo natančni recepti in katerih videz se je z leti bistveno spremenil, tako na Duchampovem originalu kot na Hamiltonovi repliki. Barve na steklih se zdaj po videzu zelo razlikujejo. Iz "Zelene škatle" in od Hamiltona vemo, da so barve "Sani", "Mlinskega kolesa" in "Škarij" vse mešanice dveh barv, svinčevega belila in kadmijeve rumene; "Sani" vsebujejo večji delež bele kot druga dva.

Edini napotek v "Zeleni škatli", ki se nanaša na barvo "Mlinčka za čokolado", je "mlečna čokolada". Hamilton se ni mogel natančno spomniti vseh barv, ki jih je uporabil v svoji mešanici, zdelo pa se mu je, da je vključil vsaj svetlo rdečo, svinčevo belilo in malo žgane umbre ter črne. Na osnovi primerjav s Hamiltonovo barvo smo zmešali in nanesli razne vzorce ter se na koncu odločili za formulo, ki je vsebovala svinčevo belilo, svetlo rdečo, žgano umbro in svetlo kadmijevo rumeno. Kot pri originalih smo tudi mi uporabili industrijsko pripravljene kvalitetne slikarske oljne barve, z izjemo minija "Polmoških kalupov", ki smo ga morali pripraviti v ateljeju, saj ni bilo na voljo primernega industrijskega proizvoda. Pobarvali smo testne vzorce. Naredili smo svetlejše mešanice kot na Hamiltonovem steklu, da upoštevamo staranje barve.

of Hamilton's glass and were drawn full size on a sheet of transparent Melinex film, which was placed beneath the full size mock-up. As the fibrous clumps soaked up the varnish from the surrounding areas, more varnish was added with a dropper to produce to produce a layer of roughly uniform thickness. This process was continued until all the larger dense masses had been positioned. Fine particulate dirt was then sprinkled onto the wet varnish with a sieve to provide the tonal gradation, working from light to dark and completing one sieve at a time. The shading was almost completed in one go by this method. The varnish was allowed to dry partially and the final adjustments were made with diluted varnish and a little sprinkled fine dust.

4 Applying the Oil Paint and Lead Foil Backing

After an interval to allow for the drying of the 'Sieves', the glass was positioned vertically and further cleaning of surplus resin was carried out. At this stage, all wiring was checked against the drawings and corrected before proceeding with the painting. The 'Malic Moulds' are the only area coloured with an unmixed colour, red lead; all the other areas are coloured with mixtures for which no precise recipes exist and which had changed dramatically in appearance with age, both on Duchamp's original and on Hamilton's replica. The colours on the two glasses now appear very different. From the 'Green Box' and Hamilton, it is known that the colours of the 'Glider', the 'Waterwheel' and the 'Scissors' are all mixtures of two colours, lead white and cadmium yellow, the 'Glider', con-

Hamilton je nanašal barvo na ploskve "Mlinčka za čokolado", "Sani" in "Mlinskega kolesa" v plasteh in pustil, da se prva plast posuši, preden je nanesel drugo. "Polmoški kalupi" in "Škarje" so poslikani samo z eno plastjo. Na vseh površinah je na barvo namestil podlogo iz svinčene folije, še preden se je barva posušila. Tudi pri rekonstrukciji smo sledili enakemu postopku. Na površine, kjer sta bili potrebni dve plasti barve, smo nanesli prvi premaz na pokončno postavljeno steklo, potem pa steklo položili vodoravno, da smo lahko namestili folijo. Steklo smo položili vodoravno na dvignjen, odprt lesen okvir, ki je omogočal pogled na prednjo stran med slikanjem. Najprej smo poslikali površino "Polmoških kalupov" (slika 8). Minij smo pripravili tako, da smo vtrli pigment v rafinirano laneno olje, na začetku z lopatico za mešanje barv, potem pa še s terilcem na plošči motnega stekla. "V ateljeju pripravljeni" minij smo s čopičem nanesli na like v zelo tankih plasteh, čeznje pa nanesli podlogo iz svinčene folije po zgolj dveh urah sušenja. Da smo dosegli enako lisast učinek kot na Hamiltonovem steklu, ki je posledica svinčene folije, ki se kaže skozi minij, smo morali biti zelo pazljivi pri redkosti barve in času sušenja. Na Duchampovem originalu je zdaj jasno vidnih le malo ploskev minija.

Like smo iz svinčene folije izrezali predhodno s šablonami iz Melinexa, in sicer malo večje, kot je bilo potrebno. Folijo smo čvrsto pritisnili na mesto, da se je prilegla površini barve in žice, potem pa smo jo ob robovih pazljivo obrezali (slika 9). Svinčena folija ni bila več dostopna v enaki širini kot tista, ki jo je uporabil Hamilton, zato je bilo za prekritje nekaterih ploskev

taining a larger proportion of white than the other two.

The only reference in the ‘Green Box’ for the colour of the ‘Chocolate Grinder’ is ‘milk chocolate’. Hamilton could not remember exactly all the colours he had used to mix this, but thought they probably included at least light red, lead white and a little burnt umber and black. Various samples based on comparisons made with Hamilton’s colour were mixed and painted out and the final formula decided upon as being acceptable comprised lead white, light red, burnt umber and light cadmium yellow. As with the originals, commercially manufactured artists’ quality oil colours were used except for the red lead of the ‘Malic Moulds’, which had to be prepared in the studio because no acceptable commercial product was now available. Test samples were painted out. The mixtures were made lighter in appearance than those on Hamilton’s glass to allow for ageing.

The painted areas of the ‘Chocolate Grinder’, the ‘Glider’ and the ‘Waterwheel’ were applied by Hamilton in layers, the first being allowed to dry before application of the second. The ‘Malic Moulds’ and the ‘Scissors’ were painted with only one layer. In all areas the lead foil backing was applied to the paint before it had dried. The same procedure was followed in the reconstruction. Those areas requiring two layers of paint had their first coat applied with the glass vertical, before laying the glass horizontally so that the foil could be applied. The glass was supported horizontally on a raised, open wooden framework which allowed the front to be viewed during painting. The first area to be painted was the ‘Malic Moulds’ (Figure 8). The red lead oil paint was prepared by grinding the pigment into refined linseed oil, initially

Slika 9. Pritiskanje podloge iz svinčene folije na mesto okrog komponent slike.

Figure 9. Pressing down the lead foil backing into position around the design components.

potrebnih več kosov, medtem ko je Hamilton uporabil eno samo polo. Da smo prikrili stike, smo jih namestili vzdolž robov stikajočih se likov. Medsebojno so se prekrivali in bili skupaj odrezani vzdolž linij žic, da so bili stiki manj vidni.

Zdaj smo nanesli tanko drugo plast barve na "Sani", "Mlinček za čokolado" in "Mlinsko kolo". Na "Mlinček za čokolado" in "Mlinsko kolo" je plast nanešena tako, da daje plosko enakomerno barvo, kadar jo gledamo od spredaj. Na "Jadralno letalo" smo tanjši drugi sloj nanesli tako, da so ostale vidne prvotne poteze s čopičem, kar je podobno efektu, ki ga je dosegel Hamilton. Pustili smo, da se barva suši približno 24 ur, tako da se je svinčena folija potem dobro prijela na lepljivo površino, ne da bi pretirano vpli-vala na plast barve. Zadnja ploskev, ki smo jo barvali, so bile "Škarje". Barva je bila nanešena v eni sami plasti, sušila pa se je 30 ur, tako da folija po aplikaciji ni prišla skozi barvo do stekla, kot je bilo potrebno pri "Polmoških kalupih".

5 Prenos Duchampovega napisa

KoščEk svinčene folije z zgornjega dela Hamiltonovega "Mlinčka za čokolado", ki nosi Duchampov napis "Richard Hamilton/pour copie conforme/Marcel Duchamp/1966" smo prenesli s poškodovanega stekla (slika 10). Da bi se izognili morebitnim poškodbam napisa in da bi ga bilo mogoče preprosto odstraniti, smo ga pritrdili na zadnjo stran nove svinčene folije, in ne neposredno na žico in barvo. Na Hamiltonovo repliko smo na mesto prenesenega kosa pritrdili nov oval folije.

Do odločitve, da Duchampov napis prenesemo na rekonstrukcijo, čeprav nismo prenesli nobenega drugega elementa spodnje plošče, smo prišli po dolgotrajnem preudarjanju. Čeprav je Duchamp videl in odobril le polovico dela, na katerega je bil zdaj pritrjen napis, so po našem mnenju sledeči dejavniki opravičevali, da ga zadržimo na razstavljenem delu. Prvič, bilo je v skladu z željo Richarda Hamiltona, da naj se ohrani kontinuiteta Duchampovega dela in da naj njegova replika Duchampovega dela šteje za "odmev mojstrovine". Drugič, napis ni del koncepta dela, temveč edinstven Duchampov dodatek v znak odobritve Hamiltonovega zaključenega dela. Nanaša se na obe plošči in je torej enako relevanten za zgornjo, nepoškodovano ploščo kot za poškodovano spodnjo ploščo, na kateri je bil po naključju vpisan. Če bi bil napis na nepoškodovani plošči, ne bi bilo o njegovem odstranjevanju niti govora. In kot zadnje, pri rekonstrukciji je v veliki meri šlo za realizacije Hamiltonovih risb, kar je zahtevalo s strani konservatorja restavrator-

with a palette knife, then with a muller on a ground glass slab. The 'studio-prepared' red lead was applied to the shapes by brush in very thin layers and the lead foil backing applied after only two hours drying. Careful attention to the thinness of the paint and its drying time was necessary to produce the same mottled effect, produced by the lead foil showing through the red lead paint, as on Hamilton's glass. Duchamp's original now has few areas of red lead clearly visible.

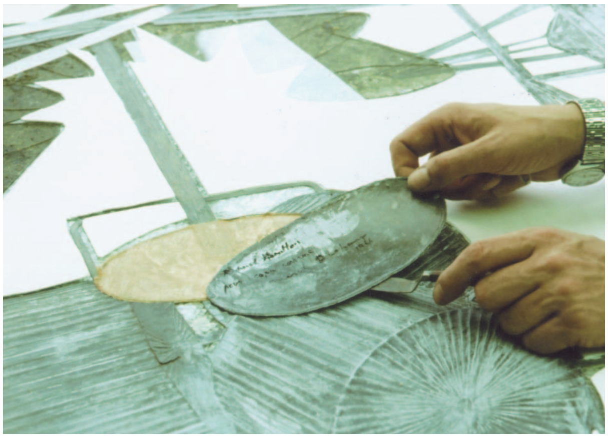
The lead foil shapes had been previously been cut, slightly larger than the required shape, using Melinex templates. The foil was pressed firmly into position to conform to the surfaces of the paint and the wire before being carefully trimmed around the edges (Figure 9). Lead foil of the same width used by Hamilton was no longer available so that some areas required several pieces to cover them where a single sheet had been used before. To disguise the joins they were located along the borders of adjoining shapes. They were overlapped and cut together along the lines of the wires to make them the joins less apparent.

The thin, second paint layer of the 'Glider', 'Chocolate Grinder' and 'Waterwheel' was now applied. On the 'Chocolate Grinder' and' Waterwheel' the layer was applied so that it produced a flat even colour when viewed from the front. On the 'Glider' a thinner second layer was applied so that the initial brushstrokes remained visible, similar to the effect obtained by Hamilton. The paint was allowed to dry for approximately 24 hours so that when the lead foil was applied it adhered well to the tacky surface without disturbing the paint layer unduly. The last area to be painted was the 'Scissors'. The single application of paint was allowed to dry for 30 hours so that when the foil was applied it did not press through to the surface of the glass as was necessary for the 'Malic Moulds'.

5 Transfer of Duchamp's Inscription

The piece of lead foil from the upper part of Hamilton's 'Chocolate Grinder', bearing Duchamp's inscription, 'Richard Hamilton/pour conforme/Marcel Duchamp/1966', was transferred from the damaged glass (Figure 10). To avoid possible damage to the inscription and to keep it easily removable, it was applied to the back of the new lead foil and not directly onto the wire and paint. A new oval shape of foil was applied to Hamilton's replica to replace the transferred piece.

The decision to transfer Duchamp's inscription to the reconstruction, when no other element from the lower panel was transferred, was reached after much deliberation. Although the inscription would now be attached to a work only half of which had been seen and approved by Duchamp the following factors seemed to justify its



Slika 10. **Prenos svinčene folije z Duchampovim napisom.**
Figure 10. Transferring the piece of lead foil bearing Duchamp's inscription.

ja minimalno invencijo. Manjše variacije, ki so posledica ravnanja z materiali, ne spremenijo glavne vsebine dela, ki še vedno v bistvu predstavlja Duchampove zamisli, kot jih je realiziral Hamilton. Tako ostaja veljavna kontinuiteta, ki jo izraža napis.

Sprememba barve med rekonstrukcijo

Med rekonstrukcijo smo opazili zanimivo spremembo barve. Na neki zgodnji fotografiji Hamiltonove replike je barva "Škarij" videti enakomerna in svetlega tona. V obdobju, preden se je steklo zdrobilo, je na večini te površine svinčevega belila in kadmijeve rumene prišlo do sivega razbarvanja; ostalo je le malo relativno majhnih predelov izvirne rumene. Prvotno smo sklepali, da je sprememba preprosto posledica tega, da se skozi barvo vidi svinčena folija. Nekaj mesecev potem, ko se je steklo razbilo, pa se je pokazalo, da se delež rumene v odnosu do sivega razbarvanja ponovno povečuje – barva se je vračala v svojo začetno barvo. Do vračanja v prvotno stanje je najhitreje prišlo na mestih razpok v steklu; na koncu je prišlo do tega, da so se oblikovali otočki sive, ki so ustrezali koscem razbitega stekla.

Kakšna je točno narava sivega razbarvanja in kako do njega pride, ostaja še naprej nejasno. Ni se pojavilo na drugih površinah, kjer sta bila zmešana

retention with the displayed work. Firstly, it agreed with Richard Hamilton's wish that the continuity of Duchamp's work be retained, and that his replica of Duchamp's work should be regarded as an 'echo of a masterpiece'. Secondly, the inscription does not form part of the concept of the work, but is a unique addition made by Duchamp in approval of Hamilton's completed work. It refers to both panels and is thus as relevant to the upper, undamaged panel as to the damaged lower panel, upon which it happened to be inscribed. If the inscription had been on the undamaged panel there would have been no question of removing it. Finally, the reconstruction consisted largely of the realisation of Hamilton's drawings, requiring minimal invention on the conservator's part. Minor variations resulting from the handling of the materials do not significantly alter the content of the work, which still essentially represents Duchamp's concepts as realised by Hamilton. Thus the continuity conveyed by the inscription remains valid.

A Colour Change During the Reconstruction

During the reconstruction an interesting colour change was observed. An early photograph of Hamilton's replica shows the paint of the 'Scissors' as uniform and light in tone. During the period up to the breaking of the glass, most of this area of lead white and cadmium yellow paint developed a grey discoloration, with a few, relatively small areas of the original yellow remaining. This change was originally assumed to be due simply to the visibility of the lead foil through the paint. However, some months after the glass shattered, it became apparent that the proportion of yellow to the grey discoloration was increasing again – the paint was reversing to its initial colour. Reversion had occurred most rapidly at the site of the cracks in the glass, and ultimately this led to the formation of small islands of grey which corresponded to the small broken pieces of glass.

The precise nature of the grey discoloration and the mechanism of its formation remain uncertain. It did not develop in other areas of lead white/cadmium yellow mixtures of paint where there were two layers of paint, with the first layer fully dry before the application of the second and the lead foil, rather than the single layer of paint of the 'Scissors'. The same type of discoloration developed in the test within a period of four months and it is also has occurred on the reconstruction. Reversion of the grey to yellow appears to involve oxidation. It occurs instantaneously upon treatment with hydrogen peroxide in

svinčevo belilo in kadmijeva rumena in je bila barva nanešena v dveh plasteh tako, da je bila prva plast popolnoma suha, preden je bila čez njo nanešena druga plast in svinčena folija, ne pa le ena plast barve kot pri "Škarjah". Do enakega razbarvanja je pri poskusu prišlo po štirih mesecih, pojavilo pa se je tudi na rekonstrukciji. Videti je, da do reverzije sive nazaj v rumeno pride ob oksidaciji. Nastopi v trenutku pri obdelavi z vodikovim peroksidom v dietiletru, prav tako pa tudi spontano ob izpostavitvi zraku; popolna reverzija v rumeno traja le kaki dve minuti. Sprememba potemtakem ne more biti optični učinek, kot na primer večja prozornost barve. Preiskava testnih vzorcev je pokazala, da se je siva barva pojavila na mestih, kjer sta se tesno stikali svinčena folija in mokra barva. Na mestih razbarvanja je bila folija v stiku z barvo na pogled svetleča in malce razjedena.

Najbolj očitna razlaga pojava, zakaj pride do sive ali črne barve pri barvnih mešanicah s svinčevim belilom in kadmijevo rumeno, bi se zdela razlaga, da kadmijeva rumena reagira ali s svinčevim belilom ali s svinčeno folijo, pri čemer se tvori črn svinčev sulfid. Le-ta se ob delovanju vodikovega peroksida pretvori v bel svinčev sulfat, ne bi pa pričakovali, da do takega oksidacijskega beljenja pride že ob stiku z zrakom. Mnogi od starejših avtorjev o kadmijevih pigmentih prav zaradi te težave svarijo pred tem, da bi jih mešali s svinčevim belilom [5]. Postopek nastanka sive barve je po vsej verjetnosti bolj zapleten; nedvomno se zdi, da pride do neke mere redukcije svinčene folije, kar sproži tvorbo svinčevih ionov (Pb^{2+}), ki lahko reagirajo s sestavinami oljnega medija in tvorijo svinčeva mila. Izključiti ne moremo tudi izločanja čiste kovine. Ne glede na vzrok razbarvanja pa se zdi, da le-to ni edinstvena lastnost materialov in tehnik, ki jih je izbral Hamilton, saj do enake spremembe prihaja na naši rekonstrukciji, v še večji meri pa je do nje prišlo, kot kaže, na Duchampovem originalu.

Sklep

Ko je bila rekonstrukcija leta 1986 dokončana, je Hamilton najprej menil, da bi jo morali pred ponovno razstavitvijo kako leto pustiti, da bi nova podloga iz svetleče svinčene folije lahko začela korodirati in bi se tako ujemalo s folijo na zgornji plošči, ki ima lisasto, motno mat površino in razjede belega svinčevega karbonata. Potem pa se je čez nekaj mesecev odločil, da se delo lahko razstavi že v svojem prvem letu. Danes, osemnajst let pozneje, je edini znak staranja folije rahla neenakomerna motnost in mat kvaliteta površine;

diethyl ether, and also spontaneously on exposure to air: full reversion to yellow takes a matter of only two minutes or so. The change cannot, therefore, be an optical effect, like increased transparency of the paint. Examination of the test samples indicated that the grey colour was observed where there was good contact between the lead foil and the wet oil paint. Where there was discoloration, the foil in contact with the paint appeared bright and slightly etched.

The most obvious explanation for the development of a grey or black colour in cadmium yellow/lead white paint mixtures would involve the formation of black lead sulphide by reaction of cadmium yellow with either the lead white or lead foil. This would be converted to white lead sulphate by hydrogen peroxide, but oxidative bleaching of this kind would not be expected to occur simply on exposure to air. Several early writers on cadmium pigments warn against mixing them with lead white because of this problem [5]. The formation of the grey colour is likely to involve more complex processes than this; certainly there seems to be some reduction of the lead foil leading to the production of lead ions (Pb^{2+}), which can react with components of the oil medium to form lead soaps. The deposition of pure metal cannot be excluded. Whatever its cause, it seems that the discoloration is not a unique feature of Hamilton's particular materials and technique: the same type of change is occurring in our reconstruction and appears to have occurred to a greater extent on Duchamp's original.

Conclusion

When the reconstruction was completed in 1986, Hamilton at first thought that it should be left for about a year before being displayed again, so that the new shiny lead foil backing had time to start corroding and match the foil on the upper panel, with its patchy, dull matt surface and white lead carbonate corrosion. However, some months later, he decided that the work could be displayed during this initial year. Today, eighteen years on, the only signs of ageing of the foil are a slight uneven dulling and mattness of the surface, with no white corrosion. The manufacturers of the lead suggested this could be due to tinned lead having been supplied instead of pure lead, as Hamilton used, but analysis we had carried out showed it to be pure lead.

The reason for the very slow ageing process would appear to be that the new lower panel has always been in a relatively 'clean' museum environment, compared with Hamilton's replica, which travelled for eight years, being exposed to various environments.

belih razjed nima. Proizvajalci svinca so kot možen vzrok navedli, da bi do tega lahko prišlo zaradi dobave zlitine svinca in kositra, in ne čistega svinca, kakršnega je uporabil Hamilton, vendar so naše analize pokazale, da je šlo za čist svinec.

Zdi se, da bi razlog za tako počasno staranje utegnil biti ta, da je bila nova spodnja plošča vedno v relativno "čistem" muzejskem okolju v primerjavi s Hamiltonovo repliko, ki je osem let potovala in bila s tem izpostavljena različnim okoljem.

Hamilton si želi, naj bi pospešili potek korozije, da bi se ujemala z zgornjo ploščo. Pred nekaj leti smo tako izvedli več poskusov na koščkih svinčene folije, ki nam je ostala od rekonstrukcije. Pri tem smo ustvarili omejena kisla okolja, ki so hitro pripeljala do nastanka belega svinčevega karbonata. Vendar pa ni bilo mogoče nadzorovati stopnje in razširjenosti korozije, čeprav je do nje prišlo. Zato smo se odločili, da bomo poskušali posnemati njen videz. Z nadaljnjimi poskusi smo ugotovili, da to lahko dosežemo z zelo redko "barvo" iz belega svinčevega pigmenta v mediju mastiksove smole, ki smo jo z raznimi tehnikami nanesli na površino s čopiči. Pri tem je bilo pomembno, da nismo uporabili nobenih novih materialov. S preizkusi moramo še ugotoviti, če se lahko zadovoljivo približamo tudi videzu površine folije na mestih, kjer ni bele razjede.

Razmišljali smo o tem, da bi simulirali starost za razstavo ob odprtju galerije Tate Modern leta 2000. O tem smo se posvetovali s kustosi in njihovo stališče je bilo, da glede na to, da se Hamiltonova replika zelo razlikuje od Duchampovega originala, odstopanje na naši rekonstrukciji ni bistvenega pomena in da naj zdaj nič več ne delamo na njej. A hkrati se je pojavil pomislek, da če smo želeli poustvariti *Steklo* iz šestdesetih let 20. stoletja – kar je v bistvu bil naš namen – , potem je potvarjanje starosti povsem sprejemljivo in še več, celo zaželeno. Obenem pa so bili mnenja, da glede na to, da je šlo pri spodnji plošči bolj za rekonstrukcijo kot za konservatorski restavratorski poseg, obstajajo močni argumenti za to, da smo glede tega odkriti in pustimo, da se razlika v starosti plošč jasno vidi. Tega vprašanja do danes še niso razrešili. Kot nam je znano, je Hamilton ponovno sprožil to vprašanje in (v času tega pisanja) razprave o tem še potekajo.

To izpostavi še eno zanimivo etično vprašanje. Ko so *Veliko steklo* po naši rekonstrukciji prvič razstavili, je bila rekonstrukcija omenjena v podpisu s stavkom: "Steklo spodnje plošče se je leta 1984 zdrobilo; leta 1985 je bilo rekonstruirano tako, da je vsebovalo napis z replike iz leta 1965." Z leti pa je bil ta podatek iz podpisa opuščen.

Hamilton is anxious for the corrosion process to be speeded up so as to match the upper panel. Some years ago, we did carry out tests on pieces of lead foil left over from the reconstruction. This was done by creating localised acidic environments, which produced the white lead carbonate very rapidly. However, although the corrosion was produced, it was not possible to control its extent and distribution. It was therefore decided to try and simulate its appearance. In further tests, we found that this could be achieved by making a very lean 'paint' of white lead pigment and mastic resin medium, applied to the surface with brushes using various techniques. Importantly, no new materials were introduced. Tests have still to be carried out to see if the appearance of the surface of the foil, where there is no white corrosion, can also be matched satisfactorily.

We considered simulating the ageing for the display at the opening of Tate Modern in 2000. The Curators were consulted about this, and their view then was that, as Hamilton's replica is very different from Duchamp's original, the difference on our reconstruction did not really matter and that we should not do any more work on it. However, the point was raised that, if we had aimed to recreate the *Glass* of the 1960s – which essentially we had – then falsifying the age is quite acceptable and, indeed, desirable. But it was also thought that, as the lower panel had been reconstructed rather than conserved, then there is a strong case for being frank about this through allowing the difference in the ages of the panels to be apparent. To date, this question has not really been resolved. We understand that Hamilton has raised this again and that (at the time of writing) discussions are taking place.

This also raises another interesting ethical issue. When the *Large Glass* first went on display after our reconstruction, this was referred to on the label with the sentence: 'The glass of the lower panel shattered in 1984 and was reconstructed in 1985 incorporating the inscription from the 1965 replica.' However, over the years this information has been dropped from the label.

Zahvale

Zahvaljujemo se: Richardu Hamiltonu za njegovo pomoč in sodelovanje. Kolegom, ki so v tistem obdobju delali na Oddelku za konservatorstvo restavratorstvo, posebno Dereku Pullenu za rekonstrukcijo "Okulistovih prič", Andrewju Durhamu za njegovo pomoč v začetnih fazah rekonstrukcije, Alanu Phenixu za rekonstrukcijo "Filtrov" in za delo na razbarvanju "Škarij", Michaelu Englandu in Petri Jaggard iz Fotografskega oddelka za fotografije. Osebju Philadelphia Museum of Art za njihovo pomoč pri proučevanju Duchampovega izvirnika in za fotografije. Timothyju Jealu (tehničnemu predstavniku podjetja Pilkington Glass Ltd.) za podatke o vzroku počenja stekla replike in za podarjeno novo stekleno ploščo.

Acknowledgements

Richard Hamilton for his help and cooperation. Colleagues working in the Conservation Department at the time, in particular Derek Pullen for the reconstruction of the 'Oculist Witnesses'; Andrew Durham for his help in the early stages of the reconstruction; Alan Phenix for the reconstruction of the 'Sieves' and work on the discolouration of the 'Scissors'; Michael England and Petra Jaggard in the Photographic Department for the photographs. Staff of the Philadelphia Museum of Art for their help when studying Duchamp's original work and for supplying photographs. Timothy Jeal (Technical representative, Pilkington Glass Ltd) for information as to the cause of the shattering of the replica glass and the gift of a new sheet of glass.

Viri in opombe

[1] Hamilton, R. (nedatirano) *The Bride Stripped Bare by Her Bachelors, Even Again*. Zapiski o "Zeleni škatli" z ilustracijami.

[2] [Duchamp, M.] (1934) "*Green Box":* ploščata škatla s 94 nevezanimi dokumenti (fotografijami, risbami in rokopisnimi zapiski za leta od 1911 do 1915). To so dokumenti, ki se nanašajo na *Veliko steklo*. Škatla dopolnjuje "*Steklo"* in je povsem prepletena z njegovim nastankom, tako da popolno razumevanje slike ni možno brez vsaj nekaj védenja o njeni vsebini. Omejena naklada 300 izvodov, podpisanih Rose Sélavy, kar je bil Duchampov psevdonim ob tej priložnosti (brez založnika, Pariz). Še 79 zapiskov je bilo objavljenih leta 1967 (*"White Box"*). Glej tudi Duchamp, M. (1960) *The Bride stripped Bare by her Bachelors, even: a typographic version, by Richard Hamilton, of Marcel Duchamp's Green Box*, Heard Hamilton, G. (prev.) (Lund, Humphries & Co., London).

[3] Alley, R. (1981) *Catalogue of the Tate Gallery's Collection of Modern Art, other than Works by British Artists*, Tate Gallery, London, 185–190.

[4] Schweig, B. (1973) *Mirrors – A Guide to the Manufacture of Mirrors and Reflecting Surfaces*, Pelham Books, London.

[5] Ward, H.W. Dudley (1927), Journal of Oil and Colour Chemists Association X, OCCA, United Kingdom, 4.

References and Notes

[1] Hamilton, R. (No date) *The Bride Stripped Bare by Her Bachelors, Even Again*. An illustrated record of the 'Green Box'.

[2] [Duchamp. M.] (1934) The '*Green Box*': a flat case containing 94 loose documents (photographs, drawings and manuscript notes of the years 1911–15). These are documents which surround the 'Large Glass'. The Box supplements the "*Glass"* and is fully integrated into its development so that a complete appreciation of the painting is impossible without some knowledge of its contents. Limited edition of 300, signed by Rrose Sélavy, a pseudonym used by Duchamp on occasion (no publisher, Paris). A further 79 notes were published in 1967 (the *'White Box'*). See also Duchamp, M. (1960) *The Bride stripped Bare by her Bachelors, even: a typographic version, by Richard Hamilton, of Marcel Duchamp's Green Box*, Heard Hamilton, G. (Trans.), Lund, Humphries & Co., London.

[3] Alley, R. (1981) *Catalogue of the Tate Gallery's Collection of Modern Art, other than Works by British Artists*, Tate Gallery, London, 185–190.

[4] Schweig, B. (1973) *Mirrors – A Guide to the Manufacture of Mirrors and Reflecting Surfaces*, Pelham Books, London.

[5] Ward, H.W. Dudley (1927), Journal of Oil and Colour Chemists Association X, OCCA, Velika Britanija, 4.

Izbrana bibliografija

▪ Hamilton, R. (1982) *Collected Works 1953–1982*, Thames and Hudson, London, 210–235.
▪ Golding, J. (1973) *Marcel Duchamp: 'The Bride Stripped Bare by her Bachelors, Even'*, Allen Lane, London.
▪ Adcock, C.E. (1983) *Marcel Duchamp's Notes from the Large Glass: An N-Dimensional Analysis*, Ann Arbor, U.M.I. Research Press.
▪ Duchamp, M. (1975) *The Essential Writings of Marcel Duchamp* (ur. Sanouillet, M. in Peterson, E.), Thames and Hudson, London.
▪ Alexandrian, S. (1977) *Marcel Duchamp*, Bonfini Press, Naefels, 28–70.

Selected Bibliography

▪ Hamilton, R. (1982) *Collected Works 1953–1982*, Thames and Hudson, London, 210–235.
▪ Golding, J.(1973) *Marcel Duchamp: 'The Bride Stripped Bare by her Bachelors, Even'* , Allen Lane, London.
▪ Adcock, C.E. (1983) *Marcel Duchamp's Notes from the Large Glass: An N-Dimensional Analysis*, Ann Arbor, U.M.I. Research Press.
▪ Duchamp, M. (1975) *The Essential Writings of Marcel Duchamp* (Edit. Sanouillet, M. and Peterson, E.), Thames and Hudson, London.
▪ Alexandrian, S. (1977) *Marcel Duchamp*, Bonfini Press, Naefels, 28–70.

Raziskave Rafaelovih slik v londonski Narodni galeriji z infrardečo reflektografijo

Infrared Examination of Paintings by Raphael at the National Gallery, London

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POVZETEK: **V pripravi na razstavo *Raphael: from Urbino to Rome (Rafael: Od Urbina do Rima)* je bilo vseh devet Rafaelovih slik iz Narodne galerije v Londonu pregledanih z infrardečo reflektografijo. Predstavljamo nekaj najbolj zanimivih rezultatov. Prikazana je Rafaelova uporaba naluknjanih kartonov kot osnove za podrisbo na slikah *Vitezove sanje* in *Sv. Katarina*. Razpravljamo o prepoznavanju materiala za podrisbo pri dveh majhnih slikah Marije z detetom, pri sliki *Mondovo Križanje* pa obstajajo dokazi za uporabo različnih materialov za podrisbo na isti sliki. *Ansideijeva Madona* kaže več različnih metod za prenos risbe na tablo.**

ABSTRACT: In preparation for the exhibition *Raphael: from Urbino to Rome* all nine of the paintings by Raphael at the National Gallery were examined using infrared reflectography. Some of the most interesting results of this work are presented. Raphael's use of pricked cartoons as the basis for the underdrawings of the *Vision of a Knight* and *Saint Catherine* is shown. The identification of the underdrawing material in the two small Virgin and Child paintings is discussed while the *Mond Crucifixion* provides evidence of the use of different underdrawing materials in the same painting. Finally the *Ansidei Madonna* reveals several different methods for transferring the design to the panel.

Ključne besede:
infrardeč;
reflektografija;
podrisba;
karton;
Rafael.

Keywords:
infrared;
reflectography;
underdrawing;
cartoon;
Raphael.

Uvod

Narodna galerija v Londonu je ponosna, da ima devet zelo lepih Rafaelovih slik, ki so dragocen primer različnih vrst dela v njegovem zgodnjem obdobju, in sicer majhna nabožna dela in posvetna dela in tudi oltarne kose. Že mnogo let so središče tehničnega pregledovanja v galeriji [1–10]: ko se je Joyce Plesters udeležila Princetonskega simpozija o Rafaelu leta 1983, je lahko obravnavala podrisbe za sedem slik. Raziskala jih je s pomočjo infrardečih fotografij in opisala raziskavo o uporabljenih materialih in slikarskih tehnikah. Priprave na razstavo v Narodni galeriji v Londonu, Raphael: from Urbino to Rome (Rafael: Od Urbina do Rima (20. oktober 2004 – 16. januar 2005) so spodbudile nove raziskave, tudi uporabo infrardeče reflektografije pri pregledu vseh slik, med njimi najnovejše pridobitve, "*Madone z nageljni*". V tem članku je na kratko opisano, kako v londonski Narodni galeriji izvajajo preiskave z infrardečo reflektografijo, sledi pa razprava o nekaterih zanimivih rezultatih nedavnih raziskav.

Introduction

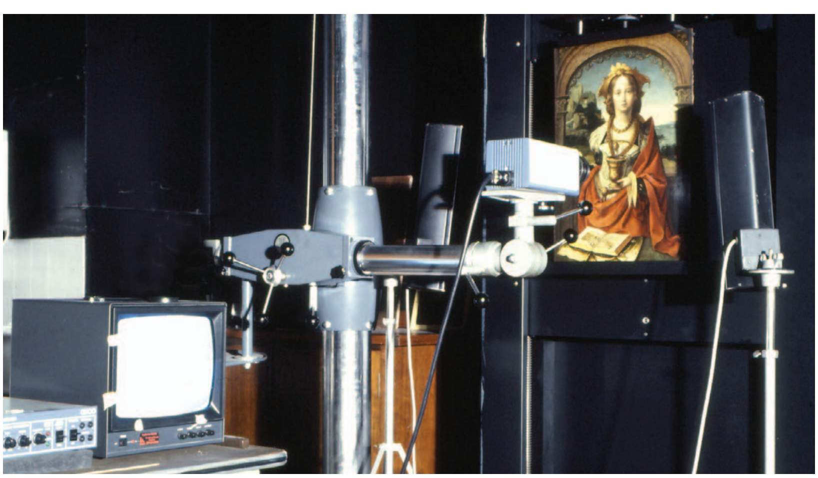
The National Gallery in London is particularly fortunate in possessing nine, very beautiful paintings by Raphael, which between them provide a valuable sample of different types of work he was pursuing in his early career, including as it does small devotional and secular works as well as large altarpieces. They have been a focus of technical examination at the Gallery for many years [1–10]: when Joyce Plesters addressed the Princeton Raphael Symposium in 1983 she was able to discuss the underdrawing of seven of the paintings, which she had studied using infrared photographs, as well as describing research on the materials and painting techniques used. Preparations for the exhibition at the National Gallery, Raphael: from Urbino to Rome (20th October 2004 – 16th January 2005) provided the stimulus for new research, including the examination using infrared reflectography of all the paintings, among them the newest acquisition, the *"Madonna of the Pinks"*. This paper will briefly describe how infrared examinations are conducted at the Gallery and then discuss some of the interesting results of the recent studies.

Oprema

Oprema, uporabljena za infrardečo reflektografijo (slika 1), je sistem Hamamatsu C2400 z infrardečo vidikonsko cevjo serije N2606. Če slika ni prevelika, jo prinesemo v posebni studio v Restavratorskem oddelku Narodne galerije, vzamemo iz okvirja in namestimo na električno slikarsko stojalo, ki ga je mogoče premikati v vodoravni in navpični smeri glede na vidikon in luči ter tako opraviti celovit pregled. Vi-

Equipment

The equipment used for infrared reflectography (Figure 1) is a Hamamatsu C2400 system containing an N2606 series infrared vidicon tube. Provided the painting is not too large, it is brought to a special studio in the National Gallery Conservation Department, removed from its frame and installed on an electrically operated



Slika 1. Oprema za infrardečo reflektografijo v Narodni galeriji. © The National Gallery, London.

Figure 1. The equipment for infrared reflectography at the National Gallery. © The National Gallery, London.

dikon, opremljen s filtrom Kodak 87A, ki blokira vso vidno svetlobo, pritrdimo na nepremičen stativ pred sliko. Osvetlitev dajeta infrardeči žarnici Philips IRK 13713X L8 v po meri narejenem ohišju, ki ju napaja za ta namen narejen reostat pri zelo nizki napetosti. Prednosti posebnih infrardečih luči, kakršne so v uporabi v Narodni galeriji, so, da oddajajo manj vidne svetlobe, ki bi tekmovala z infrardečo, da jih je lažje nadzorovati in so manj vroče. Za zapis rezultatov preiskave se reflektograme pretvori v digitalizirano obliko in shrani na računalnik za kasnejšo sestavo v mozaike infrardečih reflektogramov. Mozaičenje se izvede s programsko opremo, imenovano VIPS-ip, ki jo je razvila galerija. Z njo je združevanje posameznih reflektogramov hitro in enostavno, omogoča pa tudi razlike pri nivojih svetlosti reflektrogramov, ki se usklajujejo, nastavitev za odpravo geometričnih popačitev in izboljšavo ostrine in kontrasta. Ta program je mogoče brezplačno naložiti [11].

Študija Rafaelovih del

Za študijo Rafaelovih del je bila vsaka razstavljena slika iz Narodne galerije sistematično pregledana z vidikonom in celoviti infrardeči reflektogramski mozaiki so bili narejeni za vse, razen za *Portret papeža Julija* (NG 27) in veliki oltarni sliki, *Križani Kristus z Marijo, svetniki in angeli (Mondovo Križanje)* (NG 3943) iz okoli l. 1502–3 ter *Madono z detetom s sv. Janezom Krstnikom in sv. Nikolajem iz Barija (Ansideijevo Madono)* (NG 1171) iz l. 1505, za kateri so bili narejeni detajli zanimivih predelov. Zanimivo je bilo ugotoviti, da je infrardeča reflektografija dala nove in drugačne rezultate celo za dela, za katera so bile že narejene domnevno izredno jasne infrardeče fotografije.

1 Uporaba kartonov

Eden takih primerov je slika *Vitezove sanje* (NG 213, slika 2). Naslikana je večinoma s pigmenti, skozi katere infrardeče sevanje z lahkoto prehaja, kot so lapis lazuli (naravni ultramarin), cinober in karmin. Edini za infrardečo fotografijo težavni predeli so zeleni: naslikani so z zeleno bakreno patino, ki absorbira infrardeče sevanje uporabljenih valovnih dolžin in se prikaže kot temna lisa, toda pri figurah in krajini v ozadju je dobro vidna risba. Za to risbo se je ohranil karton, ki je bil naluknjan za prenos, torej je pri podrisbi očitno treba iskati sledi pik *(spolveri)* črnega pigmenta v prahu, običajno oglja, ki ostanejo po prenosu risbe s prašenjem. (Muslinasto vrečico z ogljem v prahu se pritiska po naluknjanem kartonu, nameščenem na priprav-

easel which can be moved horizontally and vertically in relation to the vidicon and lights, allowing full scans to be made. The vidicon, which is fitted with a Kodak 87A filter to block all visible light, is mounted on a sturdy tripod in front of the painting. Lighting is provided by two Philips IRK 13713X L8 infrared lamps in custom-made housings, run from a purpose-built rheostat at very low voltages. The advantages of special infrared lamps like those used at the National Gallery are that they give off less visible light to compete with the infrared, are more controllable and are less hot. To record the results of the examination, the reflectograms are digitised and stored on a computer for later assembly into infrared reflectogram mosaics. Mosaicing is carried out using software developed at the Gallery called VIPS-ip; this not only offers a very quick and easy way of joining the individual reflectograms, but also allows differences in lightness levels between reflectograms to be balanced, geometric distortions adjusted, and sharpness and contrast improved. This software is available free to download [11].

The Raphael Study

For the Raphael study, each of the National Gallery paintings in the exhibition was systematically examined with the vidicon and full infrared reflectogram mosaics made of all except the *Portrait of Pope Julius* (NG 27) and the two big altarpieces, *The Crucified Christ with the Virgin Mary, Saints and Angels (the Mond Crucifixion)* (NG 3943) *of about 1502–3, and The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (the Ansidei Madonna)* (NG 1171) of 1505, for which details of interesting areas were made. It was interesting to find that, even with paintings for which apparently excellently clear infrared photographs had been produced, the infrared reflectography produced new and different results.

1 The Use of Cartoons

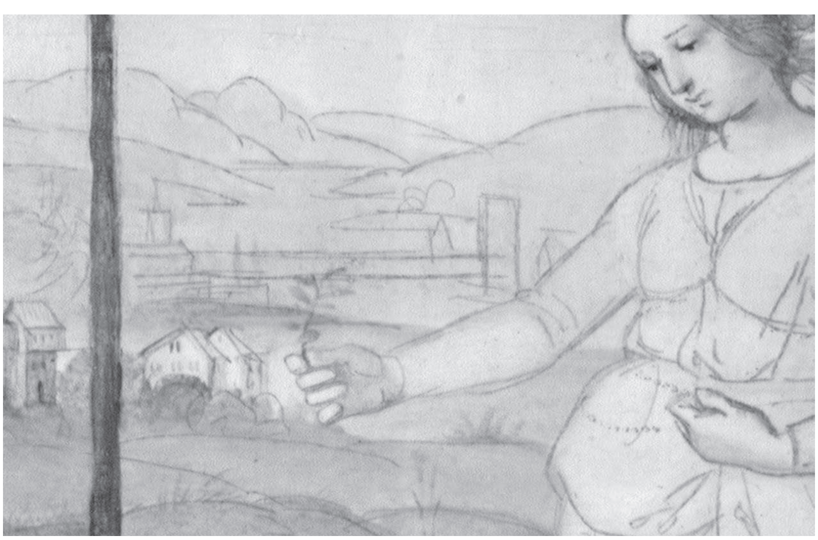
One such case is the *Vision of a Knight* (NG 213, Figure 2). It is painted using mostly pigments that are easily penetrated by infrared radiation, such as lapis lazuli (natural ultramarine), vermilion and red lake. The only problem areas for the infrared photograph are the greens: these are painted with verdigris, which absorbs infrared radiation of the wavelengths used, and appear dark, but in the figures and background landscape one sees a good image of the drawing. There is a surviving cartoon for this painting, which has been pricked for transfer, so the obvious things to look for in the underdrawing are traces of the spots *(spolveri)* of powdered black pigment, com-

Slika 2. Rafael, *Vitezove sanje* (London, The National Gallery, NG 213), okoli 1504. Olje na topolovini, 17,5 x 17,3 cm. © The National Gallery, London.

Figure 2. Raphael, *Vision of a Knight* (London, The National Gallery, NG 213), about 1504. Oil on poplar, 17.5 x 17.3 cm. © The National Gallery, London.

ljeno tablo ali drugo površino. Na tabli se risba pokaže kot niz pik.) Ko je Joyce Plesters leta 1983 razpravljala o sliki, ni mogla najti nobenega dokaza za prašenje in je morala zaključiti, da je bil karton naluknjan kasneje iz kakega drugega vzroka. Novi infrardeči reflektogramski mozaik pa povsem jasno kaže, da podrisba za *Vitezove sanje* temelji na prašenju. Slika 3 je detajl infrardečega reflektogramskega mozaika, ki kaže risbo za pokrajino na desni; prašenje je jasno vidno. Kot običajno so bile pike črnega pigmenta v prahu povezane s tekočim materialom, ki je nekatere od njih ujel, čeprav jih je večina izginila. Po povezovanju pik je Rafael podrisbo vedno dodeloval in prostoročno dodajal dodatke, kot so šrafure za sence. Na tem detajlu je tudi nekaj prostoročnih dodatkov: očarljiv prostoročno skiciran obris na desnem bregu reke nad mostom, domnevno namenjen za označitev grmovja ali drevja (čeprav ni bilo nikoli naslikano); skupina stavb z visokim stolpom takoj na levi strani drevesa, v isti ravni kot most. Zanimivo je, da sta oba dodatka tudi na kartonu, narisana, vendar ne naluknjana – in da se tudi ponekod drugod pojavlja enako. Med sliko in kartonom je seveda kar nekaj razlik: na primer pri figuri Kreposti na levi je okrašeni ovratnik z risbe na sliki poenostavljen, njegovi črni robovi na reflektrogramskem mozaiku jasno kažejo, da pokrivajo podrisbo bogateje okrašenega ovratnika, vendar je ne skrivajo popolnoma. Zdi se, da je bila zamenjava mostu pod levo roko Kreposti s tremi konjeniki zgodnja odločitev. Infrardeča reflektografija ne kaže nobenega znaka mostu, torej ta ali ni bil prenesen ali pa so bili *spolveri* odstranjeni, ne da bi bili fiksirani z mokro črto.

monly charcoal, remaining from the transfer of the image by pouncing. (A small muslin bag containing powdered charcoal is pressed over the pricked cartoon positioned on the prepared panel or other surface. The design appears on the panel as a series of dots.) When Joyce Plesters discussed the picture in 1983 she had been unable to find any evidence of pouncing and was forced to conclude that the cartoon had been pricked later for some other reason. The new infrared reflectogram mosaic, however, shows quite clearly that the underdrawing for the *Vision of a Knight* is based on pouncing. Figure 3 is a detail from the full infrared reflectogram mosaic showing the drawing for the landscape on the right; it shows the pouncing very clearly. As usual the dots of powdered black pigment have been joined using a liquid material which has trapped some of them, although many have been brushed away. After joining the dots, Raphael always elaborated his underdrawings further, adding such things as hatching for shadows freehand. In this detail there are also several freehand additions: a lovely free squiggle on the right bank of the river above the bridge, presumably intended to signify bushes or trees (although they were never painted); and a group of buildings with a tall tower just to the left of the tree, level with the bridge. Interestingly, both these additions are also present in the cartoon, drawn but not pricked – and there are several instances of the same thing happening elsewhere. There are, of course, several differences between the painting and the cartoon: for example, in the figure of Virtue on the left, the ornate collar in the drawing was simplified in the painting, its black edges showing clearly in the reflectogram mosaic, covering, but not obscuring completely, the



Slika 3. Rafael, *Vitezove sanje* (London, The National Gallery, NG 213), okoli 1504. Detajl infrardečega reflektogramskega mozaika, ki prikazuje pokrajino na desni. © The National Gallery, London.

Figure 3. Raphael, *Vision of a Knight* (London, The National Gallery, NG 213), about 1504. Detail from infrared reflectogram mosaic showing the landscape on the right. © The National Gallery, London.

Tudi na dveh drugih slikah iz Narodne galerije so jasno vidni dokazi, da sta bili preneseni s kartona: *Pot na Kalvarijo* (NG 2919; z oltarnega podstavka *oltarne slike Colonna*) in *Pridiga Janeza Krstnika* (NG 6480; z oltarnega podstavka Ansideijeve Madone) [1-5]. Pri obeh je z infrardečo reflektografijo vidna zelo detajlirana črtna risba, prenesena s kartona. Poleg črtne risbe so tudi prostoročne dodelave, na primer šrafiranje in navzkrižno šrafiranje za senčenje.

V Narodni galeriji v Londonu je še ena Rafaelova slika, za katero obstaja naluknjan karton: *Sveta Katarina* (NG 168, slika 4) [1–4]. Ko je Joyce Plesters preučevala infrardeče fotografije slike za princetonski simpozij, je povedala, da ima podrisba 'gladke tanke črte brez znakov pigmentnih pik *(spolveri)*'. Dejstvo, da je bil ta karton uporabljen za sliko iz Narodne galerije, je bilo veliko težje dokazati kot v primeru *Vitezovih sanj* in brez pomoči in velikodušnosti kustosov in znanstvenikov iz Louvra sploh ne bi bilo mogoče. Najprej smo preverili korelacijo med sliko in kartonom, in sicer tako, da smo kopijo figure na sliki odnesli v Francijo in jo položili prek risbe iz Louvra. Razen nagiba glave sta se obe tako natančno ujemali, da smo naredili še eno kopijo na papir, tokrat 'zemljevid' vseh luknjic na kartonu. To smo nesli v London in ko smo sliko ponovno pregledali z infrardečo reflektografijo, je bilo mogoče odkriti nekaj sledi pigmentnih pik *(spolveri)* (slika 5). Veliko bolj kot prisotnost nekaj pigmentnih pik *(spol-*

underdrawing of the more ornate collar. The replacement of the bridge under Virtue's left arm with three horsemen seems to have been an early decision. There is no sign of the bridge in infrared reflectography, so it was either not transferred at all or the *spolveri* were brushed away without being fixed with a wet line.

Two other pictures in the National Gallery also show clear evidence of having been transferred from cartoons: the *Procession to Calvary* (NG 2919; from the predella to the *Colonna Altarpiece*) and *John the Baptist Preaching* (NG 6480; from the predella to the *Ansidei Madonna)* [1-5]. In both, a very detailed linear drawing transferred from a cartoon is visible with infrared reflectography. In addition to the linear drawing, there are small freehand elaborations, for example hatching and cross-hatching for shadows.

Continuing the subject of cartoon transfer, there is another of Raphael's paintings in the National Gallery for which a pricked cartoon (in the collection of the Département des Arts Graphiques Musée du Louvre, Paris) exists: *Saint Catherine* (NG 168, Figure 4) [1–4]. When Joyce Plesters studied the infrared photographs of the picture for the Princeton Symposium, she reported that the underdrawing consisted of 'smooth, thin lines, with no sign of *spolveri*'. The fact that this cartoon was used for the National Gallery painting has been much more difficult to prove than was the case for the *Vision of a Knight* and would not have been possible at all without

Slika 4. Rafael, *Sv. Katarina* (London, The National Gallery, NG 168), okoli 1507. Olje na lesu, 72,2 x 55,7 cm. © The National Gallery, London.

Figure 4. Raphael, *Saint Catherine* (London, The National Gallery, NG 168), about 1507. Oil on wood, 72.2 x 55.7 cm. © The National Gallery, London.

Slika 5. **Rafael, *Sv. Katarina* (London, The National Gallery, NG 168). Detajl infrardečega reflektogramskega mozaika. © The National Gallery, London.**

Figure 5. Raphael, *Saint Catherine*, London, The National Gallery, NG 168). Detail from infrared reflectogram mosaic. © The National Gallery, London.

veri) **dokazuje uporabo kartona neovrgljivo dejstvo, da je vsako naluknjano linijo s kartona mogoče videti na podrisbi, celo tam, kjer je Rafael potem izvajal spremembe in barva ne sledi narisanim črtam. Zelo očiten je vozel na svetničini rami, ki se pojavlja, čeprav v poenostavljeni obliki, na podrisbi. Pri draperiji ob levi roki sv. Katarine je precej sprememb, na primer gube pri rumeni obrobi halje so na kartonu narisane v grobem vodoravno, naslikane pa padajo diagonalno proti levi. Z infrardečo reflektografijo je mogoče videti vodoravne črte s kartona, ki križajo risbo za gube, kakor so naslikane. Na dokončni sliki je Rafael dodal še nekaj gub, ker se obleka nekoliko pridviguje proti halji. Spremembe gub pri draperiji so bile narisane prostoročno: z infrardečo reflektografijo se kažejo linije risbe širše in temnejše od tistih, ki so prenesene s kartona; morda so**

the help and generosity of the curators and scientists at the Louvre. The correlation of sizes between the painting and the cartoon was tested first, by taking a tracing of the figure in the painting to France and laying it over the Louvre drawing. Apart from the angle of the head, the two were found to match so closely that a second tracing was made, this time a 'map' of all the pricked holes in the cartoon. This was brought back to London and when the picture was re-examined by infrared reflectography with the help of the 'map', it was possible to find a few traces of *spolveri* (Figure 5). Far more compelling as an argument for the use of the cartoon than the presence of a few *spolveri* is the fact that virtually every line in the cartoon that was pricked can be seen in the underdrawing, even where Raphael then went on to make changes so that the drawn lines are not followed in the paint. Most

narisane z drugim materialom, morda pa so v strukturi plasti barve bližje površju.

obvious is the knot on the Saint's shoulder, which does appear, although in a truncated form, in the underdrawing. In the drapery beside Saint Catherine's left hand there are a number of changes; for example, the folds in the yellow lining of the cloak are drawn roughly horizontal in the cartoon, but painted falling diagonally to the left. By infrared reflectography the horizontal lines from the cartoon can be seen crossing the drawing for the folds as painted. In the final painting Raphael added extra folds as the dress is pushed up slightly against the cloak. The changes in the drapery folds were underdrawn freehand: by infrared reflectography the lines of drawing appear broader and darker than those relating to the cartoon; possibly they are in a different material, or possibly they are closer to the surface within the layer structure of the paint.

2 Materiali, uporabljeni pri podrisbi

Pogosto se zastavlja vprašanje, kateri materiali so bili uporabljeni za podrisbo. Natančen odgovor je težko dati, ker je zelo redko na voljo primeren vzorec za analizo, in prepoznavanje večinoma temelji na tem, kakšne so videti črte na infrardečih posnetkih ali skozi barvo [3, 6]. Nekatere materiale je na ta način laže prepoznati kot druge. Na primer, pri črti tekoče barve ali črnila, nanesení s čopičem, se pogosto pojavi odebelitev tam, kjer je slikar odmaknil čopič s platna. To se pokaže na infrardečem reflektogramu in omogoča precej zanesljivo prepoznavanje tekočega medija. Takšne so črte, ki združujejo prašenje pri *Vitezovih sanjah*, risba pri *Sv. Katarini* pa ni tako lahko prepoznavna. Pri dveh slikah, pri *Madoni z nageljni* (NG 6596; slika 6) in *Garvaghovi Madoni* (NG 744; slika 8) pa podrisba sega prek barve na neposlikan rob in tako omogoča analizo. Slika 7 kaže črto podrisbe pri *Madoni z nageljni*, ki sega iz zelenega zastora na levem robu. Risba je narisana na podlogo (tanko rumenkasto plast oljne barve na gesso osnovi). Pri energetsko disperzijski analizi z rentgenskimi žarki v vrstičnem elektronskem mikroskopu

2 Materials Used for Underdrawing

The question of what material has been used for the underdrawing is frequently raised. It is one of the most difficult to answer accurately since it is very rare for a suitable sample to be available for analysis, so that most identifications rely on what the lines look like in the infrared images, or through the paint [3, 6]. Some drawing materials

Slika 6. Rafael, *Madona z nageljni* (London, The National Gallery, NG 6596), okoli 1506–7. Olje na lesu sadnega drevja, 28,8 x 22,9 cm. © The National Gallery, London.

Figure 6. Raphael, *Madonna of the Pinks* (London, The National Gallery, NG 6596), about 1506–7. Oil on fruitwood, 28.8 x 22.9 cm. © The National Gallery, London.

Slika 7. Rafael, *Madona z nageljni* (London, The National Gallery, NG 6596). Makro fotografija, ki kaže črto podrisbe s kovinskim svinčnikom na skrajnem levem neposlikanem robu. © The National Gallery, London.

Figure 7. Raphael, *Madonna of the Pinks* (London, The National Gallery, NG 6596). Macrophotograph showing a line of metalpoint underdrawing at the extreme left unpainted edge. © The National Gallery, London.

Slika 8. Rafael, *Marija z Jezusom in Janezom Krstnikom v otroških letih (Garvaghova Madona)* (London, The National Gallery, NG 744), okoli 1509–10. Olje na lesu, 38,9 x 32,9 cm. © The National Gallery, London.

Figure 8. Raphael, *The Madonna and Child with the Infant Baptist (The Garvagh Madonna)* (London, The National Gallery, NG 744), about 1509–10. Oil on wood, 38.9 x 32.9 cm. © The National Gallery, London.

(SEM–EDX) se je pokazalo, da gre za risbo s kovinskim svinčnikom, narejenim iz zlitine svinca in kositra; skoraj enaka sestava je bila ugotovljena pri risbi s kovinskim svinčnikom pri *Garvaghovi Madoni*. Risba s kovinskim svinčnikom je seveda mnogo tanjša kot s čopičem, toda ker je vidikon dovolj blizu površine slike, je črte mogoče jasno videti. Obe deli sta majhni – *Madona z nageljni* ima samo 28,8 x 22,9 cm – zaradi česar je izbira kovinskega svinčnika za podrisbo smotrna, čeprav je Rafael za podrisbo na zelo majhnih slikah uporabljal tudi tekoči medij, na primer pri *Vitezovih sanjah*. Niti pri *Madoni z nageljni* niti pri *Garvaghovi Madoni* ni bilo najti sledi prašenja. Črte, vidne z infrardečo reflektografijo, učinkujejo prosto in skicirano kot nekatere Rafaelove risbe na papirju, čeprav na nobeni od slik ni pomembnih sprememb pri figurah, tako da je morala biti kompozicija oblikovno dodelana, preden se je začelo risanje na table.

3 Rafaelov pristop k risbi

***Garvaghova Madona*, po času nastanka zadnja izmed slik, o katerih teče beseda, datira iz okoli l. 1509-10 in kaže številne vidike, značilne za Rafaelov pristop k risanju, posebej pomen geometrije in volumna (slika 9)**

are easier to identify in this way than others. For example, a line of liquid paint or ink applied with a brush will often make a blob where the brush was lifted up; this shows up in the infrared reflectogram and allows a reasonably secure identification of a liquid medium. This was the case for the lines joining up the pouncing in the *Vision of a Knight*, but the drawing in *Saint Catherine* is not so easy to identify. However, in two of the paintings, the *Madonna of the Pinks* (NG 6596; Figure 6) and the *Garvagh Madonna* (NG 744; Figure 8), the underdrawing extends beyond the paint onto an unpainted edge, allowing it to be analysed. Figure 7 shows a line of underdrawing in the *Madonna of the Pinks*, extending out from the green curtain at the left edge. The drawing has been applied on top of the priming (a thin, yellowish layer of oil paint over the gesso ground). On analysis by energy dispersive X-ray microanalysis in the scanning electron microscope (SEM–EDX), the drawing was found to be in metalpoint, made from an alloy of lead and tin; an almost identical composition was found for the metalpoint drawing of the *Garvagh Madonna*.

Metalpoint drawing is, of course, much more delicate than that made with a brush but, provided the vidicon is close enough to the surface of the painting, the lines can clearly be seen. Both of these works are

[1–4, 7–8]. Oval Marijinega obraza je skrbno izrisan in krivulji ličnic poudarjata volumen. Podobno je tudi glava Jezuščka narisana z vrsto krivulj, ki so kakor konture na zemljevidu ter poudarjajo obliko na pomembnih točkah: na vrhu glave, na vrhu čela, pri obrveh in bradi. Zelo tanko šrafiranje pomaga ustvarjati tridimenzionalnost sicer linearne risbe.

Podrisba pri *Madoni z nageljni* (slika 10) [1–3, 9] je podobna, čeprav svobodnejša v obravnavi kot pri *Garvaghovi Madoni*. Glava Jezuščka je narisana z enako mislijo na volumen in od srede njegovih prsi navzdol poteka črta. Tudi dolge, z enim zamahom izvedene krivulje pri zgornji polovici Marijinega telesa so del te težnje po volumnu in dajejo figuri telesnost, še preden so določeni lega rok in oblika prsi ter dodani detajli draperije in zapleteno šrafiranje za označitev senc. Vidni so tudi detajli, kot so členki rok, ki jih obdajajo majhne krivulje, kar je značilno za Rafaela.

***Mondovo Križanje* (NG 3943, slika 11) je sorazmerno zgodnje delo, naslikano okoli l. 1502–3, in je mnogo večje od vsega, o čemer smo govorili do zdaj, saj je skoraj tri metre visoko (283,3 x 167,3 cm) [1–3]. Podrisba je na mnogih mestih vidna pri navadni svetlobi in infrardeča fotografija jo odlično pokaže tam, kjer prodre skozi barvo. Na primer, Magdalenina rožnata draperija kaže preprosto črtno risbo, narisano jasno določljivo s tekočim medijem. Odsotnost večjih sprememb in preprosta, formulska narava risbe sta značilni za Rafaelove podrisbe s pomočjo kartona, toda kljub skrbnemu pregledu ni bilo mogoče najti nobenega**

small in scale – the *Madonna of the Pinks* is only 28.8 x 22.9 cm – which makes the choice of metalpoint for the underdrawing a reasonable one, although Raphael did use liquid underdrawing for very small paintings, as in the *Vision of a Knight*. No traces of pouncing could be found in either the *Madonna of the Pinks or the Garvagh Madonna* and the lines seen in infrared reflectography have the freedom and sketchy appearance of some of Raphael's drawings on paper, although there are no significant changes to the figures in either painting so the compositions must have reached an advanced stage of design before drawing on the actual panels began.

3 Raphael's Approach to Drawing

The *Garvagh Madonna*, which is the latest in date of all the paintings discussed here, dating from about 1509–10, shows a number of aspects which are typical of Raphael's approach to drawing, most particularly the importance to Raphael of geometry and volume (Figure 9) [1–4, 7–8]. The oval of the Virgin's face is carefully outlined and the curves for cheekbones drawn to emphasise volume. Similarly, the head of the Christ Child is drawn with a series of curves, like contour lines on a map, to stress the shape at significant points: the top of the head, the top of the forehead, the eyebrows and the chin. Very delicate hatching then helps to build up the three-dimensionality of the otherwise linear drawing.

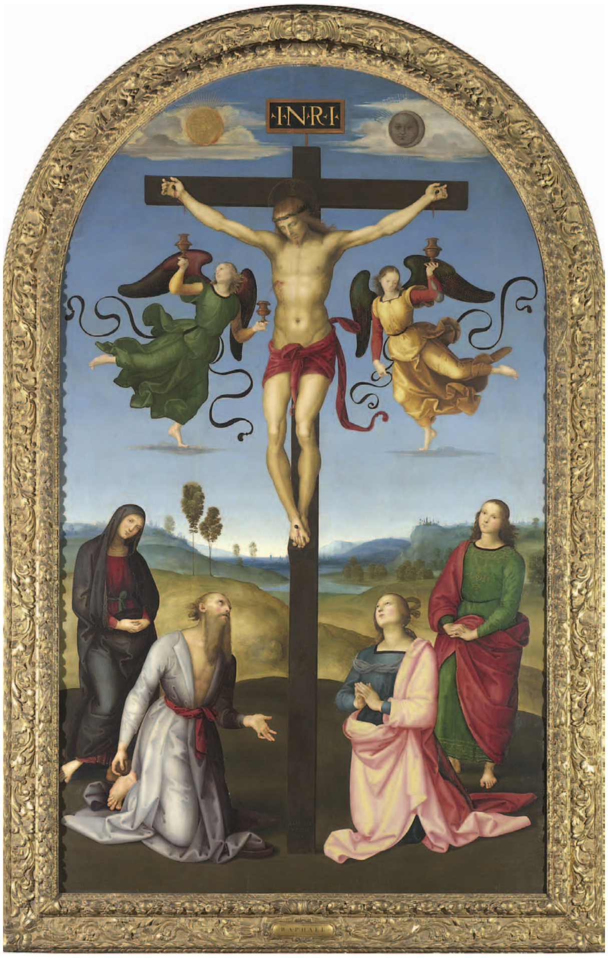
The underdrawing of the *Madonna of the Pinks* (Figure 10) [1–3, 9] is similar, although, if anything, freer in

Slika 9. Rafael, *Marija z Jezusom in Janezom Krstnikom v otroških letih (Garvaghova Madona)* (London, The National Gallery, NG 744). Detajl infrardečega reflektogramskega mozaika. © The National Gallery, London.

Figure 9. Raphael, *The Madonna and Child with the Infant Baptist (The Garvagh Madonna)* (London, The National Gallery, NG 744). Detail from infrared reflectogram mosaic. © The National Gallery, London.

Slika 10. Rafael, *Madona z nageljni* (London, The National Gallery, NG 6596). Detajl infrardečega reflektogramskega mozaika. © The National Gallery, London.

Figure 10. Raphael, *Madonna of the Pinks* (London, The National Gallery, NG 6596). Detail from infrared reflectogram mosaic. © The National Gallery, London.



Slika 11. **Rafael, *Križani Kristus z Devico Marijo, svetniki in angeli (Mondovo Križanje)* (London, The National Gallery, NG 3943), okoli 1502–3. Olje na topolovini, 283,3 x 167,3 cm. © The National Gallery, London.**

Figure 11. Raphael, *The Crucified Christ with the Virgin Mary, Saints and Angels (The Mond Crucifixion)* (London, The National Gallery, NG 3943), about 1502–3. Oil on poplar, 283.3 x 167.3 cm. © The National Gallery, London.

handling than that of the *Garvagh Madonna*. The Child's head has been drawn with the same concern for volume and a line runs down the centre of his chest. The long, sweeping curves in the Virgin's upper body are also part of this striving for volume, giving an overall bulk to the figure before the position of the arm and shape of the breast were refined and the details of the drapery added together with elaborate hatching to describe shadows. Also visible are details such as the knuckles of the hands, which are enclosed with little curved lines, a touch typical of Raphael.

The *Mond Crucifixion* (NG 3943, Figure 11) is a relatively early work, painted about 1502–3, and much larger in scale than anything so far discussed, standing almost three metres high (actual size 283.3 x 167.3 cm) [1–3]. Underdrawing is visible in normal light in many places and infrared photography produces excellent images of the underdrawing where the paint is penetrated. For example, the Magdalen's pink drapery shows simple linear drawing, clearly in a liquid medium. The lack of major changes and the simple, formulaic nature of the drawing are typical of Raphael's underdrawings made from cartoons, but in spite of careful examination, no evidence could be found of squaring or of registration lines for a cartoon and no pouncing was seen, so that the method used for transferring the design to the panel is still not known. For this picture, examination by infrared reflectography did not add a great deal to what was already known, except to highlight one interesting anomaly. In infrared reflectography some of the underdrawing clearly visible in normal light disappears, while other areas of underdrawing show clearly. Figures 12 and 13 show the left foot of the angel in green to the left of the figure of the Crucified Christ. In normal light, underdrawing can be seen all round the foot; but by infrared reflectography clear drawing for the toes can be seen, but the drawing does not continue up the leg. The fact that some of the underdrawing disappears in infrared reflectography and some does not, although all the underdrawing looks the same in normal light where visible, suggests that two different materials have been used: the one that disappears is probably iron gall ink, while the other is a carbon-containing black ink. The almost random choice of one or other material – both being used in the same figure sometimes, for example Christ, whose drawing 'disappears' in his arms and hands, but does not in his loin cloth or knees – suggests that the artist was not particular as to which black ink he used for the drawing of a particular area, but simply used whichever was nearest.

The *Ansidei Madonna* (NG1171; Figure 14) is another large panel (245 x 157 cm), dating from 1505 [1–3, 10]. It has been known for some time that there is a regular grid incised under the paint of the *Ansidei Madonna*, and it

Slika 12. **Rafael, *Križani Kristus z Devico Marijo, svetniki in angeli (Mondovo Križanje)* (London, The National Gallery, NG 3943). Detajl leve noge angela v zelenem. © The National Gallery, London.**

Figure 12. Raphael, *The Crucified Christ with the Virgin Mary, Saints and Angels (The Mond Crucifixion)* (London, The National Gallery, NG 3943). Detail of left foot of angel in green. © The National Gallery, London.

Slika 13. **Rafael, *Križani Kristus z Devico Marijo, svetniki in angeli (Mondovo Križanje)* (London, The National Gallery, NG 3943). Detajl infrardečega reflektogramskega mozaika leve noge angela v zelenem. © The National Gallery, London.**

Figure 13. Raphael, *The Crucified Christ with the Virgin Mary, Saints and Angels (The Mond Crucifixion)* (London, The National Gallery, NG 3943). Infrared reflectogram mosaic detail of left foot of angel in green. © The National Gallery, London.

dokaza o kvadratni mreži ali črtah za zaznamovanje lege kartonov, pa tudi prašenje ni bilo vidno, tako da je metoda, ki je bila uporabljena za prenos risbe na tablo, še vedno neznana. Pri tej sliki pregled z infrardečo reflektografijo ni dodal veliko novega k temu, kar je bilo že znano, je pa pokazal zanimivo anomalijo. Pri infrardeči reflektografiji del podrisbe, jasno viden pri običajni svetlobi, izgine, drugi predeli pa se jasno pokažejo. Sliki 12 in 13 kažeta levo nogo angela v zelenem na levi strani križanega Kristusa. Pri običajni svetlobi je mogoče videti podrisbo okrog celotne noge, pri infrardeči reflektografiji pa je jasno vidna risba za prste, ki pa se ne nadaljuje navzgor po nogi. Dejstvo, da del podrisbe pri infrardeči reflektografiji izgine, del pa ne, čeprav je celotna podrisba, kjer je vidna, videti enaka pri navadni svetlobi, navaja na misel, da sta bila uporabljena dva materiala: tisti, ki izgine, je verjetno železo-taninsko črnilo, drugo pa črno črnilo, ki vsebuje oglje. Skoraj naključna uporaba enega ali drugega materiala – obe sta včasih uporabljeni pri isti figuri, na primer pri Kristusu, kjer risba izgine pri rokah in dlaneh, ne pa pri ledveni prepasici ali kolenih – daje misliti, da umetnik ni izbiral, katero črno črnilo bo uporabil za risbo določenega dela, temveč je uporabil tisto, ki je bilo pri roki.

Ansideijeva Madona (NG 1171; slika 14) je druga velika tabla (245 x 157 cm), ki datira iz l. 1505 [1–3, 10]. Že nekaj časa je znano, da je pod barvo *Ansideijeve Madone* vrezana prava mreža in domnevalo se je, da se je ta mreža uporabljala za pomoč pri kopiranju risbe na tablo. Nedavne preiskave so vzbudile dvom o tej hipotezi, ki je vsekakor nekoliko neverjetna, saj so kvadrati preveliki, da bi bili uporabna vodila za kopiranje. Tudi tokrat infrardeče fotografije pomagajo pokazati

Slika 14. **Rafael, *Marija z Jezusom in sv. Janez Krstnik in sv. Nikolaj iz Barija (Ansideijeva Madonna)* (London, The National Gallery, NG 1171), 1505. Olje na topolovini, velikost table 245 x 157 cm. © The National Gallery, London.**

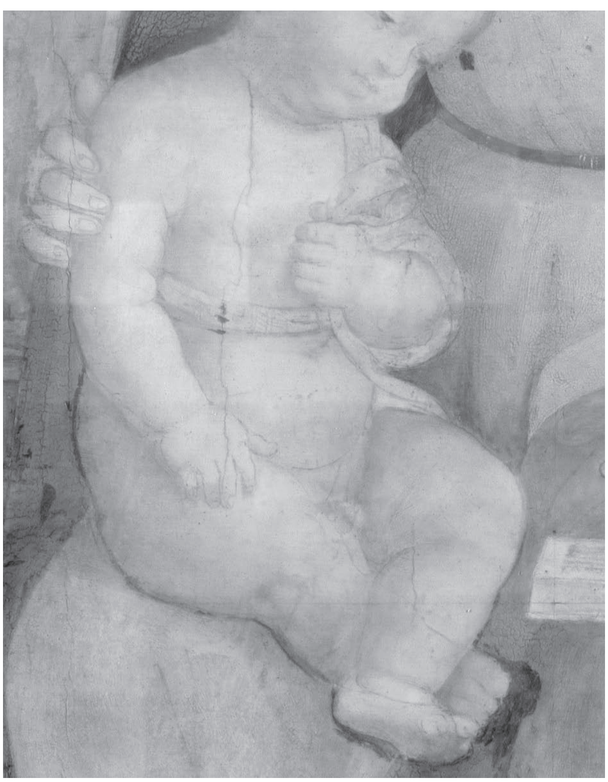
Figure 14. Raphael, *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansedei Madonna)* (London, The National Gallery, NG 1171), 1505. Oil on poplar, panel size 245 x 157 cm. © The National Gallery, London.


SALVE MATER CHRISTI

naravo podrisbe, ko odkrivajo risbo, ne nepodobno tisti z *Mondovega Križanja*, s preprostimi obrisi gub in draperije s tekočim medijem, vendar tukaj dodelano z nekaj šrafure. Jasni znaki prašenja so bili odkriti v skupini z Marijo in Jezusom; pike so bile združene, večina se jih je izbrisala in ostala je preprosta risba. Slika 15 je infrardeči reflektogramski mozaik detajla Jezusa in kaže preprosto linearno risbo, značilno za prenos s kartona, ter nekaj pigmentnih pik *(spolveri)* okoli njegovih rok in nog. Figure so bile, kot vedno pri Rafaelu, spremenjene: Jezusova glava je spremenjena in oči premaknjene, spremembe so tudi pri spodnjem delu njegovega telesa, kjer so bile spremenjene roka, dlan in noge. Nikjer na figuri sv. Janeza ni bilo mogoče najti pigmentnih pik *(spolveri)*, vendar je figura po slogu tako podobna Marijini, da zagotovo temelji na kartonu. Sv. Nikolaj iz Barija je drugačen. Podrisba (slika 16) je mnogo svobodnejša in na infrardečem reflektogramu so črte videti precej finejše. Risba na svetnikovem obrazu kaže Rafaelovo zanimanje za geometrijo in volumen, na primer pri krivuljah ličnic in strukturi nosu; podobna vrsta risbe je kasneje opazna pri *Garvaghovi Madoni*.

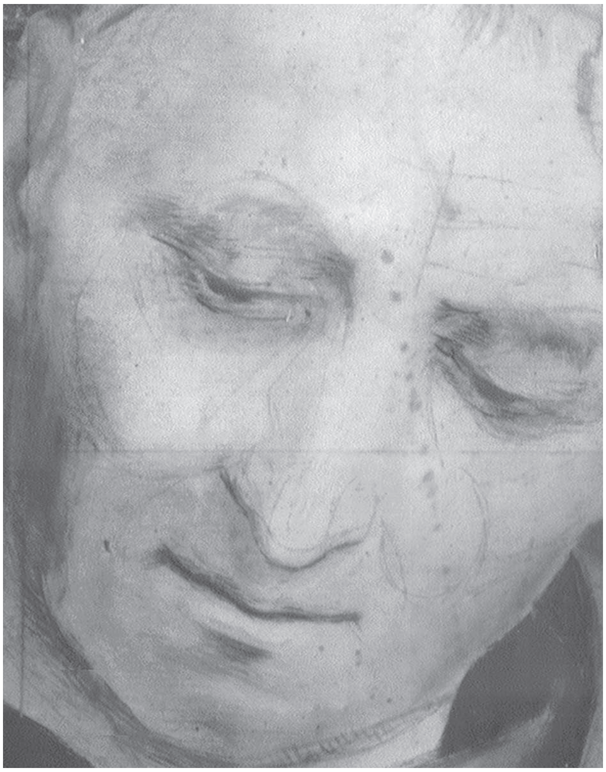
Zdi se torej, da je Rafael pri sestavi *Ansideijeve Madone* uporabil mešanico tehnik. Ključni figuri Marije

has been suggested that the grid was used to help copy a drawing onto the panel. However, recent investigations have cast doubt on this hypothesis, which in any case is somewhat improbable since the squares are rather too large to be useful guides to copying. Again, infrared photographs are helpful to show the nature of the underdrawing, revealing drawing not dissimilar to that seen in the *Mond Crucifixion*, with simple outlines of folds in the drapery, in a liquid medium, but here elaborated with some hatching. Clear signs of pouncing were found in the Virgin and Child group; the dots have been joined and most of them brushed away leaving the simple drawing. Figure 15 is an infrared reflectogram mosaic detail of the Child, showing the simple linear drawing typical of a transfer from a cartoon and some of the *spolveri* around his hands and legs. As ever with Raphael, there are changes to these figures: the Child's head has been changed and his eyes moved, and in the lower half of his body the arm and hand and the legs have been changed. No spolveri could be found anywhere in the figure of Saint John, but the underdrawing is so similar in style to that for the Virgin that it is certain he too was based on a cartoon. Saint Nicholas of Bari is different. The underdrawing (Figure 16) is much freer and the lines look much finer in the infrared reflectogram. The drawing



Slika 15. Rafael, *Marija z Jezusom in sv. Janez Krstnik in sv. Nikolaj iz Barija (Ansideijeva Madonna)* (London, The National Gallery, NG 1171). Detajl infrardečega reflektogramskega mozaika, ki kaže Jezusa. © The National Gallery, London.

Figure 15. Raphael, *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansedei Madonna)* (London, The National Gallery, NG 1171). Infrared reflectogram mosaic detail showing the Christ Child. © The National Gallery, London.



Slika 16. Rafael, *Marija z Jezusom in sv. Janez Krstnik in sv. Nikolaj iz Barija (Ansideijeva Madonna)* (London, The National Gallery, NG 1171). Detajl infrardečega reflektogramskega mozaika, ki kaže glavo sv. Nikolaja iz Barija. © The National Gallery, London.

Figure 16. Raphael, *The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansedei Madonna)* (London, The National Gallery, NG 1171). Infrared reflectogram mosaic detail showing the head of Saint Nicholas of Bari. © The National Gallery, London.

in Jezusa sta izvedeni s pomočjo kartona, prav tako sv. Janez. Ni jasno, ali je bil sv. Nikolaj narisan povsem prostoročno ali po preprostem kartonu, zaradi česar je bila potrebna zahtevnejša predelava na tabli, toda infrardeča reflektografija kaže, da so bile večje spremembe te figure izvedene precej pozno v razvoju slike: sprva je bil gologlav in je nosil krajše oblačilo, ki je odkrivalo njegove gležnje. Mreža morda ni bila uporabljena za prostoročno kopiranje, temveč za pomoč pri vzpostavitvi geometrije kompozicije, za merilo, v katerem so morali biti narejeni kartoni, in za postavitev kartonov na tablo.

in the Saint's face shows aspects of Raphael's interest in geometry and volume, drawing the curves of the cheekbones, and the structure of the nose for example; this is similar to the kind of drawing seen later in the *Garvagh Madonna*.

It would therefore appear that Raphael used a mixture of techniques when assembling the *Ansidei Madonna* on its panel. The key figures of the Virgin and Child had a cartoon, as did Saint John. Whether Saint Nicholas was drawn entirely freehand or had a simpler cartoon, which needed more elaborate reworking on the panel, is not clear, but infrared reflectography also shows that significant changes were made to this figure quite late in the picture's development: he was initially bareheaded and wearing shorter robes which revealed his ankles. The grid may not have been used for freehand copying of the underdrawing, but would have helped in establishing the geometry of the composition, the scale to which the cartoons had to be made and in positioning the cartoons on the panel.

Zahvale

Velik del veselja pri delu v Narodni galeriji izvira iz sodelovanja s kolegi in preiskave Rafaela so bile resnično skupinsko delo. Posebej bi rada omenila Carol Plazzotta in Toma Henrya, znanstvenike Mariko Spring, Ashoka Roya in Jo Kirby ter konservatorko - restavratorko Jill Dunkerton; za pomoč pri študiji kartona za Sv. Katarino se zahvaljujem tudi Catherine Goguel iz Département des Arts Graphiques, Musée du Louvre, Paris (Oddelka za grafične umetnosti, Muzej Louvre, Pariz).

Opomba

Ta zapis je razširjena različica tistega, ki je bil predstavljen na simpoziju ‘Raphael's Painting Technique: Working Practices before Rome’ (Rafaelova tehnika slikanja: praksa pri delu pred Rimom), ki je potekal v Narodni galeriji v Londonu pod pokroviteljstvom projekta Evropske unije Eu-ARTECH. Izsledke tega simpozija bo objavil Nardini Editore kot posebno številko *Kermes Quaderni.*

Viri

Op. To ni celovit seznam znanstvenih del o Rafaelu, navaja dela, ki so jih napisali uslužbenci Narodne galerije v Londonu in se nanašajo na slike, o katerih govorim v tem članku. Mnogo popolnejšo bibliografijo o Rafaelu najdete pri [2], str. 307–315, o podrisbah pa pri *Art in the Making: Underdrawings in Renaissance Paintings* (ur. Bomfordu, D.), 187–191 (navedeno pri [5], [6] in [8]).

[1] Plesters, J. (1990) *Technical Aspects of Some Paintings by Raphael in the National Gallery, London,* The Princeton Raphael Symposium: Science in the Service of Art History, Princeton Monographs in Art and Archaeology XLVII (ur. Shearman, J. in Hall, M.B.), Princeton University Press, New Jersey, 15–37 in slike 1–29.

[2] Chapman, H., Henry, T. Plazzotta, C. et. al. (2004) *Raphael: From Urbino to Rome*, katalog razstave, The National Gallery, London.

[3] Roy, A., Spring, M. in Plazzotta, C. (2004) *Raphael’s Early Work in the National Gallery: Paintings before Rome,* National Gallery Technical Bulletin 25, National Gallery, London, 4–35 (predvsem 5–7 za podrisbo).

Acknowledgements

Much of the pleasure of working at the National Gallery derives from collaboration with colleagues and the Raphael examinations were real teamwork. In particular I would like to mention curators Carol Plazzotta and Tom Henry, scientists Marika Spring, Ashok Roy and Jo Kirby and conservator Jill Dunkerton; also, for her help with the study of the Saint Catherine cartoon, Catherine Goguel of the Département des Arts Graphiques, Musée du Louvre, Paris.

Note

This paper is an expanded version of one presented at ‘Raphael’s Painting Technique: Working Practices before Rome’, a symposium held at the National Gallery under the auspices of the European Union Eu-ARTECH project. The proceedings of this symposium are to be published by Nardini Editore as a special volume of *Kermes Quaderni.*

References

N.B. This is not intended to be a comprehensive list of Raphael scholarship, but to list works written by members of staff at the National Gallery about the National Gallery paintings discussed in this paper. For a much fuller bibliography on Raphael see [2], 307–315, and on underdrawings see *Art in the Making: Underdrawings in Renaissance Paintings* (Ed. Bomford, D.), 187–191 (cited in [5], [6] and [8]).

[1] Plesters, J. (1990) *Technical Aspects of Some Paintings by Raphael in the National Gallery, London,* The Princeton Raphael Symposium: Science in the Service of Art History, Princeton Monographs in Art and Archaeology XLVII (Edit. Shearman, J. and Hall, M.B.), Princeton University Press, New Jersey, 15–37 and photo 1–29.

[2] Chapman, H., Henry, T. Plazzotta, C. et. al. (2004) *Raphael: From Urbino to Rome*, exhibition catalogue, The National Gallery, London.

[3] Roy, A., Spring, M. and Plazzotta, C. (2004) *Raphael’s Early Work in the National Gallery: Paintings before Rome*, National Gallery Technical Bulletin 25, National Gallery, London, 4–35 (especially 5–7 for underdrawing).

[4] Dunkerton, J., Foister, S. and Penny, N. (1999) *Dürer to Veronese: Sixteenth-Century Painting in The National*

[4] Dunkerton, J., Foister, S. in Penny, N. (1999) *Dürer to Veronese: Sixteenth-Century Painting in The National Gallery*, Yale University Press, New Haven in London, 225–231.

[5] Plazzotta, C. (2002) *Raphael, The Procession to Calvary,* Art in the Making: Underdrawings in Renaissance Paintings, katalog razstave (ur. Bomford, D.), The National Gallery, London, 122–127.

[6] Kirby, J., Roy, A. in Spring, M. (2002) *The Materials of Underdrawing*, Art in the Making: Underdrawings in Renaissance Paintings, katalog razstave (ur. Bomford, D.), The National Gallery, London, 26–37.

[7] Dunkerton, J. in Penny, N. (1993) The Infra-red Examination of Raphael's 'Garvagh Madonna', National Gallery Technical Bulletin 14, National Gallery, London, 6–21.

[8] Plazzotta, C. (2002) *Raphael*, *The Madonna and Child with the Infant Baptist (The Garvagh Madonna)*, Art in the Making: Underdrawings in Renaissance Paintings, katalog razstave (ur. Bomford, D.), The National Gallery, London, 128–135.

[9] Penny, N. (1992) *Raphael's 'Madonna dei garofani' rediscovered*, Burlington Magazine CXXXIV, The Burlington Magazine Publications, London, 66–81.

[10] Cooper, D. in Plazzotta, C. (2004) *Raphael's Ansidei altarpiece in the National Gallery*, Burlington Magazine CXLVI, The Burlington Magazine Publications, London, 720–731.

[11] Več informacij o programski opremi najdete na www.vips.ecs.soton.ac.uk. (Dostop 17. februarja 2007.)

Napisi (podnapisi) k slikam

(Op. Avtorske pravice za vse ilustracije v tem članku so last The National Gallery, London)

Gallery, Yale University Press, New Haven and London, 225–231.

[5] Plazzotta, C. (2002) *Raphael, The Procession to Calvary*, Art in the Making: Underdrawings in Renaissance Paintings, exhibition catalogue (Edit. Bomford, D.), The National Gallery, London, 122–127.

[6] Kirby, J., Roy, A. and Spring, M. (2002) *The Materials of Underdrawing*, Art in the Making: Underdrawings in Renaissance Paintings, exhibition catalogue (Edit. Bomford, D.), The National Gallery, London, 26–37.

[7] Dunkerton, J. and Penny, N. (1993) *The Infra-red Examination of Raphael's 'Garvagh Madonna',* National Gallery Technical Bulletin 14, National Gallery, London, 6–21.

[8] Plazzotta, C. (2002) Raphael, *The Madonna and Child with the Infant Baptist (The Garvagh Madonna),* Art in the Making: Underdrawings in Renaissance Paintings, exhibition catalogue (Edit. Bomford, D.), The National Gallery, London, 128–135.

[9] Penny, N. (1992) *Raphael's 'Madonna dei garofani' rediscovered*, Burlington Magazine CXXXIV, The Burlington Magazine Publications, London, 66–81.

[10] Cooper, D. and Plazzotta, C. (2004) *Raphael's Ansedei altarpiece in the National Gallery, Burlington* Magazine CXLVI, The Burlington Magazine Publications, London, 720–731.

[11] For more information on the software see www.vips.ecs.soton.ac.uk. (Accessed 17 February 2007.)

Captions

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Rdeča in modra: nedavne raziskave pigmentov, barvil in spremembe barvnih plasti v londonski Narodni Galeriji

Red and Blue: Recent Work on Pigments, Paint and Colour Change at the National Gallery, London

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POVZETEK: V Znanstvenem oddelku londonske Narodne galerije so bili nedavno izvedeni trije raziskovalni projekti o vplivu relativne vlažnosti na spremembo barve pigmenta zaradi svetlobe in vplivu proizvodne metode na bledenje pariško modre ter preiskava substratov organskih barvil iz obdobja od petnajstega do zgodnjega dvajsetega stoletja. Podajamo nekatere vidike teh raziskav. Prvič, za organske pigmente karmin, cinober in minij je znano, da so v določenih okoliščinah občutljivi na svetlobo; opisani so dodatni učinki relativne vlažnosti in učinki na azurit. Drugič, ugotovljeno je bilo, da je način priprave pariško modre v starih receptih iz posušene krvi, alkalne soli, ki vsebuje kalij, galunovca in železovega (II) sulfata v nekaterih ozirih vplival na obstojnost pigmenta na svetlobi. Nazadnje, ugotovljeno je bilo, da je na sestavo karminastih pigmentov vplival natančen način priprave substrata karminastega pigmenta z vsebnostjo aluminija. To je obravnavano v kontekstu o pigmentih iz brošča v devetnajstem stoletju.

Ključne besede:
relativna vlažnost;
sprememba barve;
svinčeva bela;
karmin;
cinober;
minij;
azurit;
pariško modra;
aluminijev oksid;
brošč.

Keywords:
relative humidity;
colour change;
lead white;
lac lake;
vermilion;
red lead;
azurite;
prussian blue;
alumina;
madder lake.

ABSTRACT: Three recent research projects carried out in the Scientific Department of the National Gallery, London have been concerned with the effect of relative humidity on light-induced colour change of pigments; the effect of the method of manufacture on the fading of Prussian blue; and an investigation of the substrates of red lake pigments, dating from the fifteenth to the early twentieth centuries. Particular aspects of each of these studies are discussed. Firstly, the lake pigment lac lake, vermilion and red lead are known to be vulnerable to light under certain circumstances; the additional effects of relative humidity are described, together with the effects on azurite. Secondly, it was found that the method of preparation of Prussian blue, in early recipes from dried blood, a potassium-containing alkaline salt, alum and iron(II) sulphate, influenced the permanence of the pigment to light in certain respects. Finally, the precise method of preparation of an aluminium-containing red lake pigment substrate has been found to affect its constitution. This is discussed in the context of nineteenth-century madder lake pigments.

Uvod

Preiskava slik v londonski Narodni galeriji je običajno kolektivna naloga. Na neki stopnji, morda med pripravo kataloškega vnosa za sliko ali med rutinsko konservatorsko obravnavo, se kustosi, restavratorji in znanstveniki dobijo pred sliko in med razpravo, ki sledi, se lahko pojavijo vprašanja, na katera ni takojšnjega odgovora. Ta vprašanja lahko postanejo osnova za ploden umetnostnozgodovinski in znanstveni raziskovalni projekt. Ta članek na kratko povzema tri študije, ki so bile pred kratkim opravljene v Znanstvenem oddelku Narodne galerije in so vse temeljile na opažanjih pri preiskavi slik. Poleg tega vse zadevajo barvo, v tem primeru rdeče in modre pigmente.

V prvi študiji preučujemo vpliv temperature in vlažnosti na spremembe barv, do katerih pride pri različnih pigmentih zaradi izpostavljenosti svetlobi [1]. Ta razprava se osredotoča na učinek spremembe relativne vlažnosti na izbor rdečih in modrih pigmentov, za katere je znano, da posebej nagibajo k spremembam barve zaradi svetlobe. V drugi preučujemo bledenje pariško modre, pojav, ki ga pogosto opažamo pri slikah iz osemnajstega stoletja, in vpliv priprave pigmenta na to [2]. Tu razpravljamo o značilnih lastnostih zgodnjih pariško modrih in njihov vpliv na obstojnost pigmentov. Ti študiji se ukvarjata s spremembami, ki so jasno vidne na površini slike, v tretji pa smo preučevali kemično sestavo organskih barvil, pigmentov, narejenih z usedanjem organskega barvila na primeren substrat [3]. Posebne lastnosti sestave pigmentov, ki so bile odkrite med analizo vzorcev, odvzetih med preiskavo slik, so se izkazale kot značilne za organska barvila iz devetnajstega stoletja in jih je mogoče razložiti z raziskavo načina, kako so bili pigmenti verjetno narejeni.

Introduction

Examination of a painting at the National Gallery, London, is usually a collaborative exercise. At some stage, perhaps during the preparation of a catalogue entry for the picture, or during routine conservation treatment, curators, restorers and scientists may meet in front of the painting and during the ensuing discussions, questions to which there is no immediate answer may arise. These may later form the basis of fruitful research projects, both art historical and scientific. This paper gives a brief account of three recent studies carried out in the National Gallery Scientific Department, all of which were founded on observations made during examination of paintings. In addition, all are concerned with colour, in this case, with red and blue pigments.

The first study examined the influence of temperature and humidity on colour changes that occur in various pigments as a result of exposure to light [1]. The present discussion concentrates on the effect of changes in relative humidity on a selection of red and blue pigments known to be particularly liable to show light-induced colour changes. The second examined the fading of Prussian blue, a phenomenon quite frequently observed in eighteenth-century paintings, and how this is influenced by the method of pigment preparation [2]. Here, a characteristic features of early Prussian blues and its effect on the permanence of the pigments is discussed. These two studies were concerned with changes clearly visible on the surface of the painting: the third study investigated the chemical composition of red lake pigments, pigments made by precipitating an organic dyestuff onto a suitable substrate [3]. Particular features of the constitution of the pigments, revealed during analysis of samples taken during examination of the paintings, were found to be characteristic of nineteenth-century lakes and could be explained by research into how the pigments were probably made.

Vpliv relativne vlažnosti na spremembo barve v odvisnosti od svetlobe pri izbranih rdečih in modrih pigmentih

Pred petimi leti sta dva izmed avtorjev tega članka vodila poskus primerjave opreme in metod za pospešeno staranje v različnih laboratorijih ob uporabi omejenega izbora vzorcev, ki so jih pripravlili v Narodni galeriji in poslali vsem sodelujočim [4]. Med tem poskusom je bila skupina vzorcev izpostavljena trem različnim temperaturam (10, 25 in 60° C) pri stalni rela-

Influence of Relative Humidity on Light-induced Colour Change in Selected Red and Blue Pigments

Five years ago, two of the present authors conducted an experiment to compare the equipment and methods used for light-accelerated ageing in different laboratories, using a limited range of samples prepared at the National Gallery and supplied to all the participants [4]. During this experiment, a set of samples was exposed to three different temperatures,10, 25 and 60 °C,

tivni vlažnosti 55 %, druga skupina pa trem različnim stopnjam relativne vlažnosti (20, 55 in 85 %) pri stalni temperaturi 60° C. Poskusi so bili izvedeni v komercialni okoljski komori, opremljeni s fluorescenčnimi cevmi Philips *Colour 84*, pri katerih je osvetlitev relativno enakomerno porazdeljena po vidnem spektru. Ugotovljeno je bilo, da sta povišanje temperature pri stalni relativni vlažnosti in, kar je še bolj zanimivo, povišanje relativne vlažnosti pri stalni temperaturi v vsakem primeru povzročila večjo spremembo barve.

Učinki povečane relativne vlažnosti na spremembo barve so bili posebej zanimivi, ker so v konservatorski literaturi pogosta poročila o učinkih vlažnosti na nekatere pigmente. Med najbolj občutljivimi so pigmenti, ki vsebujejo svinec – minij [5–6] in svinčeva bela (bazični svinčev karbonat) [7–8], cinober (rdeči živosrebrni sulfid) [9–10] in modri pigment azurit (bazični bakrov karbonat) [11].

1 Primeri spremembe barve

V številnih primerih se je spreminjanje barve nanašalo na stenske slikarije ali pobarvan kamen. V teh primerih je težko ločiti učinke vlažnosti od dodatnega dejavnika prisotnosti ionov v raztopini: veliko je bilo že razprav o gibanju soli v raztopini znotraj zidov. Primeri stenskih poslikav so bili zagotovo najbolj dramatični, o učinkih na enake pigmente pri tabelnem slikarstvu pa je manj poročil. Pri miniju lahko pride tako do temnenja kot do bledenja, odvisno od razmer. Primer temnenja pigmenta in tvorbo črnega ali rjavega svinčevega dioksida je mogoče videti pri slikah v ladji iz l. 1275 v cerkvi v Gundsømagleu, Severna Zelandija, Danska [5–6]; drugi primer je zasnova okrasja na oboku Kapele svetega groba, Winchesterska katedrala, Anglija [9]. O temnenju pigmenta so občasno poročali tudi pri rokopisih in japonskih tiskih. Tudi o bledenju pigmenta in tvorbi cerusita (svinčevega karbonata) ali svinčevega belila obstajajo občasna poročila, znan primer so romanske poslikave v apsidi Kapele sv. Gabriela, Canterburyska katedrala [12–13].

Temnenje cinobra in tvorbo domnevnega metacinobra je mogoče videti na stenskih slikarijah, kot je okrasje v Kapeli svetega groba, omenjenih zgoraj [9]. To tudi pri tabelnem slikarstvu ni nenavadno, še posebej če barva ni dobro povezana: če je kot vezivo uporabljena jajčna tempera (ali raztopina lepila ali gumija), se predvsem pri cinobru rada pojavi ta sprememba, ki jo lahko vidimo npr. v *Križanju* florentinskega slikarja Jacopa di Cione in njegove delavnice iz okoli 1368–70 (London, The National Gallery, NG 1468) [10]. Tudi druge soli, ki nastopajo kot nečistoče med izdelavo cinobra po mokrem postopku ali so prisotne v

at a constant relative humidity of 55%, and another set to three different relative humidities, 20, 55 and 85%, at a constant temperature of 60 ºC. The experiments were carried out in a commercial environmental chamber fitted with Philips *Colour 84* fluorescent tubes, which have a relatively even distribution of illumination across the visible spectrum. It was found that an increase in temperature at a constant relative humidity and, more interestingly, an increase in relative humidity at constant temperature caused a greater colour change in every case.

The effects of increased relative humidity on colour change were particularly interesting as the effects of damp conditions on certain pigments have frequently been reported in the conservation literature. The most vulnerable pigments include the lead-containing pigments red lead (minium) [5–6] and lead white (basic lead carbonate) [7–8], vermilion (red mercuric sulphide) [9–10], and the blue pigment azurite (a basic copper carbonate) [11].

1 Examples of Colour Change

In many cases, examples given of the colour changes have referred to wall paintings or to painted stone. In these cases, it is difficult to dissociate the effects of humidity from the additional factor of the presence of ions in solution: the movements of salts in solution within walls have been much discussed. Wall paintings have certainly provided the most dramatic examples; the effects on the same pigments in easel paintings have been reported less often. In the case of red lead, both darkening and lightening may occur, depending on the conditions. An example of darkening of the pigment to form black or brown lead dioxide may be seen in the nave paintings of about 1275 in the church of Gundsømagle, North Zealand, Denmark [5–6]; another example is seen in the thirteenth-century decorative scheme on the vault of the Holy Sepulchre Chapel, Winchester Cathedral, England [9]. Darkening of the pigment has also occasionally been reported in manuscripts and Japanese prints. Lightening of the pigment to form cerussite (lead carbonate) or lead white has also occasionally been reported, notably in Romanesque paintings in the apse of St Gabriel's Chapel, Canterbury Cathedral [12–13].

Darkening of vermilion to form what is thought to be black metacinnabar can be seen in wall paintings, such as the Holy Sepulchre Chapel scheme mentioned above [9]. It is not uncommon on easel paintings, particularly if the paint is not well bound: vermilion bound in egg tempera (or in a solution of glue or gum) is therefore particularly likely to show this change, seen, for example, in *The Crucifixion*, painted by the Florentine painter Jacopo di Cione and his workshop in about 1368–70 (London,

okolju, predvsem alkalni kovinski kloridi – na primer sol (natrijev klorid) – prispevajo svoj delež k temnenju [14–15]. Ker lahko temnenje spremlja tudi tvorba kalomela (živosrebrnega (I) klorida), je splošni videz barve prej bledo vijoličast kot črn, kar je vidno pri *Mariji z Jezusom na prestolu* (1461–2; London, The National Gallery, NG 283) Benozza Gozzolija [10].

Pretvorba modrega azurita v zeleno spojino je bila pogosto opažena pri stenskih slikarijah. Znan primer spremembe barve lahko vidimo pri ciklu Legenda sv. Frančiška v zgornji cerkvi sv. Frančiška v Assisiju, Italija [11]; prej omenjene stenske slikarije v Gundsømagleu kažejo enako spremembo [5–6]. Rezultat so bakrove soli, ki vsebujejo klor, na primer paratacamit in atacamit [16], v nekaterih primerih (vključno s cerkvijo v Gundsømagleu) pa je težko izključiti možnost, da je bil kateri od teh bazičnih kloridov uporabljen v originalni zasnovi.

2 Oprema in postopek

Tako smo te štiri pigmente – minij, svinčevo belilo, cinober in azurit – skupaj z drugimi, ki se pogosto uporabljajo v tabelnem slikarstvu [1], vključili v novo skupino poskusov. Za nekatere od njih, na primer za rdeče in rumene organske pigmente ter za pariško modro, je bilo znano, da so občutljivi na svetlobo [17–18], dodatni učinki vlažnosti pa so bili manj znani. Kot vezivo so služili hidrofobni – olja – in tudi hidrofilni mediji – gumi ali klej; tudi jajčna tempera, kazein in akrilna veziva so bili uporabljeni z izborom pigmentov. Pri teh poskusih smo uporabili svetlobno komoro (slika 1) ter vzdrževali povprečno temperaturo okoli 25° C. Pigmenti so bili izpostavljeni svetlobi dveh 65 W fluorescenčnih cevi *Artificial Daylight* (umetna dnevna

The National Gallery, NG 1468) [10]. Other salts present as impurities during manufacture of wet process vermilion, or in the environment, particularly alkali metal chlorides or other halides – salt (sodium chloride), for example – play a part in the darkening [14–15]. As the darkening may be accompanied by the formation of calomel (white mercury(I) chloride), the overall appearance of the paint may be lilac rather than black, as seen in Benozzo Gozzoli's *The Virgin and Child Enthroned* (1461–2; London, The National Gallery, NG 283) [10].

The transformation of blue azurite to a green compound has frequently been observed in wall paintings. A well-known example of the colour change may be seen in the *Legend of St Francis* cycle in the Upper Church of St Francis at Assisi, Italy [11]; the wall paintings at Gundsømagle, mentioned previously, show the same change [5–6]. The products are chlorine-containing copper salts, such as paratacamite and atacamite [16], but in some cases (including the Danish church of Gundsømagle) it is difficult to exclude the possibility that one of these basic copper chlorides may have been used in the original scheme.

2 Equipment and Procedure

These four pigments – red lead, lead white, vermilion and azurite – were thus included in a new set of experiments, together with others commonly used in easel painting [1]. Some of these, such as the red and yellow lake pigments and Prussian blue, were known to be light sensitive [17–18], but the additonal effects of moisture were less well known . The pigments were bound in both hydrophobic oil and hydrophilic – gum or glue – media; egg tempera, casein and acrylic binding media were also used with a selection of the pigments. In these experi-

Slika 1. Svetlobna komora, uporabljena za poskuse pri bledenju. V njej se vzdržuje povprečna temperatura okoli 25° C; dno je perforirano, da omogoča pretok zraka, ventilatorji v pokrovu odvajajo toploto, ki jo ustvarjajo fluorescentne cevi, iz naprave. Na desni je vidnih pet komor, v katerih vzdržujejo različne stopnje relativne vlažnosti.

Figure 1. Light box used for fading experiments. The box is maintained at an average temperature of about 25 °C; the floor is perforated to allow air flow and heat generated by the fluorescent tubes is drawn out of the apparatus by fans mounted in the roof. The five chambers maintained at different relative humidities are seen on the right.

svetloba) proizvajalca General Electric s svetilnostjo do 22.000 luksov. Spektralna moč teh svetil je razmeroma enakomerno razporejena po obsegu od 300–760 nm in daje več osvetlitve v ultravijoličnem delu spektra kot svetila, uporabljena v prejšnjih poskusih [4]. Vzorce na ploščicah PTFE smo dali v majhne komore (slika 2), vsak je bil pri drugačni relativni vlažnosti, ki smo jo dosegali z uporabo raztopine nasičene soli: 11 % [litijevega klorida], 32 % [magnezijevega klorida], 51 % [magnezijevega nitrata], 75 % [natrijevega klorida] in 90 % [barijevega klorida]. Neosvetljene primerjalne vzorce za vsak poskus smo položili pod neprozorne črne kartice v iste predele kot vzorce, izpostavljene svetlobi. Merjenje barve smo izvedli s kromometrom Minolta CR200 ali CR221 z geometrijo 45/0 (razen odbleskov); spekter nekaterih vzorcev pa smo posneli s spektrometrom Minolta CM-2600d [17]. Podatke smo pretvorili v koordinate Commission Internationale de l'Eclairage (CIE) L*, a*, b*, pri čemer smo kot primerjalni vir uporabili standardni iluminator D65; koordinata a*

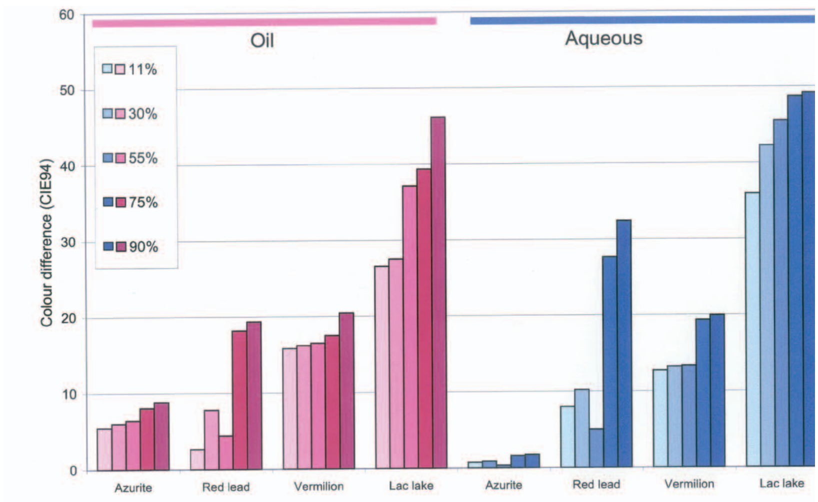
Slika 2. Komora, v kateri vzdržujejo konstantno relativna vlažnost. Nasičena raztopina soli je v steklenem kozarcu, pokritem z membrano iz GORE-TEX®-a. Vzorci na PTFE ploščicah so nameščeni nad kozarcem, med temnimi kontrolnimi vzorci in svetlobi izpostavljenimi vzorci so neprozorne črne kartice.

Figure 2. Box maintained at a constant relative humidity. The saturated salt solution is contained in a glass jar covered by a GORE-TEX® membrane. The samples, mounted on PTFE tiles, are supported above the jar, with opaque black card between the dark control samples and the light-exposed samples.

ments, a light box was used (Figure 1), maintained at an average temperature of about 25 °C. The pigments were exposed to light from twelve 65 W General Electric *Artificial Daylight* fluorescent tubes, giving an illuminance of up to 22,000 lux. The spectral power distribution of these lamps is reasonably even across the range 300–760 nm and more illumination is provided in the ultraviolet region of the spectrum than with the lamps used in the earlier experiments [4]. The samples, mounted on PTFE tiles, were placed in small chambers (Figure 2), each maintained at a different relative humidity using a saturated salt solution: 11% [lithium chloride], 32% [magnesium chloride], 51% [magnesium nitrate], 75% [sodium chloride], and 90% [barium chloride]. The dark control samples for each experiment were placed beneath opaque black card in the same enclosures as the light-exposed samples. Colour measurement was carried out using either a Minolta CR200 or CR221 chroma meter, using a 45/0 geometry (excluding gloss); a Minolta CM-2600d spectrophotometer was used to record spectra for some samples [17]. The data were converted to Commission Internationale de l'Eclairage (CIE) L*, a*, b* co-ordinates using the standard illuminant D65 as reference; the a* co-ordinate indicates redness–greenness (positive values are red, negative, green), while b* is a measure of yellowness–blueness (positive, yellow, negative, blue). Colour changes were expressed either as overall colour change (ΔE, calculated using the CIE 1994 formula), or as a change in lightness ΔL [19–20].

3 The Behaviour of Lac Lake, Vermilion, Red Lead and Azurite

For some pigments, including lead white, it was found that an increase in relative humidity has no effect on the degree of colour change. In other cases, such as lac lake – a crimson pigment widely used in medieval and Renaissance Europe, made from the dyestuff produced by the lac insect, *Kerria lacca* (Kerr, 1782) – an increase in relative humidity was accompanied by a greater degree of colour change. It is noticeable, however, that the changes were less pronounced when the pigment was bound in linseed oil. The colour changes observed in lac lake, together with the three pigments known to be affected by relative humidity – red lead, vermilion and azurite – bound in oil or an aqueous medium, after a total exposure of 60 Mlux hours, is shown in Figures 3 and 4. The colour change of vermilion is not straightforward, as factors other than light and humidity, including trituration (grinding) of the pigment during its preparation and and the presence of impurities, may also be involved in its deterioration [10, 14–15]. However, it was found to behave in a rather similar way to the lake pigment: the greater



Slika 3. Vpliv relativne vlažnosti na spremembo barve azurita, minija, cinobra in karmina v oljnih in vodnih medijih.

Figure 3. Effect of relative humidity on the colour change of azurite, red lead, vermilion and lac lake in oil and aqueous media.

Slika 4. Spremembe barve pri različnih relativnih vlažnostih za štiri pigmente. Kontrolni vzorci so bili v temi pri 11 % RV.

Figure 4. Colour changes at different relative humidities for the four pigments. The control samples had been kept in the dark at 11% RH.

navaja rdečino-zelenino (pozitivne vrednosti so rdeče, negativne zelene), b* pa je mera za rumenino-modrino (pozitivna je rumena, negativna modra). Spremembe barve so bile izražene kot splošna sprememba barve (ΔE, izračunano po formuli CIE 1994) ali kot sprememba svetlosti ΔL [19–20].

3 Karmin, cinober, minij in azurit

Za nekatere pigmente, s svinčevim belilom vred, je bilo ugotovljeno, da povečanje relativne vlažnosti nima vpliva na stopnjo spremembe barve. V drugih primerih, na primer pri karminu – škrlatnem pigmentu, pogosto uporabljanem v srednjeveški in renesančni Evropi, narejenem iz barvila, ki ga izloča insekt *Kerria lacca* (Kerr, 1782) – je povečanje relativne vlažnosti spremljala večja sprememba barve. Vendar pa je treba omeniti, da so bile spremembe manj izrazite, če je bilo za vezivo pigmentov uporabljeno laneno olje. Spremembe barve, opažene pri karminu in pri treh pigmentih, za katere je znano, da nanje vpliva relativna vlažnost – minij, cinober in azurit – in pri katerih so bili kot vezivo uporabljeni oljni ali vodni mediji, po izpostavljenosti 60 Mlux ur, so prikazane na slikah 3 in 4. Sprememba barve pri cinobru ni enoznačna, saj nanjo vplivajo tudi drugi dejavniki, ne samo svetloba in vlažnost, med njimi tudi drobljenje pigmenta med pripravo in prisotnost nečistoč [10, 14–15]. Ugotovljeno pa je bilo, da se obnaša precej podobno kot karmin: kolikor večja je relativna vlažnost, bolj izrazito je temnenje na svetlobi. Cinober, narejen po mokrem postopku, je potemnel bolj kot tisti, ki je bil narejen po suhem postopku, poleg tega so bile spremembe manj izrazite, če je bil pigment dobro vezan v

the relative humidity, the more pronounced the darkening with exposure to light. Vermilion made by the wet process method darkened more than that made by the dry process method and, again, the changes were less marked when the pigment was well bound in a hydrophobic linseed oil medium. These findings support the observations made on the behaviour of the pigment in both wall paintings and easel paintings.

Red lead has recently been the subject of detailed studies [21–22]. The pattern observed is quite complicated, but explains the fact that both darkening and lightening of the pigment have been reported. Exposure of the pigment to light under the experimental conditions described produced a slight darkening initially, thought to be caused by the formation of lead dioxide. At lower relative humidities (32% or less), this dark product persisted, resulting in an overall darkening of the samples. At a relative humidity of 51% or higher, the samples subsequently lightened as this lead dioxide, and the remaining red lead, were converted to lead white. These changes occurred more rapidly in the paint films exposed to light. The change occurred in all binding media, but was slower for those samples bound in a medium that protected the pigment particles most effectively, generally the hydrophobic linseed oil. It can be seen from Photo 3 that the colour difference in samples of the pigment maintained at relative humidities of 75% and 90% is markedly greater for samples bound in aqueous media.

The azurite samples examined were bound in linseed oil, acrylic medium, casein and glue; a layer of azurite bound in casein was applied over lime, intended to represent the layer structure supposed to have been used in some wall paintings; lime was added to one sam-

hidrofobni medij iz lanenega olja. Ti izsledki podpirajo opažanja o obnašanju pigmenta tako pri stenskem kot tudi pri tabelnem slikarstvu.

O miniju so bile pred kratkim izdelane podrobne študije [21–22]. Opazovani vzorec je precej zapleten, pojasnjuje pa poročila o temnenju in bledenju pigmenta. Izpostavljenost pigmenta svetlobi v razmerah poskusa je na začetku povzročila rahlo potemnitev, za katero menimo, da je posledica tvorjenja svinčevega dioksida. Pri nižji relativni vlažnosti (32 % ali manj) je ta temni produkt ostajal in povzročil splošno temnenje vzorcev. Pri relativni vlažnosti 51 % ali več so vzorci posvetleli, ko sta se svinčev dioksid in preostali minij pretvorila v svinčevo belilo. Te spremembe so se zgodile hitreje pri nanosih barve, ki so bili izpostavljeni svetlobi. Do spremembe je prišlo pri vseh vezivih, vendar je bila počasnejša pri vzorcih, kjer je vezivo učinkoviteje ščitilo pigmentne delce, večinoma je bilo vezivo hidrofobno laneno olje. S slike 3 je razvidno, da je razlika v barvi pri vzorcih pigmentov, ki so bili izpostavljeni 75 % in 90 % relativni vlažnosti, precej večja pri tistih, kjer je bilo vezivo vodni medij.

ple of azurite, which was then bound in glue medium. Light exposure had no effect on any of these samples, whatever the relative humidity. It was only possible to observe a colour change from blue to green, like that seen in wall paintings, at relative humidities greater than 75% in a sample of azurite mixed with sodium chloride in a medium of animal skin glue (photo 4). Examination of the sample by Fourier transform infrared spectroscopy (FTIR) showed that the colour changes was due to the formation of a green basic copper chloride, general formula $Cu_2(OH)_3Cl$, similar to the green products identified in wall paintings. It should be noted that, although the saturated salts used to produce these relative humidities were chlorides (sodium chloride for the 75% relative humidity; barium chloride for 90%) there was no evidence of colour change in the sample of azurite alone in glue, indicating firstly, that no deposition of chloride on the surface of the samples had taken place, and, secondly, that there were no aerosol effects. This suggests that the presence of dissolved salts, very frequently present in wall paintings, is an important factor in the deterioration of azurite.

Karmin v oljnem mediju
Lac lake in oil medium

Karmin v vodnem mediju
Lac lake in aqueous medium

Cinober v oljnem mediju
Vermilion in oil medium

Cinober v vodnem mediju
Vermilion in aqueous medium

Minij v oljnem mediju
Red lead in oil medium

Azurit v vodnem mediju
Azurite in aqueous medium

Azurit + sol v vodnem mediju
Azurite + salt in aqueous medium

Pri pregledanih vzorcih azurita so bili za vezivo uporabljeni laneno olje, akrilni medij, kazein in klej; plast azurita, povezanega s kazeinom, smo nanesli na apno, da bi predstavljal strukturo plasti, kakršna je bila domnevno uporabljena pri nekaterih stenskih poslikavah; enemu vzorcu azurita smo dodali apno, nato pa kot medij za vezivo uporabili klej. Izpostavljenost svetlobi ni vplivala na nobenega od teh vzorcev, ne glede na to, kolikšna je bila relativna vlažnost. Opaziti je bilo mogoče samo spremembo modre barve v zeleno, kakršno vidimo pri stenskih slikarijah, pri relativni vlažnosti, večji od 75 %, pri vzorcu azurita, zmešanega z natrijevim kloridom v mediju iz kožnega kleja (fotografija 4). Pregled vzorca s Fourierjevo transformacijsko infrardečo spektroskopijo (FTIR) je pokazal, da se je barva spremenila zaradi tvorbe zelenega bazičnega bakrovega klorida (splošna formula $Cu_2(OH)_3Cl$), podobnega zelenim produktom s stenskih slik. Čeprav so bile nasičene soli, uporabljene za doseganje teh relativnih vlažnosti, kloridi (natrijev klorid za 75 % relativno vlažnost, barijev klorid za 90 %), ni bilo znakov spremembe barve pri vzorcu azurita samega v kleju. To pomeni, prvič, da ni prišlo do nalaganja klorida na površino vzorcev, in drugič, da ni bilo učinka aerosola. To navaja na misel, da je prisotnost raztopljenih soli, zelo pogosta pri stenskih poslikavah, pomemben dejavnik pri deterioraciji azurita.

Prisotnost tekoče vode, izrazito alkalnih razmer in ionov iz soli v raztopini, je verjetnejša pri stenskem kot pri tabelnem slikarstvu. Številne slike, ki so zdaj v muzejih in galerijah, so bile prvotno del dekorativnih zasnov in so bile zelo blizu zidov, vendar ne v stiku z njimi, njihovo vsebnostjo vlage in raztopljenih soli, ki so se premikale po njihovi strukturi. Med primeri so Veronesejeve štiri *Alegorije ljubezni* (London, The National Gallery, NG 1318, 1324, 1325 in 1326), naslikane na platno verjetno v sedemdesetih letih 16. stoletja in originalno del stropne strukture. Če platno ni pritrjeno neposredno na steno, s čimer bi postalo del njene strukture, slike kažejo malo znakov prizadetosti. Poleg tega večina pigmentov prenese vpliv vlažnosti bolje, če jih ščiti bogat nanos medija, predvsem na primer nanos sušečega se olja, ki je hidrofoben.

Vpliv načina izdelave na obstojnost pariško modre pri svetlobi

Pariško modra je bila eden od pigmentov, pregledanih v zgoraj opisanem poskusu. Vpliv izpostavljenosti svetlobi je bil dobro znan, saj je bil razis-

The presence of liquid water, markedly alkaline conditions, and ions from salts in solution are all more likely to be encountered in wall paintings than in easel paintings. Many paintings now in museums and galleries were originally part of decorative schemes that were quite close to, but not in contact with, walls with their content of moisture and dissolved salts moving through their structure. Examples include Veronese's four *Allegories of Love* (London, The National Gallery, NG 1318, 1324, 1325 and 1326), painted on canvas, probably in the 1570s, and originally part of the structure of a ceiling. Unless the canvas is attached directly to the wall, effectively becoming part of its structure, paintings such as these show few signs of having suffered. In addition, most pigments withstand the effects of damp better when they are protected in a medium-rich film, particularly one, like a drying oil film, that is hydrophobic.

Influence of Method of Manufacture on the Lightfastness of Prussian Blue

Prussian blue was one of the pigments examined in the experiment described above as the effect of light exposure on the pigment was well known, having been investigated in another series of experiments under conditions similar to those described above, but without varying the temperature and humidity [2]. Like other samples of the pigment investigated in that series of experiments, this sample turned slightly grey on exposure to light. Although it is well known that Prussian blue is sensitive to an alkaline environment, including freshly plastered walls [23], its fading was not much affected by increases in relative humidity. The fact that the fading of the pigment in general has been observed more frequently in paintings and decorative schemes of the eighteenth century, the period in which the pigment was first invented, is particularly interesting [18]. As its colour is so intense, it was (and is) almost always used mixed with white in oil paintings, and as a thin wash in watercolour, and because its tinting strength is so high, the proportion of Prussian blue in the mixture used for a pale blue sky, for example, may be very low indeed. The colour of the skies seen in paintings by Canaletto, for example, can be matched by a mixture of one part of a modern, high quality Prussian blue with two hundred, or even four hundred, parts of lead white [2]. When the pigment fades, as seen, for example, in the sky of Canaletto's *Venice: Campo San Vidal and Santa Maria della Carità ('The Stonemason's Yard')* (London, The National Gallery, NG 127), painted between 1726 and 1730 [24], the resulting pallid and often greyish hues may

kan v neki drugi seriji poskusov v podobnih razmerah, vendar brez sprememb temperature in vlažnosti [2]. Kot drugi vzorci pigmenta, pregledani v tisti seriji poskusov, je tudi ta vzorec pri izpostavljenosti svetlobi postal nekoliko sivkast. Čeprav je dobro znano, da je pariško modra občutljiva na alkalno okolje, vključno s sveže ometanimi zidovi [23], povečanje relativne vlažnosti ni veliko vplivalo na njeno bledenje. Posebej zanimivo je, da je bilo bledenje pigmenta pogosteje opaženo pri slikah in dekorativnih zasnovah iz osemnajstega stoletja, obdobja, ko je bil pigment odkrit [18]. Ker je njegova barva tako intenzivna, se je na oljnih slikah skoraj vedno uporabljal (in se še) zmešan z belo, pri akvarelu pa kot tanek voden nanos. Ker je njegova moč toniranja tako velika, je količina pariško modre v mešanici za, na primer, bledo modro nebo zares zelo majhna. Barvo neba, kakršno vidimo na primer na Canalettovih slikah, je mogoče dobiti z mešanjem enega dela sodobne visokokakovostne pariško modre in dvesto ali celo štiristo delov svinčeve bele [2]. Ko pigment obledi, kot lahko vidimo na primer pri nebu Canalettove slike *Benetke*: *Campo San Vidal in Santa Maria della Carità ('Kamnosekovo dvorišče')* (London, The National Gallery, NG 127), naslikani med l. 1726 in 1730 [24], lahko posledični bledi in pogosto sivkasti od-change our impressions of the scene depicted. Darker coloured blue paint, such as that seen in darker areas of the woman's dress in Thomas Gainsborough, *Portrait of the Artist with His Wife and Daughter,* of about 1748 (London, The National Gallery, NG 6547; Figure 5) is very much better preserved.

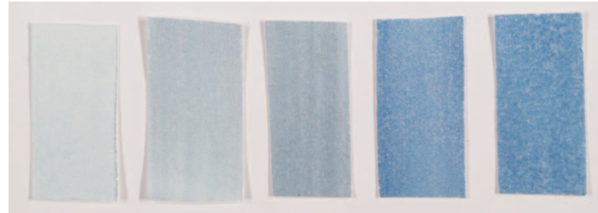
1 Preparation of the Pigment

The fact that Prussian blue was not particularly permanent, particularly when mixed with large amounts of white pigment, was already noticed in the eighteenth century. In order to investigate the fading behaviour of early and modern Prussian blues, samples from late eighteenth - to early nineteeth-century paint boxes and pigment collections were collected to compare with modern batches of the pigment. Comparative samples made using the original ingredients of blood (dried, in this case), potassium carbonate (pearl ashes), potassium aluminium sulphate (potash alum) and iron(II) – ferrous – sulphate (green vitriol), were prepared in the laboratory. The recipe for Prussian blue was first published by John Woodward in 1724 [25]; however, after comparing the proportions of ingredients given in several eighteenth-century recipes, the recipe followed was that published by Robert Dossie

Slika 5. Thomas Gainsborough, *Portret umetnika z ženo in hčerko* (London, The National Gallery, NG 6547), okoli 1748. Olje na platnu, 92,1 x 70,5 cm. © The National Gallery, London.

Figure 5. Thomas Gainsborough, *Portrait of the Artist with His Wife and Daughter* (London, The National Gallery, NG 6547), about 1748. Oil on canvas, 92.1 x 70.5 cm. © The National Gallery, London.

tenki spremenijo vtis, ki ga upodobljeni prizor naredi na gledalca. Temneje obarvana modra slikarska barva, kakršno vidimo na temnejših predelih ženske obleke na sliki Thomasa Gainsborougha *Portret umetnika z ženo in hčerko* iz okoli l. 1748 (London, The National Gallery, NG 6547; slika 5), je veliko bolje ohranjena.



Slika 6. **Vzorci pariško modre v mediju gumiarabikuma na papirju Silversafe. Od leve proti desni: škatla za barve, 1770–1831 (London, Victoria & Albert Museum); mehur barve, ekstrahiran oljni medij, 1830–40; laboratorijska priprava iz posušene krvi; pigment Winsor & Newton (moderen); železov(III) heksacianoferat(II) (dobavitelj Aldrich Chemicals).**

Figure 6. Samples of Prussian blue in gum arabic medium on Silversafe paper. From left to right: paint box, 1770–1831 (London, Victoria & Albert Museum); paint bladder, oil medium extracted, 1830–40; laboratory preparation from dried blood; Winsor & Newton pigment (modern); iron(III) hexacyanoferrate(II) (supplied by Aldrich Chemicals).

1 Priprava pigmenta

Dejstvo, da pariško modra ni posebej obstojna, predvsem če je zmešana z velikimi količinami belega pigmenta, so opazili že v osemnajstem stoletju. Za preiskavo obnašanja pri bledenju zgodnje in moderne pariško modre so bili zbrani vzorci iz škatel za barve in zbirk pigmentov od poznega osemnajstega do zgodnjega devetnajstega stoletja za primerjavo z modernimi primerki pigmenta. Primerjalne vzorce, narejene z uporabo originalnih primesi krvi (v tem primeru posušene), kalijevega karbonata (pepelike), kalijevega aluminijevega sulfata (kalijevega galuna) in železovega II sulfata (zelene galice), smo pripravili v laboratoriju. Recept za pariško modro je prvi objavil John Woodward leta 1724 [25]; vendar smo po primerjavi razmerij sestavin v več receptih iz osemnajstega stoletja uporabili recept, ki ga je objavil Robert Dossie leta 1758 [2, 26]. Mešanico posušene krvi (kakršno se uporablja za vrtno gnojilo) in kalijevega karbonata smo segrevali v peči, zaradi česar je gorela in oddajala neprijeten, jedek dim. Vsebino talilnega lončka smo dodali vreli destilirani vodi; mešanica je vrela 45 minut, nato smo jo filtrirali in dobili čist, bledo rumen filtrat. Železov (II) sulfat in kalijev galun smo raztopili ločeno v destilirani vodi, ju zmešali in hitro dodali vroči rumeni raztopini. Tako smo dobili zeleno-modro oborino, ki vsebuje nekaj z vodikom spojenega aluminijevega oksida, in tako zaželeno modro. Po obdelavi s klorovodikovo kislino za odstranitev aluminijevega oksida smo dobili pariško modro. Njeno identiteto smo potrdili s Fourierjevo transformacijsko infrardečo spektroskopijo (FTIR).

Vsi vzorci – moderni, tisti iz poznega osemnajstega in devetnajstega stoletja in tisti, ki so bili pripravljeni v laboratoriju – so bili pregledani s FTIR in z energetsko razpršitveno mikroanalizo z rentgenskimi žarki v vrstičnem elektronskem mikroskopu (SEM–EDX). Pregledi so odkrili, da so skoraj vsi pigmenti poleg železa vsebovali tudi kalij. Najčistejša oblika pariške modre je železov (III) heksacianoferat (II), morda bolje znan kot železov ferocianid $Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}xH_2O$, kjer je x = 14–16. Vendar pa večina umetniških pigmentov in drugih komercialnih različic pigmenta vsebuje tudi alkalni kovinski ion. Do zgodnjega dvajsetega stoletja je bil to običajno kalij: $KFe^{III}[Fe^{II}(CN)_6]{\cdot}xH_2O$, kjer je x

in 1758 [2, 26]. The mixture of dried blood (as supplied for use as a garden fertiliser) and potassium carbonate was heated in a furnace, causing it to burn with unpleasant, acrid fumes. The contents of the crucible were added to boiling distilled water; the mixture was boiled for 45 minutes, then filtered, giving a clear, pale yellow filtrate. The iron(II) sulphate and potash alum were dissolved separately in distilled water, mixed and added rapidly to the hot yellow solution. This gave a greenish-blue precipitate which contains some hydrated alumina as well as the desired blue. After treatment with hydrochloric acid to remove the alumina, Prussian blue was obtained. Its identity was confirmed by Fourier-transform infrared analysis (FTIR).

All samples – modern, those dating from the late eighteenth and nineteenth centuries and those prepared in the laboratory – were examined by FTIR and by energy dispersive X-ray microanalysis in the scanning electron microscope (SEM–EDX). This revealed that, in addition to iron, almost all the pigments contained potassium. The purest form of Prussian blue is hydrated iron(III) hexacyanoferrate(II), perhaps better known as ferric ferrocyanide, $Fe^{III}_4[Fe^{II}(CN)_6]_3{\cdot}xH_2O$, where x = 14–16. However, most artists' pigments and other commercial varieties of the pigment also contain an alkali metal as counter ion and, until the early twentieth century, this was usually potassium: $KFe^{III}[Fe^{II}(CN)_6]{\cdot}xH_2O$, where spremenljivka, za nekatere primere pa poročila omenjajo 5. (Danes se navadno pripravlja varianta, ki vsebuje amoniak.) Zanimivo je, da so bile nedavno izražene domneve, da je razmerje kalija v kristalnih mrežah vzorcev pigmenta iz osemnajstega in devetnajstega stoletja mogoče povezati z zgodovinskim načinom izdelave [27].

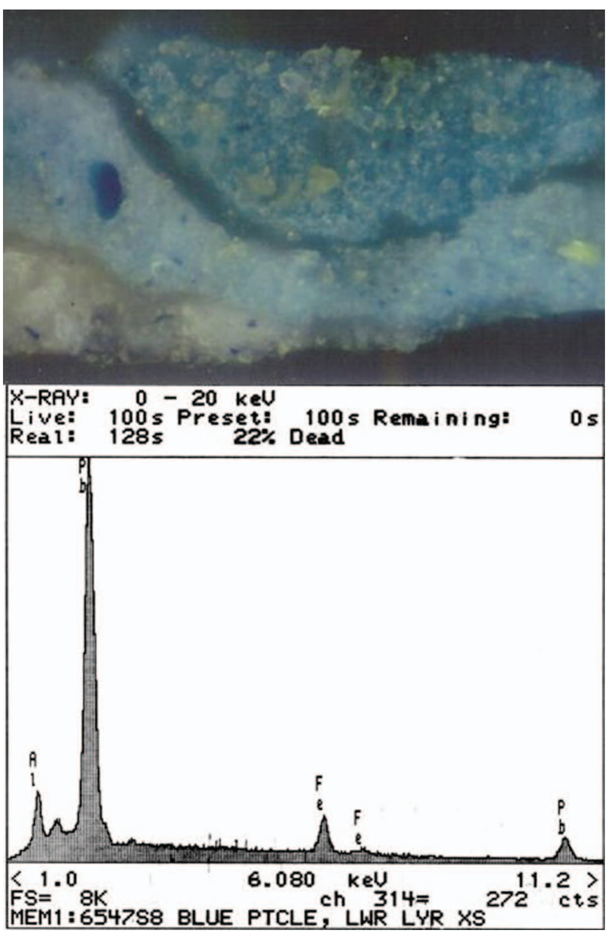
x is variable but in some cases has been reported to be 5. (Nowadays the ammonium-containing variety is commonly prepared.) Interestingly, it has recently been suggested that the proportion of potassium present in the crystal lattice of eighteenth- and nineteenth-century samples of the pigment can be related to the historical method of manufacture [27].

2 Primerjava v laboratoriju pripravljenih in zgodovinskih vzorcev

Pigmenti, pripravljeni po receptu iz osemnajstega stoletja, so bili zelo podobni pristnim vzorcem iz poznega osemnajstega in zgodnjega devetnajstega stoletja tako po videzu in pod mikroskopom kot tudi po svoji kemični sestavi. Akvarelna raztopina laboratorijsko pripravljenega vzorca je bila podobne barve kot vzorci iz škatel za barvo iz poznega osemnajstega in zgodnjega devetnajstega stoletja; vse barve so bile manj žive kot moderne modre (slika 6).

2 Comparison of Laboratory-Prepared and Historical Samples

The pigments prepared according to the eighteenth-century recipe were found to be quite similar to the genuine late eighteenth- and early nineteenth-century samples, both in appearance, by eye and under the microscope, and in thier chemical constitution. A watercolour wash of a laboratory-prepared example of the pigment was a similar colour to late eighteenth- and early nineteenth-century paint box samples; all were less bright than the modern blues (Figure 6).



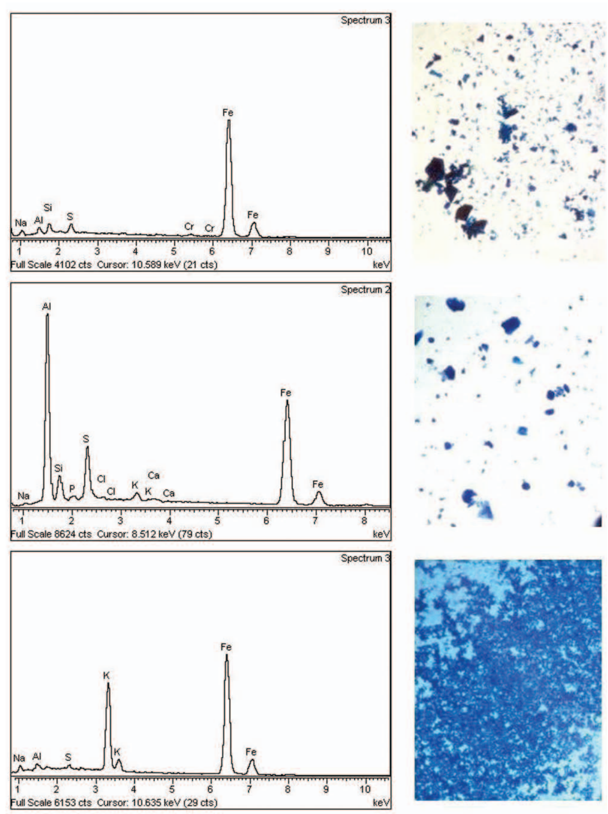
Slika 7. **Thomas Gainsborough, *Portret umetnika z ženo in hčerko.* Prerez srednje modre barve obleke Margaret Gainsborough: pariško modra je zmešana s svinčevo belo in malo neapeljsko rumene v obeh plasteh barve. EDX spekter pariško modrih delcev v spodnji plasti kaže prisotnost železa in aluminija; vrhovi za svinec se pojavljajo zaradi svinčeve bele in neapeljsko rumene.**

Figure 7. Thomas Gainsborough, *Portrait of the Artist with his Wife and Daughter*. Cross-section of mid-blue paint of Margaret Gainsborough's dress: Prussian blue is mixed with lead white and a little Naples yellow in both paint layers. The EDX spectrum of a Prussian blue particle in the lower layer shows the presence of iron and aluminium; the peaks for lead are due to the lead white and Naples yellow.

Pariško modra slikarska barva iz osemnajstega stoletja – in včasih iz zgodnjega devetnajstega stoletja – se od modernega pigmenta zelo značilno razlikuje: pogosto vsebuje oglate kosmiče pigmenta, ki so lahko precej veliki in prosojni [2]. Vidni so v barvi obleke Gainsboroughove žene, prikazani v prerezu na sliki 7. Posebej veliki kosmiči so opazni v barvi modrega neba na sliki Nicolasa Lancreta *Štiri obdobja dneva: Popoldan* (1739–41; London, The National Gallery, NG 5869) [28]. Pregled vzorcev pigmenta iz poznega osemnajstega in zgodnjega devetnajstega stoletja z optičnim mikroskopom je pokazal, da so tudi mnogi od njih vsebovali te oglate delce. Značilno je, da so bili podobni oglati delci prisotni v vzorcih, narejenih v laboratoriju po receptu iz osemnajstega stoletja. Moderne pariško modre, pripravljene brez uporabe posušene krvi, temveč iz čistega ferocianida – heksacianoferata (III) – kalijevih soli, amoniaka ali natrija, lahko vsebujejo okrogle aglomerate delcev, odvisno od razmer sedimentacije pigmenta, ne pa oglatih kosmičev. Domneva, da je prav ta oblika delcev povezana z originalnim načinom priprave pigmenta iz organske snovi, tipično iz posušene krvi, je bila izražena pred skoraj dvajsetimi leti [29]. To hipotezo so tu opisani poskusi potrdili [2].

Analiza SEM–EDX v laboratoriju narejenih pigmentov in tistih iz poznega osemnajstega in zgodnjega devetnajstega stoletja je pokazala, da poleg železa in kalija vsebujejo aluminij iz aluminijevega oksida, prisotnega v pigmentu zaradi načina priprave (slika 8). Kosmičem podobni delci so bili posebej bogati z aluminijem. Analiza delcev podobnih oblik, kakršne najdemo na slikah iz osemnajstega stoletja, na primer v pigmentu, ki ga je Thomas Gainsborough uporabil pri slikanju ženine obleke (slika 7), je dala podobne rezultate.

Med poskusi z bledenjem smo opazili, da je prisotnost polnila v pigmentih (številni vzorci iz devetnajstega stoletja so vsebovali polnila, kot so škrob, barijev sulfat in kalcijeve soli, dodana za izboljšanje delovnih lastnosti pigmenta ali iz drugih vzrokov) delovala na enak način kot dodajanje belega pigmenta: povečala je tendenco bledenja pigmenta. Aluminijev oksid, prisoten v pigmentu zaradi načina izdelave, deluje na natanko enak način kot dodano polnilo. To smo prikazali na naslednji način. Med laboratorijsko pripravo enega od "tradicionalnih" vzorcev pariško modre smo klorovodikovo kislino dodali samo polovici bledozelene usedline, da smo izločili aluminijev oksid in dobili temnomoder produkt, ki je vseboval malo ali nič aluminijevega oksida; drugo polovico smo posušili, da je dala svetel modrozelen pigment, bogat z aluminijevim oksidom. Ko smo primerjali rezultate bledenja obeh pigmentov, smo ugotovili, da je pigment, bogat z aluminijevim oksidom, bolj obledel (slika 9) [2]. Presoj-



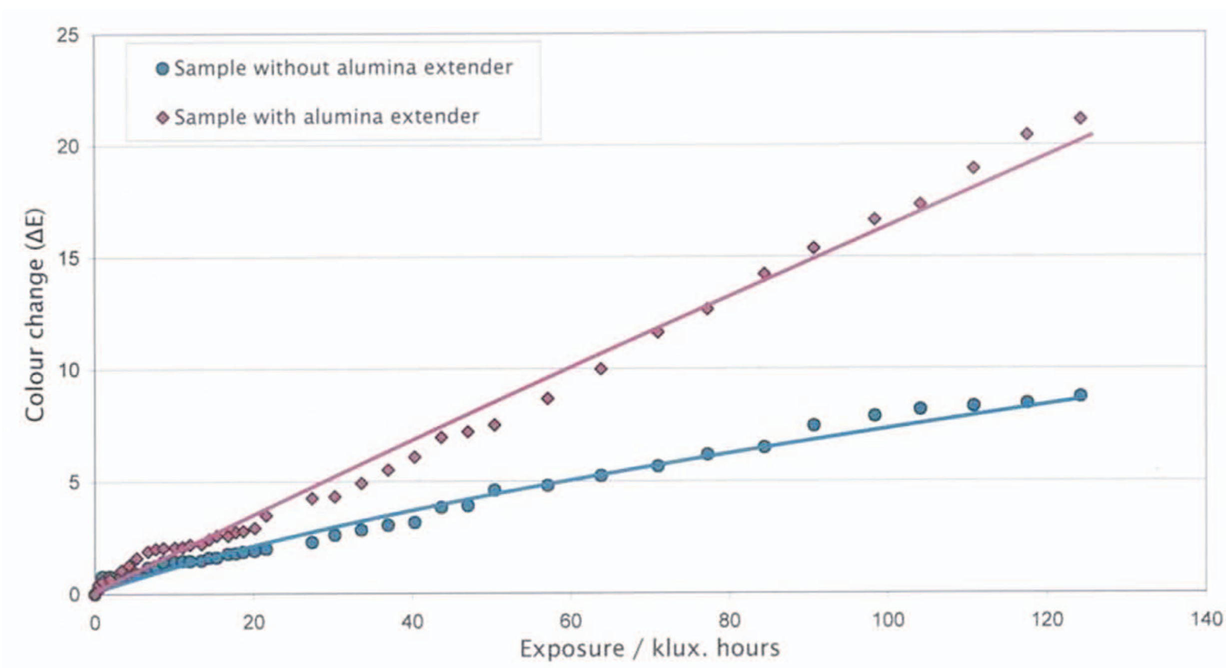
Slika 8. Primerjava moderne in stare pariško modre, ki kaže videz delcev in EDX spektre: zgoraj – laboratorijsko pripravljen vzorec; na sredi – vzorec iz škatle za barve; spodaj – vzorec Winsor & Newton.

Figure 8. Comparison of modern and old style Prussian blues, showing appearance of particles and EDX spectra: top, laboratory-prepared sample; middle, paint box sample; bottom, Winsor & Newton sample.

The Prussian blue seen in eighteenth-century – and sometimes early nineteenth-century – paint differs from the modern pigment in a particularly characteristic way: it often contains angular flakes of pigment, which may be quite large and translucent [2]. These are seen in the paint of Gainsborough's wife's dress, illustrated in the cross-section in Figure 7. Particularly large flakes are seen in the paint of the blue sky in Nicolas Lancret's *The Four Times of Day: Afternoon* (1739–41; London, The National Gallery, NG 5869) [28]. Examination of the late-eighteenth and early nineteenth-century pigment samples by optical microscopy revealed that many of these also contained the angular particles particles. Significantly, similar angular particles were present in the samples prepared in the laboratory according to the eighteenth-century recipe. Modern Prussian blues, prepared using, not dried blood, but pure ferrocyanide – hexacyanoferrate(II) – or ferricyanide – hexacyanoferrate(III) – salts of potassium, ammonium or sodium, may contain rounded agglomerates of particles, depending on the conditions of precipitation of the pigment, but not the angular flakes. The sug-

Slika 9. Vpliv polnila iz aluminijevega oksida na spremembo barve (ΔE) pri pariško modri, pripravljeni po tradicionalnem receptu iz 18. stoletja, ter vzorci pariško modre brez polnila iz aluminijevega oksida (levo) in z njim (desno).

Figure 9. The effect of alumina extender on colour change (ΔE) in Prussian blue prepared according to a traditional 18th-century recipe, and samples of Prussian blue without (left) and with (right) alumina extender.



ni kosmiči pigmenta z večjo vsebnostjo aluminijevega oksida bodo najverjetneje bolj obledeli.

Značilni rezultat načina priprave pigmenta iz organskega začetnega materiala, v tem primeru posušene krvi, je prisotnost oglatih, z aluminijevim oksidom bogatih, presojnih, kosmičem podobnih delcev v pigmentu. Priprava torej vpliva na obstojnost pigmenta pri svetlobi, če uvede polnilo – aluminijev oksid.

Podlaga organskih barvil iz devetnajstega stoletja

Tudi tretja študija se ukvarja z različico vodikovih spojin aluminijevega oksida, vendar v tem primeru aluminijev oksid ni prisoten po naključju, kot pri pariško modri iz osemnajstega stoletja, temveč je bistven sestavni del pigmenta: broščevi organski pigmenti, kakor so jih pripravljali v devetnajstem stoletju in ki so jih uporabljali slikarji Monet, Degas in številni drugi.

Tradicionalni rdeči pigment sestavlja naravno organsko barvilo, ki se nalaga na podlago iz amorfne vodikove spojine aluminijevega oksida. V primeru karmina, uporabljenega v prvi zgoraj opisani študiji, je bila vir barvila indijska žuželka, ki izloča smolnato snov, in sicer *Kerria lacca* Kerr 1782; v primeru brošča je barvilo izvleček iz korenin brošča, *Rubia tinctorum* L.

Organska barvila v vzorcih, odvzetih s slik, ki datirajo od petnajstega stoletja do zgodnjih let dvajsetega stoletja, so analizirali v Znanstvenem oddelku (Scientific Department) londonske Narodne galerije in jih primerjali z barvili, pripravljenimi po receptih iz časa od petnajstega do devetnajstega stoletja. Substrati so bili pregledani s SEM–EDX in FTIR, barvila pa z visokozmogljivostno tekočinsko kromatografijo (HPLC). Ta analiza je pokazala, da so podlage za organska barvila mnogo bolj zapletene, kot bi sodili po preprostem opisu, in sicer zaradi številnih dodatnih elementov in zaradi vsega, kar se nanaša na naravo in kemijo aluminijeve soli. Ugotovljeno je bilo, kakor pri opisani zgoraj pariško modri, da je natančen način priprave substrata, ki je vseboval aluminij, vplival na njeno sestavo [3]. Objavljeno delo se osredotoča na slike, nastale pred poznim osemnajstim stoletjem; v naslednji razpravi pa so opisane lastnosti pigmentov iz devetnajstega stoletja, po katerih se razlikujejo od zgodnejših različic.

Brošči iz devetnajstega in zgodnjega dvajsetega stoletja so pogosto oranžno-rdeči, precej svetli, zelo živi in transparentni, pogosto oranžno fluorescentni. Organsko barvilo tega tipa je uporabil Claude-Oscar Monet na sliki *Irisi*, naslikani okoli l. 1914–17 (London,

gestion that this particular particle form is connected with the original method of preparation of the pigment from organic matter, typically dried blood, was put forward nearly twenty years ago [29]; this hypothesis has been confirmed by the experimental work described here [2].

SEM–EDX analysis of both the laboratory-prepared and the late eighteenth-and nineteenth-century pigments showed that, in addition to iron and potassium, they contained aluminium, derived from the alumina present in the pigment as a result of the method of preparation (Figure 8). The flake-like particles were particularly rich in aluminium. Analysis of the similarly-shaped particles seen in eighteenth-century paintings, such as those seen in the pigment used by Thomas Gainsborough to paint his wife's dress (Photo 7), gave similar results.

During the fading experiments, it was noticed that the presence of any extender in the pigments (and many of the nineteenth-century samples contained extenders such as starch, barium sulphate and calcium salts, added to improve the working properties of the pigment or for other reasons) acted in the same way as adding white pigment: it increased the tendency of the pigment to fade. The alumina present in the pigment as a result of the method of manufacture acts in exactly the same way as an added extender. This was demonstrated in the following manner. During the laboratory preparation of one of the 'traditional' samples of Prussian blue, hydrochloric acid was added to only half the pale blue-green precipitate to dissolve out the alumina, giving a dark blue product containing little or no alumina; the other half was dried to give a pale blue-green, alumina rich pigment. When the results of fading the two pigments were compared, it was found that the alumina-rich pigment faded more (Figure 9) [2]. The translucent flakes of pigment, which contain more alumina, are likely to show a greater degree of fading.

The method of preparation of the pigment from an organic starting material, in this case dried blood, typically results in the presence of angular, alumina-rich, translucent flake-like particles in the pigment. It thus affects the light-fastness of the pigment in so far as it introduces an extender, alumina.

The Substrate of Nineteenth-century Red Lake Pigments

The third study is also concerned with a variety of hydrated alumina, but in this case the alumina is not present incidentally, as it is in the eighteenth-century Prussian blues, but is an essential constituent of the pigment:

The National Gallery, NG 6383), katere detajl prikazuje slika 10; poteze z rožnato broščevo barvo so vidne na poti. Močna fluorescenca fragmenta rožnatega brošča pri UV osvetlitvi je prikazana na sliki 11. Pri analizi s SEM–EDX je bilo ugotovljeno, da je podlaga tega pigmenta in drugih podobnih na slikah sodobnikov, vključno z Edgarjem Degasom, Georgesom Seuratom in drugimi, poleg aluminija vsebovala presenetljivo veliko žvepla. To je bilo precej nepričakovano, saj substrati rdečih barvil iz vodikovih spojin aluminijevega oksida iz prejšnjih obdobij ne kažejo te značilnosti. Za pojav je mogoče predlagati več možnih razlag, ki se nanašajo na vir broščevega barvila in na način izdelave podlage.

Leta 1826 sta Robiquet in Colin ekstrahirala in identificirala alizarin, najpomembnejšo sestavino brošča; temu je sledila identifikacija purpurina [30]. Ta raziskava je privedla do precej bolj učinkovite ekstrak-

Slika 10. Claude-Oscar Monet, *Irisi* (London, The National Gallery, NG 6383), c. 1914–17. Olje na platnu, 200,7 x 149,9 cm. © The National Gallery, London.

Figure 10. Claude-Oscar Monet, *Irises* (London, The National Gallery, NG 6383), c. 1914–17. Oil on canvas, 200.7 x 149.9 cm. © The National Gallery, London.

madder lakes, as they were prepared in the nineteenth century and used by painters such as Monet, Degas and many others.

A traditional red lake pigment consists of a natural organic dyestuff precipitated onto a substrate consisting of some form of amorphous hydrated alumina. In the case of the lac lake used in the first study, described above, the source of dyestuff was the Indian lac insect, *Kerria lacca* Kerr 1782; in the case of a madder lake, the dyestuff is extracted from the root of the madder plant, *Rubia tinctorum* L.

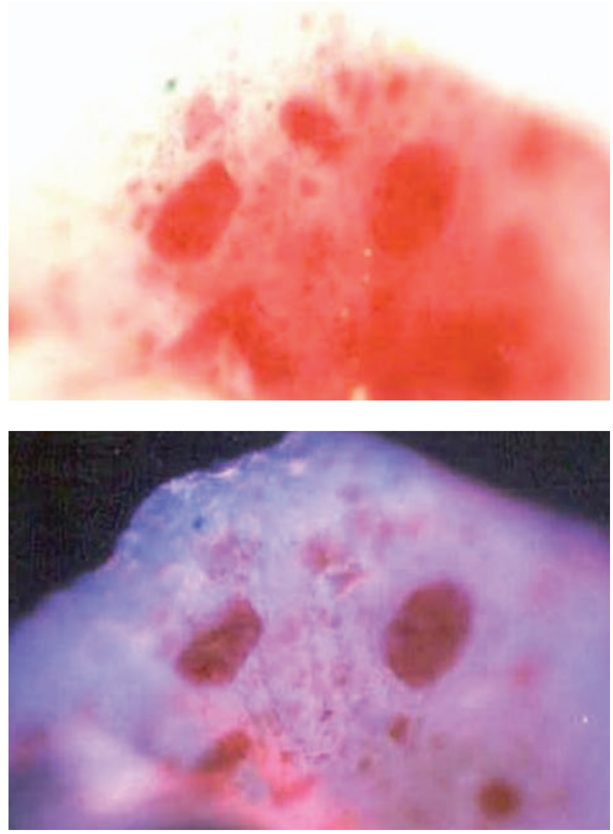
Lake pigments in samples taken from paintings dating from the fifteenth to the early years of the twentieth centuries were analysed in the Scientific Department of the National Gallery, London, comparing them with lakes prepared using recipes dating from the fourteenth to the nineteenth centuries. The substrates were examined by SEM–EDX and FTIR, the dyestuffs by high-performance liquid chromatography (HPLC). This analysis has shown that lake pigment substrates are very much more complex than the simple description suggests, both in the range of additional elements present and as far as the nature and chemistry of the aluminium salt is concerned. It has been found that, as with the Prussian blues described above, the precise method of preparation of the aluminium-containing substrate has been found to affect its constitution [3]. The work published has concentrated on paintings dating from before the late eighteenth century; the discussion that follows describes a feature of nineteenth-century pigments in which they differ from the earlier varieties.

Nineteenth- and early twentieth-century madder lakes are often an orange-red, quite light in colour, very vivid and transparent, frequently with an orange fluorescence. A lake of this type was used by Claude-Oscar Monet in *Irises*, painted in about 1914–17 (London, The National Gallery, NG 6383), a detail of which is shown in Figure 10; strokes of pink madder lake paint may be seen on the path. The strong fluorescence of a fragment of the pink madder lake under UV-illumination is seen in Figure 11. When analysed by SEM–EDX, it was found that the substrate of this lake and those of similar pigments in paintings by contemporary artists, including Edgar Degas, Georges Seurat and others, contained a surprisingly large amount of sulphur, in addition to aluminium. This was quite unexpected since hydrated alumina substrates of the red lakes of earlier periods did not show this feature. However, several possible explanations can be suggested for the phenomenon, relating firstly to the source of madder dyestuff, secondly to the method of making the substrate.

In 1826, alizarin, the most important constituent of the madder dyestuff, was extracted and identified by Rocije barvila iz korenine. Robiquet and Colin (1828) sta ugotovila, da z obdelavo broščeve korenine z vodeno žvepleno kislino dobita rjav material, 'garancin', ki ima precej več barvilnih sestavin (alzarina, purpurina in drugih antrachinonov) kot originalna korenina [31]. Nekoliko kasneje so odkrili nove načine za obdelavo svežih korenin. Koppov purpurin (1864), na primer, je bil pripravljen iz zmletih broščevih korenin, namočenih v vodi, nasičeni z žveplasto kislino (H_2SO_3). Po nadaljnji obdelavi je izdelek vseboval purpurin, psevdopurpurin in druge antrachinone [32]. Garancin, Koppov purpurin in drugi podobni derivati so se nato lahko uporabljali za izdelavo alizarina ali barvanje. Kot se je pokazalo, je pojasnitev strukture alizarinske molekule, ki sta jo izvedla Graebe in Liebermann leta 1868, ter njena posledična sinteza privedla do hitrega zatona francoske industrije brošča, toda Koppov purpurin se je v Franciji še naprej uporabljal do okoli leta 1900 [33]. Ugotovljeno je bilo, da vzorec Koppovega purpurina, narejenega v laboratoriju, vsebuje nekaj žvepla (slika 12) ter tako mogoče pojasnjuje prisotnost žvepla v Monetovem pigmentu. Alizarin, izdelan iz laboratorijsko pripravljenega 'Koppovega purpurina', je tudi drugače primerljiv z umetnikovim pigmentom: je močno fluorescenten in iz njega narejena slikarska barva je podobne barve kot moderni rožnati brošč.

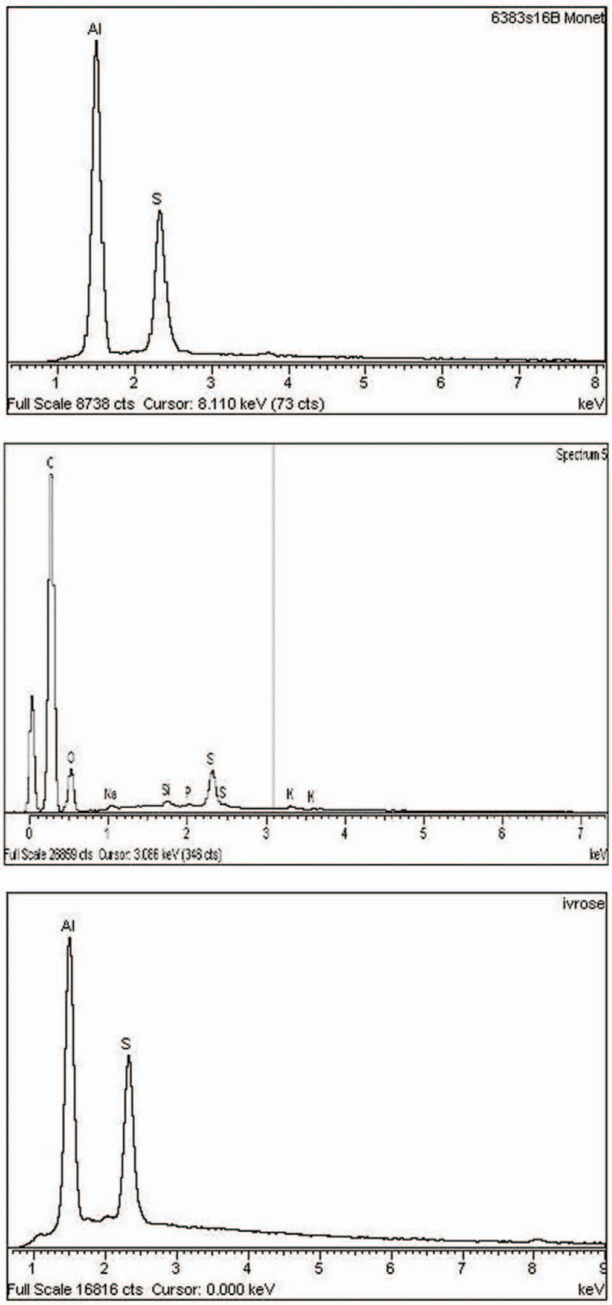
Obstaja pa še ena možna razlaga. Aluminij vsebujoča podlaga rdečega barvila nastane z reakcijo med lužnino in kalijevim galunovcem (kalijevim aluminijevim sulfatom) ali aluminijevim sulfatom. Ker je ta substrat amorfen in zelo spremenljiv, ga je težko okarakterizirati, toda nedavne analize kažejo, da substrati, ki vsebujejo aluminij, v bistvu pripadajo dvema skupinama [3]. Prva vsebuje večinoma aluminij in kisik (Al–O vezi se opazuje s FTIR); najbolje jo opišemo kot amorfen aluminijev oksid z vodikovo spojino [3, 34]. Večina rdečih organskih barvil s slik iz osemnajstega stoletja in zgodnejših vsebuje substrate te vrste. Druga skupina dodatno vsebuje še večjo količino žvepla. FTIR je pokazal, da je ta prisotna kot sulfat in da je ta vrsta substrata običajno prisotna v vzorcih barvil iz dvajsetega stoletja.

Pomemben dejavnik pri določanju, katero različico pridobimo, je vrstni red dodajanja reagentov. V receptih za karmin pred osemnajstim stoletjem je bil izvleček barvila pogosto narejen z lužno raztopino in nato so dodali kalijev galunovec, kar je povzročilo, da se je aluminijev oksid z vodikovo spojino usedal skupaj z barvilom, s katerim je bil vezan. To so substrati prve skupine. V receptih iz devetnajstega stoletja pa so raztopini barvila in aluminijevega sulfata ali kalijevega galunovca zmešali in nato dodali lužilo, da se je pigment usedel. V laboratorijskih vzorcih tako nare-



Slika 11. Claude-Oscar Monet, *Irisi*. Vzorec barve, ki vsebuje brošč, fotografiran z odbojno svetlobo in UV osvetlitvijo, kaže fluorescenco pigmenta.

Figure 11. Claude-Oscar Monet, *Irises*. Paint sample containing madder lake photographed by reflected light and UV illumination, showing fluorescence of pigment.



Slika 12. EDX spektri brošča, ki ga je uporabljal Monet (zgoraj); laboratorijsko pripravljeni 'Koppov purpurin' (na sredi); moderni rožnati brošč (spodaj).

Figure 12. EDX spectra of madder lake used by Monet (top); laboratory prepared 'Kopp's purpurin' (middle); a modern rose madder (bottom).

biquet and Colin in 1826; this was followed by the identification of purpurin [30]. This research led to considerable improvements in the efficiency of the extraction of the dyestuff from the root. Robiquet and Colin (1828) found that, by treating the madder root with aqueous sulphuric acid, they obtained a brown material, 'garancine' which was very much richer in the dyeing constituents (alizarin, purpurin and other anthraquinones) than the original root [31]. Slightly later in the century, other methods of processing the fresh root were devised. Kopp's purpurin (1864), for example, was prepared from ground madder root soaked in water saturated in sulphurous acid (H_2SO_3). After further treatment, the resulting product contained purpurin, pseudopurpurin and other anthraquinones [32]. Garancine, Kopp's purpurin and other similar derivatives could then be used for lake making or dyeing. As it turned out, the elucidation of the structure of the alizarin molecule by Graebe and Liebermann in 1868, and its subsequent synthesis, led to the rapid decline of the French madder industry, but Kopp's purpurin continued to be used in France for pigment preparation until about 1900 [33]. A sample of Kopp's purpurin made in the laboratory was found to contain some sulphur (Figure 12) and this is, therefore, one possible explanation for the presence of sulphur in Monet's pigment. The lake made from the laboratory-prepared 'Kopp's purpurin' was comparable to the artist's pigment in other ways: it fluoresced strongly and the paint made using it was a similar colour, reminiscent of a modern rose madder.

There is, however, another possible explanation. An aluminium-containing lake pigment substrate is produced by the reaction between an alkali and potash alum (potassium aluminium sulphate), or aluminium sulphate. As this substrate is amorphous and highly variable it is difficult to characterise, but recent analysis has shown that aluminium-containing substrates essentially fall into two groups [3]. The first contains mostly aluminium and oxygen (Al–O bands are observed by FTIR); this is best described as amorphous hydrated alumina [3, 34]. Most red lake pigments in paintings dating from the eighteenth century and earlier contain substrates of this type. The second group contains a significant amount of sulphur in addition. FTIR reveals that this is present as sulphate and that this is the type of substrate commonly present in nineteenth-century lake samples.

An important factor in determining which variety is obtained is the order in which the reagents are added. In recipes for lake pigments dating from before the eighteenth century, the dyestuff was often extracted by an alkaline solution and potash alum was then added, causing the hydrated alumina to precipitate together with the dyestuff with which it is bonded. These are substrates of the first group. In nineteenth-century recipes, how-

jenih substratov pigmenta je bilo žveplo v obliki sulfata prisotno v večjih količinah, kot so pokazali EDX spektri; tudi S–O (sulfatne) vezi (identificirane s FTIR) so bile podobne velikosti kot Al–O vezi aluminijevega oksida [3]. Ta vrsta substrata je podobna t.i. lahkemu aluminijevemu oksidu v spojini z vodikom (to je bazični aluminijev sulfat, čigar natančna sestava se spreminja v skladu z načinom priprave), opisanemu v literaturi o moderni tehnologiji barve. Lahki aluminijev oksid v spojini z vodikom je izredno presojen, nestanoviten in želatinast ter daje površino, zelo dovzetno za adsorpcijo barvil [35].

Recepti za pigmente iz devetnajstega stoletja pogosto bolj priporočajo izdelavo substrata iz bazičnega aluminijevega substrata kot iz aluminijevega oksida z vodikovo spojino, in sicer tako, da se namenoma doda dve tretjini količine lužine (običajno natrijevega karbonata), potrebne za nevtralizacijo galunovca, nato pa zavre mešanico, da se pigment usede. Vzrok za to je, da je filtriranje tako mnogo lažje [36]. To utegne biti poglavitna razlaga za prisotnost žvepla v broščcu, ki ga je uporabljal Monet, čeprav je mogoče, da so bili v praksi prisotni vsi trije viri žvepla.

Zaključek

Članek se z namenom, da bi prikazal sliko razsežnosti nedavnih projektov, izvedenih v Znanstvenem oddelku londonske Narodne galerije, osredotoča na posebne vidike treh študij, ki so v večjem obsegu objavljene drugje. Ne smemo pa pozabiti, da je bila izhodišče za vse tri študije slika z nekaterimi njenimi značilnostmi, ki so vodile do nadaljnjih vprašanj in končno do poskusov. Namen vseh treh študij je prispevati k večjemu razumevanju materialov, ki jih uporabljajo umetniki, in slik, ki jih slikajo.

ever, the solutions of dyestuff and aluminium sulphate or potash alum were mixed and alkali was then added to precipitate the pigment. In laboratory samples of lake pigment substrates made in this way, sulphur in the form of sulphate was present in marked amounts, seen in the EDX spectra; also the S–O (sulphate) bands (identified by FTIR) were of similar size to the Al–O bands of the alumina [3]. This type of substrate is similar to the so-called light alumina hydrate (actually a basic aluminium sulphate, the precise composition of which varies according to the method of peparation) described in modern paint technology literature. Light alumina hydrate is valued as a substrate for present-day lakes as it is extremely transparent, fluffy and gelatinous and provides a highly receptive surface for for the adsorption of dyestuffs [35].

Nineteenth-century pigment recipes in fact often recommend making a substrate of basic aluminium sulphate, rather than hydrated alumina, by deliberately adding only two-thirds of the amount of alkali (commonly sodium carbonate) required to neutralise the alum and then boiling the mixture to precipitate the lake. The reason given was that the lake formed was much easier to filter [36]. This may be the principal explanation for the presence of the sulphur in the madder lake used by Monet, although in practice the three possible sources of sulphur may all have made a contribution..

Conclusion

In order to give a picture of the range of recent projects carried out in the Scientific Department of the National Gallery, London, this paper has focused on particular aspects of the three studies published at greater length elsewhere. It should not be forgotten, however, that the starting point for all three studies was a painting and some characteristic it showed that led to further questions and ultimately to experimental work. The intention of all three studies was that the results of the research should contribute to a greater understanding of the materials used by artists and of the paintings they produced.

Viri

[1] Saunders, D. in Kirby, J. (2004) *The effect of relative humidity on artists' pigments*, National Gallery Technical Bulletin 25, 62–72.

[2] Kirby, J. in Saunders, D. (2004) *Fading and colour change of Prussian blue: Methods of manufacture and the influence of extenders*, National Gallery Technical Bulletin 25, 73–99.

[3] Kirby, J., Spring, M. in Higgitt, C. (2005) *The technology of red lake pigment manufacture: Study of the dyestuff substrate*, National Gallery Technical Bulletin 26, 71–88.

[4] Saunders, D. in Kirby, J. (2001) *A comparison of light-accelerated ageing regimes in some galleries and museums*, The Conservator 25, ICCROM, 95–104.

[5] Bøllingtoft, P. in Christensen, M.C. (1993) *Early Gothic wall paintings: An investigation of painting techniques and materials of 13th-century mural paintings in a Danish village church*, ICOM Committee for Conservation, 10th Triennial Meeting (ur. Bridgland, J), Washington, DC, USA, 22–27 August 1993: Preprints, ICOM Committee for Conservation, Paris, 531–535.

[6] Padfield, T., Bøllingtoft, P., Eshøj, B. in Christensen, M.C. (1994) *The wall paintings of Gundsømagle Church, Denmark*, Preventive Conservation: Practice, Theory and Research: Preprints of the Contributions to the Ottawa Congress, (ur. Roy, A. in Smith, P), 12–16 September 1994, International Institute for Conservation of Historic and Artistic Works, London, 94–98.

[7] Giovannoni, S., Matteini, M. in Moles, A. (1990) *Studies and developments concerning the problem of altered lead pigments in wall painting*, Studies in Conservation 35, International Institute for Conservation of Historic and Artistic Works, London, 21–25.

[8] Matteini, M. in Moles, A. (1981) *The reconversion of oxidized white lead in mural paintings: a control after a five year period*, ICOM Committee for Conservation, 6th Triennial Meeting (ur. van Asperen de Boer, J.R.J. in Berends-Albert, M.), Ottawa 1981, ICOM, Paris, 81/15/1–81/15/8.

[9] Howard, H. C. (1995) *Techniques of the*

References

[1] Saunders, D. and Kirby, J. (2004) *The effect of relative humidity on artists' pigments*, National Gallery Technical Bulletin 25, 62–72.

[2] Kirby, J. and Saunders, D. (2004) *Fading and colour change of Prussian blue: Methods of manufacture and the influence of extenders*, National Gallery Technical Bulletin 25, 73–99.

[3] Kirby, J., Spring, M. and Higgitt, C. (2005) *The technology of red lake pigment manufacture: Study of the dyestuff substrate*, National Gallery Technical Bulletin 26, 71–88.

[4] Saunders, D. and Kirby, J. (2001) *A comparison of light-accelerated ageing regimes in some galleries and museums*, The Conservator 25, ICCROM, 95–104.

[5] Bøllingtoft, P. and Christensen, M.C. (1993) Early Gothic wall paintings: *An investigation of painting techniques and materials of 13th-century mural paintings in a Danish village church*, ICOM Committee for Conservation, 10th Triennial Meeting (Edit. Bridgland, J), Washington, DC, USA, 22–27 August 1993: Preprints, ICOM Committee for Conservation, Paris, 531–535.

[6] Padfield, T., Bøllingtoft, P., Eshøj, B. and Christensen, M.C. (1994) *The wall paintings of Gundsømagle Church, Denmark*, Preventive Conservation: Practice, Theory and Research: Preprints of the Contributions to the Ottawa Congress (Ed. Roy, A. and Smith, P.), 12–16 September 1994, International Institute for Conservation of Historic and Artistic Works, London, 94–98.

[7] Giovannoni, S., Matteini, M. and Moles, A. (1990) *Studies and developments concerning the problem of altered lead pigments in wall painting*, Studies in Conservation 35, International Institute for Conservation of Historic and Artistic Works, London, 21–25.

[8] Matteini, M. and Moles, A. (1981) *The reconversion of oxidized white lead in mural paintings: a control after a five year period*, ICOM Committee for Conservation, 6th Triennial Meeting , (Edit. van Asperen de Boer, J.R.J. and Berends-Albert, M.), Ottawa 1981, ICOM, Paris, 81/15/1–81/15/8.

[9] Howard, H.C. (1995) *Techniques of the Romanesque and Gothic wall paintings in the Holy Sepulchre Chapel, Winchester Cathedral* Historical Painting Techniques, Materials and Studio Practice: Preprints of a Symposium (Edit. Wallert, A., Hermens, E. and Peek, M.), University

Romanesque and Gothic wall paintings in the Holy Sepulchre Chapel, Winchester Cathedral, Historical Painting Techniques, Materials and Studio Practice: Preprints of a Symposium (ur. Wallert, A., Hermens, E. and Peek, M.), University of Leiden, the Netherlands, 26–29 June 1995, Getty Conservation Institute, Los Angeles, 91–104.

[10] Spring, M. and Grout, R. (2002) _The blackening of vermilion: An analytical study of the process in paintings_, National Gallery Technical Bulletin 23, 50–61.

[11] Gettens, R. J. in FitzHugh, E. W. (1993) _Azurite and Blue Verditer_, Artists' Pigments: A Handbook of their History and Characteristics, 2. zvezek, (ur. Roy, A.), National Gallery of Art, Washington; Oxford University Press, Oxford, 27.

[12] Emoto, Y. (1980) _Deterioration of a Japanese wooden panel painting – an approach to study of malachite staining, 'Rokushō-Yake'_, International Symposium on the Conservation and Restoration of Cultural Property – Conservation of Far Eastern Art Objects, November 26–29, 1979, Tokyo, Japan,Tokyo National Research Institute of Cultural Objects, Tokyo, 50.

[13] Cather, S. in Howard, H. (1994) _Romanesque wall paintings in the apse of St Gabriel's Chapel, Canterbury Cathedral: Their technique, condition and environment reassessed_, Forschungprojekt Wandmalerei-Schäden, Arbeitshefte zur Denkmalpflege in Niedersachsen 11 (ur. Segers-Glocke, C.), Niedersächsisches Landesverwaltungsamt Institut für Denkmalpflege, Hannover, 141–156.

[14] Feller, R. L. (1967) _Studies in the darkening of vermilion by light_, Report and Studies in the History of Art, National Gallery of Art, Washington, 99–111.

[15] Daniels, V. (1987) _The blackening of vermilion by light_, Recent Advances in the Conservation and Analysis of Artifacts; University of London, Institute of Archaeology Jubilee Conference Papers (ur. Black, J.), Institute of Archaeology, London, 280–282.

[16] Dei, L., Ahle, A., Baglioni, P., Dini, D. in Ferroni, E. (1998) _Green degradation products of azurite in wall paintings: identification and conservation treatment_, Studies in Conservation 43, International Institute for Conservation of Historic and Artistic Works, London, 80–88.

of Leiden, the Netherlands, 26–29 June 1995, Getty Conservation Institute, Los Angeles, 91–104.

[10] Spring, M. and Grout, R. (2002) *The blackening of vermilion: An analytical study of the process in paintings*, National Gallery Technical Bulletin 23, 50–61.

[11] Gettens, R.J. and FitzHugh, E.W. (1993) *Azurite and Blue Verditer*, Artists' Pigments: A Handbook of their History and Characteristics, Vol. 2 (Edit. Roy, A.), National Gallery of Art, Washington; Oxford University Press, Oxford, 27.

[12] Emoto, Y. (1980) *Deterioration of a Japanese wooden panel painting – an approach to study of malachite staining, 'Rokushō-Yake'*, International Symposium on the Conservation and Restoration of Cultural Property – Conservation of Far Eastern Art Objects, November 26–29, 1979, Tokyo, Japan, Tokyo National Research Institute of Cultural Objects, Tokyo, 50.

[13] Cather, S. and Howard, H. (1994) *Romanesque wall paintings in the apse of St Gabriel's Chapel, Canterbury Cathedral: Their technique, condition and environment reassessed*, Forschungprojekt Wandmalerei-Schäden, Arbeitshefte zur Denkmalpflege in Niedersachsen 11 (Edit. Segers-Glocke, C.), Niedersächsisches Landesverwaltungsamt Institut für Denkmalpflege, Hannover, 141–156.

[14] Feller, R.L. (1967) *Studies in the darkening of vermilion by light*, Report and Studies in the History of Art, National Gallery of Art, Washington, 99–111.

[15] Daniels, V. (1987) *The blackening of vermilion by light*, Recent Advances in the Conservation and Analysis of Artifacts; University of London, Institute of Archaeology Jubilee Conference Papers (Edit. Black, J.), Institute of Archaeology, London, 280–282.

[16] Dei, L., Ahle, A., Baglioni, P., Dini, D. and Ferroni, E. (1998) *Green degradation products of azurite in wall paintings: identification and conservation treatment*, Studies in Conservation 43, International Institute for Conservation of Historic and Artistic Works, London, 80–88.

[17] Saunders, D. and Kirby, J. (1994) *Light-induced colour changes in red and yellow lake pigments*, National Gallery Technical Bulletin 15, 79–97.

[18] Kirby, J. (1993) *Fading and colour change of*

[17] Saunders, D. in Kirby, J. (1994) *Light-induced colour changes in red and yellow lake pigments*, National Gallery Technical Bulletin 15, 79–97.

[18] Kirby, J. (1993) *Fading and colour change of Prussian blue: Occurrences and early reports*, National Gallery Technical Bulletin 14, 62–71.

[19] Commission Internationale de l'Eclairage (1978) *Recommendations on uniform color spaces, color difference equations, psychometric color terms*, Supplement No. 2 to CIE Publication No. 15 (E-2.3.1), 1971/(TC-1.3), Commission Internationale de l'Eclairage, Vienna.

[20] McDonald, R. in Smith, K. J. (1995) *CIE94 – a new colour difference formula*, Journal of the Society of Dyers and Colourists 111, 376–379.

[21] Saunders, D., Spring, M. in Higgitt, C. (2002) *Colour change in red lead-containing paint films*, ICOM Committee for Conservation, 13th Triennial Meeting (ur. Vontobel, R.), Rio de Janeiro, 22–27 September 2002: Preprints, James and James, London, 455–463.

[22] Aze, S. in Vallet, J.-M. (2002) *Chromatic degradation processes of red lead pigment*,. ICOM Committee for Conservation, 13th Triennial Meeting (ur. Vontobel, R), Rio de Janeiro, 22–27 September 2002: Preprints, James and James, London, 549–555.

[23] Dayes, E. (1805) *The Works of the late Edward Dayes*, Mrs Dayes, London, 300–301.

[24] Bomford, D. in Roy, A. (1993) *Canaletto's 'Stonemason's Yard' and 'San Simeone Piccolo'*, National Gallery Technical Bulletin 14, 34–41: glej sliko 4, 39.

[25] Woodward, J. (1724) *Praeparatio caerulei Prussiaci ex Germania missa ad Johannem Woodward*, Philosophical Transactions XXXIII (381), 15–17.

[26] Dossie, R. (1758) *The Handmaid to the Arts* 1. zvezek, 77–8; za recept 1724 gl. 2. zvezek, izdajatelj ni naveden, London, 387–391.

[27] Asai, C. (2004) *'Handmade' Berlinerblau, Zeitschrift für Kunsttechnologie und Konservierung* 18(2), ICCROM, 261–292.

Prussian blue: Occurrences and early reports, National Gallery Technical Bulletin 14, 62–71.

[19] Commission Internationale de l'Eclairage (1978) *Recommendations on uniform color spaces, color difference equations, psychometric color terms*, Supplement No. 2 to CIE Publication No. 15 (E-2.3.1), 1971/(TC-1.3), Commission Internationale de l'Eclairage, Vienna.

[20] McDonald, R. and Smith, K.J. (1995) *CIE94 – a new colour difference formula*, Journal of the Society of Dyers and Colourists 111, 376–379.

[21] Saunders, D., Spring, M. and Higgitt, C. (2002) *Colour change in red lead-containing paint films*, ICOM Committee for Conservation, 13th Triennial Meeting (Edit. Vontobel, R.), Rio de Janeiro, 22–27 September 2002: Preprints, James and James, London, 455–463.

[22] Aze, S. and Vallet, J.-M. (2002) *Chromatic degradation processes of red lead pigment*, ICOM Committee for Conservation, 13th Triennial Meeting (Edit. Vontobel, R.), Rio de Janeiro, 22–27 September 2002: Preprints, James and James, London, 549–555.

[23] Dayes, E. (1805) *The Works of the late Edward Dayes*, Mrs Dayes, London, 300–301.

[24] Bomford, D. and Roy, A. (1993) *Canaletto's 'Stonemason's Yard' and 'San Simeone Piccolo'*, National Gallery Technical Bulletin 14, 34–41: see Plate 4, 39.

[25] Woodward, J. (1724) *Praeparatio caerulei Prussiaci ex Germania missa ad Johannem Woodward*, Philosophical Transactions XXXIII (381), 15–17.

[26] Dossie, R. (1758) *The Handmaid to the Arts* Vol. I, 77–8; for the 1724 recipe see Vol. 2, no publisher cited, London, 387–391.

[27] Asai, C. (2004) *'Handmade' Berlinerblau*, Zeitschrift für Kunsttechnologie und Konservierung 18(2), ICCROM, 261–292.

[28] Ackroyd, P., Roy, A. and Wine, H. (2004) *Nicolas Lancret's The Four Times of Day*, National Gallery Technical Bulletin 25, 48–61: see Plate 7, 54.

[29] Welsh, F.S. (1988) *Particle characteristics of Prussian blue in an historical paint*, Journal of the American Institute for Conservation 27, American Institute for

[28] Ackroyd, P., Roy, A. in Wine, H. (2004) *Nicolas Lancret's The Four Times of Day*, National Gallery Technical Bulletin 25, 48–61: glej sliko 7, 54.

[29] Welsh, F. S. (1988) *Particle characteristics of Prussian blue in an historical paint*, Journal of the American Institute for Conservation 27, American Institute for Conservation, Washington, 55–63.

[30] B., A. (1826) *Sur un nouveau principe immédiat des végétaux (l'alizarin) obtenu de la garance*. *Note extraite d'un travail de MM*. Colin et Robiquet, Journal de Pharmacie et de Chemie 12, 407–412.

[31] Anon. (1828) *Mémoire de MM. Robiquet et Colin sur la question, 'Séparer la matière colorante de garance, et déterminer la quantité qu'un poids donné de garance peut en contenir'*, Bulletin de la Société industrielle de Mulhouse (1828), 126–145.

[32] Kopp, E. (1861) *Recherches sur la garance d'Alsace*, Répértoire de chimie appliquée III, 85–97.

[33] Perkin, A.G. in Everest, A.E. (1918) *The Natural Organic Colouring Matters*, Longmans, Green & Co., London, 27.

[34] Williams, J. (1973) *Hydrated Aluminium Oxide*, Pigment Handbook, 1. zvezek (ur. Patton, T.C.), John Wiley & Sons, New York, 293–304.

[35] Patton, T. C. (1973) *Light Alumina Hydrate and Gloss White*, Pigment Handbook, 1. zvezek (ur. Patton, T.C), John Wiley & Sons, New York, 319–321.

[36] Halphen, G. (1895) *Couleurs et vernis*, J. B. Baillière et fils, Paris, 178–179.

Conservation, Washington, 55–63.

[30] B., A. (1826) *Sur un nouveau principe immédiat des végétaux (l'alizarin) obtenu de la garance. Note extraite d'un travail de MM. Colin et Robiquet*, Journal de Pharmacie et de Chemie 12, 407–412.

[31] Anon. (1828) *Mémoire de MM. Robiquet et Colin sur la question, 'Séparer la matière colorante de garance, et déterminer la quantité qu'un poids donné de garance peut en contenir'*, Bulletin de la Société industrielle de Mulhouse (1828), 126–145.

[32] Kopp, E. (1861) *Recherches sur la garance d'Alsace*, Répértoire de chimie appliquée III, 85–97.

[33] Perkin, A.G. and Everest, A.E. (1918) *The Natural Organic Colouring Matters*, Longmans, Green & Co., London, 27.

[34] Williams, J. (1973) *Hydrated Aluminium Oxide*, Pigment Handbook, Vol. 1 (Edit. Patton, T.C.), John Wiley & Sons, New York, , 293–304.

[35] Patton, T.C. (1973) *Light Alumina Hydrate and Gloss White*, Pigment Handbook, Vol. 1 (Edit. Patton, T.C.), John Wiley & Sons, New York, 319–321.

[36] Halphen, G. (1895) *Couleurs et vernis*, J.B. Baillière et fils, Paris, 178–179.

Alkalni kronski etri v umetnosti in konservatorstvu

Alkali-crown-ether in Art and Conservation

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POVZETEK: Lak na slikah starih mojstrov je izpostavljen mnogim procesom deterioracije. Oksidacija npr. povzroča postopno tvorbo karboksilnih skupin, možne pa so tudi oslabitve estrskih vezi. Hidroksidi alkalijskih kovin so močne baze, znane po tem, da burno in nekontrolirano reagirajo s karboksilnimi kislinami. Pričakovali pa smo, da bo reakcija potekala kontrolirano, če bo potekala v makromolekularnem matriksu. Kot zelo obetajoče orodje za cepljenje estrskih vezi pri sobni temperaturi in za reagiranje z ostanki prostih karboksilnih kislin, nastalih med procesom staranja, ne da bi deloval na barvne plasti, se je izkazal stabilen RbOH polietilen glikol kompleks. Kontrolne študije z ^{86}RbOH in ^{14}C poliakrilatom so pokazale, da na površini slike ni ostankov čistil.

Ključne besede:
laneno olje;
RbOH-PEG 400;
kronski eter;
odstranjevanje laka.

Keywords:
linseed oil;
RbOH–PEG 400;
crown ether;
varnish removal.

ABSTRACT: The varnish of aged Old Master paintings is exposed to many different deterioration processes. For example, oxidative attacks lead to progressive formation of carboxylic acid groups while many ester bondings are expected to be weakened. Alkali hydroxides are strong bases, known to attack ester bondings and to react vigorously and in an uncontrolled manner with carboxylic acids. However, embedded in a macromolecular matrix a controlled reaction was expected. A stable RbOH–polyethylene glycol complex was a promising tool to cleave the ester bondings at room temperature and to react with the exposed carboxylic acid residues generated in the course of the ageing process without affecting the paint layers. Control studies employing $^{86}RbOH$ and ^{14}C polyacrylate showed the complete absence of residual cleansing components on the paint surface.

Uvod

Stare lakirane površine slik so izpostavljene mehanskim vplivom in vplivom okolja, ki povzročajo bolj ali manj ekstremne spremembe, vključujoč rumenenje, zamreženje in razpokanost.
Te spremembe v stanju slike in barvnih tonih na koncu zahtevajo odstranitev plasti laka. Do srednjega veka so prvi laki primarno temeljili na sušečih se oljih [1]. Izdelovali so jih s preprostim postopkom vrenja nekaterih olj ali vrenja olj z naravnimi smolami. Tako nastale visoko viskozne temne tekočine so na slike nanašali s čopičem ali ročno. Kot lak so priložnostno nanašali tudi čisto, nepredelano olje.

Na zraku se lak počasi suši nekaj mesecev ali let. Proces sušenja lahko pospešimo s sončno svetlobo ali sušilci (sikativi). Tradicionalno so v te namene uporabljali svinčevo belilo (bazičen svinčev karbonat) ali svinčeve okside, moderni sušilci pa vsebujejo svinčeve, manganove ali kobaltove oleate ali rezinate. Ponovno odkritje destilacije v poznem srednjem veku je vodilo do uporabe terpentinskega olja in drugih hitro hlapljivih snovi kot topil za smole in laki so postali boljši. Ker se smolni etrski laki sušijo hitreje in so precej lažji kot oljni laki, jih v modernih slikah v veliki meri nadomeščajo. Kemijska sorodnost med starimi lanenimi in smolnimi laki je v tem, da imajo delno ali v celoti strukturo poliestrskega tipa.

Etrske smolne lake je ponavadi mogoče preprosto odstraniti z organskimi topili, stari oljni laki pa so lahko odporni na ta topila. Včasih, ko je vezivo za barve podobno ali bolj topno kot pokrivni premaz (lak), lahko postane selektivno odstranjevanje lakov skoraj nemogoče. Podobna situacija se pojavi ob poskusu odstranjevanja preslikav iz oljnih barv, če je preslikava nanesena neposredno na originalno plast. Kemija starih oljnih barv in lakov ter njihovo nežno odstranjevanje so torej pri ohranjanju naše kulturne dediščine posebno zanimivi. Trenutna tehnologija kemijsko tega problema ne more rešiti. Za čiščenje površin slik so bile vpeljane nove obetajoče tehnike, ki uporabljajo lipaze. Na lipazah temelječe odstranjevanje starih oljnih lakov naj bi bilo bolj nežno in varovalno [2, 3]. Žal se je ta metoda izkazala kot nekakšen placebo [4].

Kot alternativa je bil razvit nov koncept alkalnega odstranjevanja lakov, ki je upošteval reaktivnost močnih baz in večjih protiionov – kationov. Od topila PEG 400 z veliko relativno molekulsko maso smo pričakovali tvorbo kompleksov z ioni alkalijskih kovin kot makromolekularnih kronskih etrov, ki bi ovirali difuzijo njihovih bazičnih protiionov v spodnje plasti laka ali barve. Po tej novi metodi so bili na primer pripravljeni in uporabljeni RbOH-PEG 400 kronski

Introduction

Aged varnished paint surfaces are exposed to mechanical and environmental influences causing more or less extreme changes, including yellowing, cross-linking and crazing. These changes to the shape and tonal balance of a painting ultimately necessitate the removal of the varnish layer. Early varnishes for paintings were based primarily on drying oils until the late Middle Ages [1]. These varnishes were made by the simple process of boiling certain oils or boiling them with natural resins. The resulting highly viscous, dark liquids were applied to the paintings using a brush or with the hand. Occasionally, pure, unadulterated oil was applied as a varnish.

Upon exposure to air, a varnish will dry slowly over a period of months or years. This drying process can be accelerated by sunlight or driers (siccatives). Whereas traditionally lead white (basic lead carbonate) or lead oxides were used, modern driers contain lead, manganese or cobalt oleates or resinates. The rediscovery of distillation in the late Middle Ages led to the application of terpentine oil and other volatile substances as resin solvents, resulting in improved varnishes. These resin ethereal varnishes dry faster and are considerably lighter than oil varnishes – very likely the reason they have largely replaced oil varnishes in modern painting. There is a chemical relationship between aged linseed and resinous varnishes in that they represent in part or in full a polyester-type structure.

While resin ethereal varnishes are usually easily removable with organic solvents, aged oil varnishes can be resistant to these solvents. Sometimes selective removal of varnish becomes almost impossible if the paint binder is of similar or greater solubility than the covering varnish. A similar situation occurs when trying to remove overpaint consisting of oil paint, if the overpaint was applied directly onto the original layer. The chemistry of aged oil paint and varnishes, as well as the gentle removal of such layers, is accordingly of special interest in the conservation of our cultural heritage. Current technology cannot solve this problem chemically. A promising new technique for the cleaning of painting surfaces was introduced employing lipase. The lipase-based removal of aged oil varnishes was claimed to be both gentle and protective [2, 3]. Unfortunately, this method turned out to be a placebo phenomenon [4].

As an alternative, a new concept in alkaline varnish removal was developed, taking into account the reactivity of strong bases and larger counter cations. The large relative molecular mass solvent PEG 400 was expected to form complexes with alkaline ions as macromolecular crown ethers, impeding the diffusion

etri, ki naj bi stare oljne lake odstranili v celoti ali jih le stanjšali. Prav tako se zdi na ta način obetajoče odstranjevanje preslikav. Tehnika naj bi se izvajala kontrolirano, ne da bi poškodovala spodnje plasti slike ali podsnove. Poleg cepitve estrskih vezi naj bi ta rubidijev kronski eter reagiral z ostanki prostih kislin, prisotnimi v laku. Reaktivnost uporabljene alkalne raztopine predstavlja dodatno prednost. Polietilen glikol polimerni kelatni rubidij v obliki kronskega etra ovira difuzijo bazičnih protiionov Rb^+ v globlje plasti laka ali barvne plasti. Prepričljivo je bila prikazana tvorba visoko stabilnega polietilen RbOH kompleksa z uporabo gelske kromatografije (long range CG). Poleg tega je bil možna migracija alkalnih ionov v plast barve med alkalnim odstranjevanjem laka kontrolirana z ^{86}RbOH polietilen glikolom. Na srečo lak propada le na površini. Globlje plasti barve ali laka niso ogrožene niti v primeru, ko so kemijsko sorodne laku ali preslikavi, ki naj bi ju odstranili, kar kaže dejstvo, da na površini slike ^{86}Rb skorajda ni bil odkrit. Tudi za nevtralizacijo uporabljena poliakrilna kislina se na površini slike ni absorbirala. V primerih, ko je bila uporabljena polialkrilna kislina s ^{14}C, niso izmerili nobene radioaktivnosti.

Rezultati in razprava

1 Kemijske lastnosti in molekularna zgradba starih lakov na osnovi lanenega olja

Žal ne poznamo kemijskih lastnosti in molekulske zgradbe starih lakov, kakršenkoli zanesljiv koncept konserviranja pa bi moral temeljiti na natančnem in popolnem poznavanju kemijske narave lakov in veziv [5]. Laneno olje sestavljajo različni trigliceridi, ki vsebujejo linolensko (cis-9, cis-12, cis-15-oktadekatrienojsko) in linolno (cis-9, cis-12-oktadekadienojsko) kislino. Po predpostavljenem reakcijskem mehanizmu naj bi se sušenje lanenega olja začelo z avtooksidacijo gliceridnih maščobnih kislin v olju. Poleg tega postopoma oksidirajo ostanki polinenasičenih maščobnih kislin, kar vodi do nekontroliranega zamreževanja in kislinskih ostankov (slika 1).

Včasih se ti karboksilatni ostanki lahko zasidrajo v globino do podsnove. Dodatek alkalijskih hidroksidov ali ionskih izmenjevalcev lahko te vezi razcepi in sprosti preostanke laka. Končni produkt se imenuje linoksin in njegova struktura ostaja neznana. Olje v prisotnosti kisika prehaja iz tekočega stanja prek poltrdnih intermediatov v trdno, čvrsto, elastično plast. Ta plast lahko zadrži pigmente in jih tako "veže" na nosilec.

Z namenom, da bi pridobili nekatere informacije

of their basic counter ions into lower varnish or paint layers. In this new method, for example, RbOH–PEG 400 crown ethers were prepared and employed to remove aged oil varnishes at full strength or thinned. The removal of overpaint, similarly, seemed promising. This technique is designed to proceed in a controlled manner without damaging lower paint or base layers. In addition to the cleavage of the ester bondings this rubidium crown ether reacted with carboxylic acid residues present in the varnish. The reactivity of the alkaline solution employed is an additional benefit here. The polyethylene glycol polymer chelates rubidium in a crown ether mode, impeding the diffusion of the basic Rb^+ counter ions into lower varnish or paint layers. The formation of a highly stable polyethylene–RbOH complex was convincingly demonstrated by the use of long-range gel chromatography. Furthermore, possible migration of alkali metal ions into the paint layer during alkaline varnish removal was controlled using ^{86}RbOH polyethylene glycol. Fortunately, the varnish is degraded on the surface only. Lower paint or varnish layers are not attacked, even if chemically similar to the varnish or overpaint to be removed, shown by the fact that virtually no ^{86}Rb was detected on the paint surface. In the same way, the polyacrylic acid used for neutralisation was not absorbed onto the paint surface: no radioactivity was measured when ^{14}C polyacrylic acid was employed.

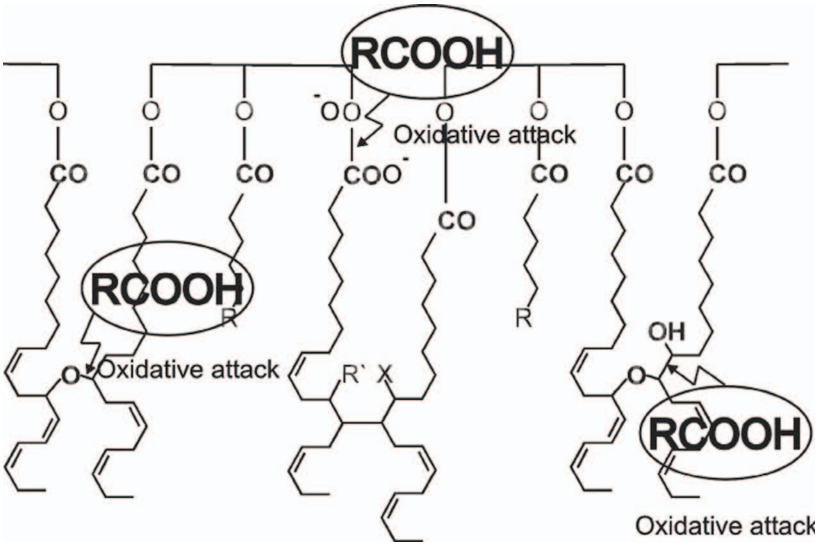
Results and Discussion

1 Chemistry and Molecular Architecture of Aged Linseed Oil Varnish

Unfortunately, we do not know the chemistry and molecular architecture of aged varnishes. Any reliable conservation concept would have to be based on a thorough and complete knowledge of the chemical nature of varnish and binder [5].

Linseed oil consists primarily of various triglycerides containing linolenic (*cis*-9, *cis*-12, *cis*-15-octadecatrienoic acid) and linoleic acid (*cis*-9, *cis*-12-octadecadienoic acid). The current reaction mechanism postulates that the drying of linseed oil begins with an autoxidation of the glyceride fatty acids within the oil. In addition, polyunsaturated fatty acid residues are progressively oxidized, leading to uncontrolled cross-linking and carboxylic acid residues (Figure 1).

Occasionally these carboxylate residues may be anchored to the paint ground. Addition of alkali hydroxides or ion exchange materials may break these bondings and liberate varnish remnants. The end product is called linoxin and its structure remains unknown. In the



Slika 1. Shematski načrt progresivnega staranja in oksidacije lanenega olja. Možne oslabitve estrskih vezi med staranjem, ki povzroči dodatno cepitev teh delov v prisotnosti polimernega RbOH-PEG-kompleksa, ne moremo izključiti.

Figure 1. Schematic proposal of progressive linseed oil ageing and oxidation. Possible weakening of ester bondings during the ageing process, resulting in the additional cleavage of these moieties in the presence of the polymeric RbOH–PEG-complex, cannot be excluded.

o strukturi, so proces sušenja lanenega olja nadzorovali z infrardečo spektrometrijo. Spekter sušenega lanenega olja se razlikuje od spektra svežega olja; število dvojnih vezi se med sušenjem zmanjša. Vibracijski pasovi z vrhovi pri 3011cm^{-1} (alkil-H valenčne vibracije), 1652 cm^{-1} (C=C valenčne vibracije) in 722 cm^{-1} (cis olefinske, deformacijske vibracije) so se zožili ali popolnoma izginili.

Spekter suhega lanenega olja kaže močan, intenziven OH valenčni pas z vrhom pri 3450 cm^{-1}, ki je posledica absorbirane vode (OH skupin, povezanih z vodikovo vezjo) ali nastalih karboksilnih skupin. Vibracijski pasovi estrskih skupin v linoksinu so v primerjavi s svežim lanenim oljem nespremenjeni (C=O valenčne vibracije pri 1745 cm^{-1} in C-O valenčne vibracije pri 1163 cm^{-1}). Sušenje zato ne vpliva na funkcijo olja.

Emulzija svežega lanenega olja je v prisotnosti hladnega natrijevega hidroksida nenavadno odporna na hidrolizo. Pomembna hidroliza lanenega in podobnih rastlinskih olj zahteva podaljšan proces vrenja v močnih alkalnih raztopinah, nasprotno pa karboksilne kisline počasi sušečega se premaza lanenega olja učinkovito reagirajo z natrijevim hidroksidom. Tako so izvedli primerjalne eksperimente retitracije svežega in starega lanenega olja. Vsaka komponenta je bila tretirana s hladno raztopino natrijevega hidroksida. Retitracija je bila izvedena z uporabo žveplove kisline. V nasprotju s svežim lanenim oljem, ki je v prisotnosti NaOH ostalo nespremenjeno, so pomembne koncentracije karboksilnih skupin pri starem lanenem olju (ali

presence of oxygen, the state of the oil molecule progresses from a liquid, through semi-solid intermediates, to a firm, elastic layer. This layer can retain pigments, thus 'binding' them to the support.

In an attempt to obtain some structural information, the drying process of linseed oil was monitored by infrared spectrometry. The spectrum of dried linseed oil differs from that of fresh oil: the number of double bonds decreases in the course of drying. The vibrational bands at 3011 cm^{-1} (alkenyl-H valence vibrations), 1652 cm^{-1} (C=C valence vibrations) and 722 cm^{-1} (*cis* olefines, deformational vibrations) diminish or disappear completely.

The spectrum of dried linseed oil shows an intense OH valence band at 3450 cm^{-1}, resulting either from absorbed water, from hydrogen-bonded OH groups, or from the carboxylic acid groups generated. The vibrational bands of the ester groups in linoxin are essentially unchanged compared to fresh linseed oil (C=O valence vibrations at 1745 cm^{-1} and C–O valence vibrations at 1163 cm^{-1}). Consequently, the drying process does not affect the glyceride ester function.

An emulsion of fresh linseed oil is extraordinarily resistant to hydrolysis by cold sodium hydroxide. Significant hydrolysis of linseed or similar vegetable oils requires prolonged boiling in strong alkaline solutions. By way of contrast, the carboxylic acid groups of a slowly dried linseed oil film react effectively with sodium hydroxide. Comparative back titration experiments using both fresh and aged linseed oil were performed. Each component was treated with cold, aqueous sodium hydroxide.

linoksinu) reagirale z NaOH. To lahko sklepamo iz dejstva, da se je porabilo 55 % dodanega natrijevega hidroksida (slika 2).

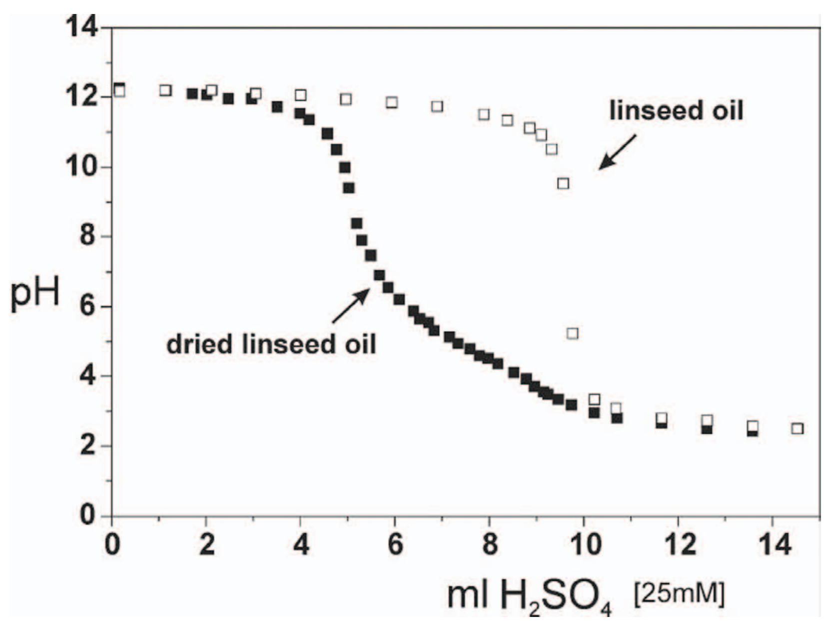
2 Nov koncept

Lak se učinkovito odstranjuje z alkalijskimi hidroksidi; ta že dolgo znani pojav smo ponovno pretehtali in izvedli reakcijo v nadzorovanih okoliščinah. Alkalna tehnika odstranjevanja laka se pri čiščenju slik uporablja priložnostno. V ekstremnih primerih običajnim vodnim raztopinam amonijaka dodajo alkoholne raztopine natrijevega hidroksida. Čeprav se zdi uporaba alkoholnega natrijevega hidroksida na slikah na začetku nezaslišana, nadaljnji premislek pokaže, da so lahko zelo močne baze daleč manj nevarne kot šibki alkalni puferski sistemi in jih lahko uporabimo pri odstranjevanju laka, če upoštevamo naslednja pravila:

Back titration was performed using sulphuric acid. Unlike fresh linseed oil, which remained unaffected in the presence of NaOH, marked concentrations of carboxylic acid groups of aged linseed oil – or linoxin – reacted with the NaOH added, demonstrated by the fact that 55% of the sodium hydroxide solution was consumed (Figure 2).

2 The New Concept

Taking into account the effective removal of varnish by alkali hydroxides, this long-known phenomenon was reconsidered in applying this reaction in a controlled manner. Alkaline varnish removal techniques are occasionally applied in the cleaning of paintings. In extreme cases, alcoholic solutions of sodium hydroxide are used to supplement the usual aqueous solutions of ammonia. While the application of alcoholic sodium hydroxide to paintings may initially appear outrageous, the following considerations show that very strong bases may be far



Slika 2. Titracija umiljenega–saponificiranega linoksina. Linoksin in laneno olje (84,1 mg vsakega) sta bila tretirana 1 uro z 10 ml mrzle vodne raztopine 50-mM natrijevega hidroksida. Retitracija je bila izvedena s 25-mM žveplovo kislino. Strma krivulja prikazuje laneno olje (□), medtem ko nižja krivulja predstavlja linoksin (■). Količina žveplove kisline, uporabljene za titracijo lanenega olja, je povsem ekvivalentna količini uporabljenega natrijevega hidroksida (hiter padec pH vrednosti v ekvivalentni točki 10 ml). Laneno olje potemtakem ni bilo umiljeno. Titracijska krivulja linoksina pade strmo pri uporabi 4,5 ml žveplove kisline. Razlika do teoretično potrebne količine žveplove kisline (10 ml) kaže, da je bilo porabljeno 5,5 ml 50-mM natrijevega hidroksida.

Figure 2. Titration of saponified linoxin. Linoxin and linseed oil (84.1 mg each) were treated for 1 hour with 10.0 ml cold, aqueous 50mM sodium hydroxide. Back titration was performed with 25mM sulphuric acid. Linseed oil (□) results in the steep curve, while a more shallow curve originates from linoxin (■). The amount of sulphuric acid used to titrate linseed oil is exactly equivalent to the amount of sodium hydroxide applied (steep drop of the pH value at the equivalence point 10.0 ml). Linseed oil was accordingly not saponified. The titration curve of linoxin drops steeply at 4.5 ml sulphuric acid. The difference to the theoretical amount of sulphuric acid required (10.0 ml) shows that 5.5 ml of the 50mM sodium hydroxide were consumed.

Pravilo 1: Uporabljaj topila z visoko relativno molekulsko maso (M_r).
Topila z nizko relativno molekulsko maso (M_r) (voda, etanol in podobna topila) povzročajo nabrekanje in mehčanje plasti laka. Posledično lahko topilo prodre skozi plast laka in povzroči velike poškodbe na barvnih plasteh pod lakom. Zaradi tega bi morali za restavriranje slik uporabljati topila z visoko relativno molekulsko maso (M_r).

Pravilo 2: Nizke koncentracije močnih baz so varnejše kot visoke koncentracije šibkih baz.
Zelo razredčene raztopine močnih baz so dovolj bazične za odstranjevanje laka. Ko jih nanesemo na plasti laka, hitro reagirajo in se iztrošijo že na površinskih plasteh. V globlje plasti torej nimajo časa prodreti. Močne baze prav tako praktično kvantitativno hidrolizirajo estrske skupine laka in na ta način se uporabljena baza učinkovito odstrani, kar pomeni dodatno prednost. Šibke baze laka ne hidrolizirajo popolnoma. V puferskih raztopinah prisotnost ustreznih kislin še bolj zmanjša njihovo učinkovitost, zato moramo uporabiti šibke kisline ali pufre v visokih koncentracijah, da dosežemo primerljive učinke. Ker laki hidrolizirajo veliko počasneje v šibko alkalnih raztopinah kot v močnih bazah, imajo majhni puferski ioni več časa za prodiranje v spodnje plasti in za povzročanje škode. Hidroksidni (–OH) ion je zelo močna baza. Razredčene raztopine natrijevega hidroksida so zato popolnoma primerne za odstranjevanje starih lakov.

Pravilo 3: Uporaba kationov z visoko (M_r).
Ker hidroksidni ioni lahko difundirajo skozi lak in spodnje plasti barv, bi se morali uporabi natrijevega hidroksida ali amonijaka izogibati. Difuzija hidroksidnih ionov je možna, če jih spremljajo majhni, difuzirajoči protiioni. Zaradi njihove permeabilnosti lahko gledamo na lakirane površine kot na "kationske gobe". Vdirajoči hidroksidni ioni hidrolizirajo estrske skupine in spremeljevalni kationi nevtralizirajo nastale karboksilatne skupine. Pri restavriranju slik bi se zato morali izogibati majhnim kationom. Tega pravila bi se morali držali ne le v primerih, ko delamo z močnimi bazami, kot so npr. hidroksidni ioni, ampak tudi v primerih, ko uporabljamo šibke baze za nevtralizacijo kislin. Domnevamo lahko, da pride do škodljivega učinka dezoksiholata [6] ali smolnih detergentov [7] predvsem zaradi prodiranja majhnih kationov v veziva in posledične hidrolize.

Pri postopkih konserviranja slik bi se morali zato izogibati uporabi blagih detergentov. Edina izjema bi morali biti primeri, v katerih nobena plast (lak, barva ali osnovna plast) ne vsebuje estrske komponente, ki lahko hidrolizira. Izmenjava malih kationov z velikimi praktično "naplavi" hidroksidne ione na površino slike.

less dangerous than weakly alkaline buffer systems and may be employed in varnish removal if the following guidelines are observed:

Rule 1: Use large relative molecular mass (M_r) solvents.
Small M_r solvents, such as water, ethanol and similar solvents, cause varnish layers to swell and soften. As a result, the solvent can penetrate the varnish layer and cause severe damage to the paint layers below. Consequently, large M_r solvents should preferably be used during the restoration of paintings.

Rule 2: Low concentrations of strong bases are safer than high concentrations of weak bases.
Very dilute solutions of strong bases are alkaline enough to remove varnish. When applied to varnish layers, these dilute solutions react quickly and are consumed at the surface layer. They therefore lack the time to penetrate into deeper layers. Strong bases also hydrolyse varnish ester groups almost quantitatively, effectively eliminating the base used at the same time, an additional advantage. Weak bases do not hydrolyse varnish completely. In buffered solutions, the presence of their corresponding acids reduces their efficacy even further. Therefore, weak bases or buffers must be applied in high concentrations to achieve comparable effects. However, varnish hydrolyses much more slowly in weak alkaline solutions than in strong, allowing the small buffer ions more time to penetrate lower layers and cause damage. The hydroxide (–OH) ion is a very strong base. Accordingly, dilute solutions of sodium hydroxide are perfectly suitable for the removal of aged varnish.

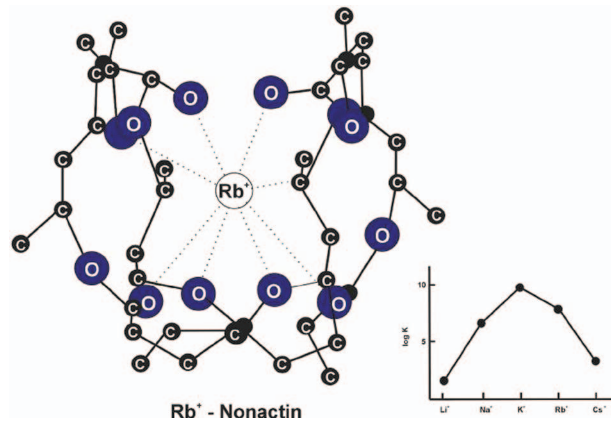
Rule 3: Employing large M_r cations.
The application of sodium hydroxide or ammonia should, however, be avoided as hydroxide ions may diffuse into lower paint and varnish layers. This diffusion is possible if the hydroxide ions are accompanied by small, diffusible counter ions. Due to their permeability, varnish layers can be viewed as a 'cation sponge'. Invading hydroxide ions hydrolyse the ester groups and the accompanying cations neutralise the resulting carboxylate groups. Consequently, small cations should be avoided wherever possible in the restoration of paintings. This rule should be observed not only when working with strong bases such as hydroxide ions, but also in cases where weak bases are employed to neutralise acids. As such, the damaging effect of desoxycholate [6] or resin detergents [7] can be assumed to be due primarily to penetration of small cations into the binder and its consequent hydrolysis.

Accordingly, the application of these 'mild' detergents in the conservation of paintings should be avoided. The only exception should be cases in which none of the

3 Uporaba alkalnega kronskega etra z visoko M_r

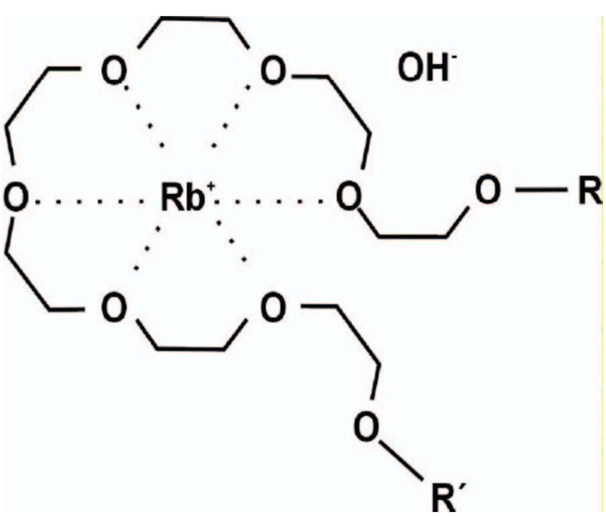
Primerni topili sta polarni polietilen glikol 400 (PEG 400) ali manj polarni polipropilen glikol. Prav tako se lahko uporabljajo alkoholi z visoko M_r, npr. dodekanol. Veliki protiioni (kationi) preprečujejo hidroksidnim ionom prodiranje v globino barvne plasti. Na ta način omejimo učinek hidroksidnih ionov na površino laka. V nevodnih topilih se lahko uporabijo tudi druge anionske baze. V tem kontekstu mislimo na PEG 400 in alkalijske hidrokside. PEG 400 ni samo topilo z visoko M_r, ampak ima tudi odlične kompleksirajoče lastnosti, npr. za alkalijske kovinske ione [8]. Veliki kompleksi, podobni kronskim etrom, nastanejo, ko se hidroksidi alkalijskih kovin, alkoholati in podobne spojine raztopijo v PEG 400 [9], ki obkroža kation alkalijske kovine (slika 3).

Ionski radij določa končno velikost obroča. Najbolj stabilni alkalnoionski kronski etri nastanejo v prisotnosti kalija (K^+), sledijo Rb^+, Cs^+, Na^+ in Li^+ [10] (slika 3). Velikost obroča makrocikličnega kovinskega kompleksa je določena z velikostjo ionskega radija alkalijske kovine. Ta fenomen se imenuje "templatni učinek" [11]. Predlagani model kompleksa alkalnega kronskega etra lahko primerjamo z Rb nonaktinom, naravnim kronskim etrom [12] (slika 4).



Slika 4.
Struktura Rb nonaktina, primer biološkega kompleksa tipa kronskega etra z alkalijskim ionom. *Spodaj desno:* Konstante stabilnosti alkalno ionskih kriptatov, ponovno narisano (prilagojeno po: Da Silva and Williams 1991).

Figure 4. The structure of Rb Nonactin, an example of a biological alkali ion crown ether-type complex. *Lower right:* Stability constants of alkali ion cryptates, redrawn after da Silva and Williams 1991.



Slika 3. Struktura Rb+ polietilen glikol 400 (PEG 400) kronskega etra.

Figure 3. The structure of rubidium ion (Rb+) polyethylene glycol 400 (PEG 400) crown ether.

layers (varnish, paint or base) contains hydrolysable ester components. Exchanging small cations for large in effect 'docks' the hydroxide ions onto the surface of the painting.

3 The Application of High M_r Alkali Crown Ether

Appropriate solvents are the polar polyethylene glycol 400 (PEG 400) or the less polar polypropylene glycol. Large M_r alcohols such as dodecanol can also be employed. Large countercations prevent hydroxide ions from penetrating into lower paint layers. This has the desirable effect of limiting the effect of hydroxide ions to the surface of the varnish. In non-aqueous solvents, other anionic bases may be employed as well. In this context, our interest fell on PEG 400 and alkali hydroxides. PEG 400 is not only a large M_r solvent, but also has excellent complexing characteristics, for alkali metal ions, for example [8]. Large complexes resembling crown ethers are formed when alkali metal hydroxides, alcoholates and similar compounds are dissolved in PEG 400 [9], which encircles an alkali metal cation (Figure 3).

The ionic radius determines the resulting ring size. The most stable alkali ion crown ethers were obtained in

4 Sestava in stabilnost RbOH polietilen glikol kompleksa

Naravni RbOH PEG 400 kompleks je bil uspešno demonstriran z gelsko filtracijo zmesi RbOH in PEG 400 prek Bio Gel P 2 kolone. Jasno je bilo prikazano, da Rb^+ ioni ostanejo trdno vezani v polietilen glikolnih frakcijah. Obstojnost oz. stabilnost *in situ* generiranega kompleksa tipa kronskega etra je morala biti presenetljivo visoka, da se je lahko obdržal med gelsko filtracijo (long range CG) (slika 5). Glavnina vzorca je rahlo premaknjena, neposredno pod "ramo" PEG 400 absorpcije pri $A_{210\ nm}$. Pred ali za PEG 400 absorpcijskim pasom nismo ugotovili nobenih disociiranih Rb^+ ionov, kar potrjuje ugotovitev o visoki stabilnosti kompleksa.

Uporaba Rb^+ je bila zelo pomembna, saj smo v kasnejših fazah uporabili ^{86}R za študij možne migracije v spodnje barvne plasti. Ta čistilni postopek v prisotnosti Rb^+ je bil bolj podrobno dokumentiran (slika 6). Odstranjevanje laka s tem postopkom je v primerjavi z vodnimi ali alkoholnimi raztopinami enake koncentracije počasnejše. K sreči je zmes s PEG omejena na površino laka. Odstranjevanje laka je še posebej počasno, če raztopino PEG 400 po nanosu na površino slike pustimo pri miru. Visoka viskoznost in visoka M_r znižujeta stopnjo difuzije in konvekcije produktov hidrolize laka. Restavrator lahko torej določi stopnjo odstranjevanja laka z nežnim premikanjem reakcijske raztopine (npr. z bombažno blazinico ali polipropilensko lopatico). Produkti razgradnje oljnih lakov se raztapljajo v PEG 400 in raztopino obarvajo oranžno-rjavo.

Ko dosežemo želeno stopnjo čiščenja, z odstranitvijo te raztopine končamo reakcijo. Preostalo reakcijsko raztopino odstranimo s spiranjem. Prednost te tehnike odstranjevanja laka v primerjavi s konvencionalnimi metodami je, da lak hidrolizira le na površini. Istočasno so karboksilni ostanki izvlečeni iz podsnove. Tako se kaže učinek te tehnike na kemijski ravni. Lak lahko odstranimo ali stanjšamo, celo če sta lak in osnova kemijsko podobna (npr. oljni lak na oljni barvi).

Po čiščenju nismo niti vizualno niti pri pregledu pod mikroskopom odkrili nobenih površinskih razjed ali izravnav površine barve. Podrobno so koraki odstranjevanja laka z metodo RbOH-PEG kronskega etra opisani pri sliki 6.

5 Uporaba RbOH-PEG 400 kronskega etra za odstranjevanje laka na starih slikah

Nova metoda je bila prikazana na dveh ohranjenih fragmentih starih slik. Med delavnico na Courtauld Institute of the History of Art v Londonu smo zaporedoma očistili delca platna dveh oljnih slik iz

the presence of potassium (K^+) followed by Rb^+, Cs^+, Na^+ and Li^+ [10](Figure 3). The ring size of the macrocyclic metal complex is determined by the size of the alkali metal ion radius. This phenomenon is called the ‘template effect’ [11]. The suggested model crown ether alkali complex can be compared with Rb nonac-tin, a naturally occurring crown ether [12] (Figure 4).

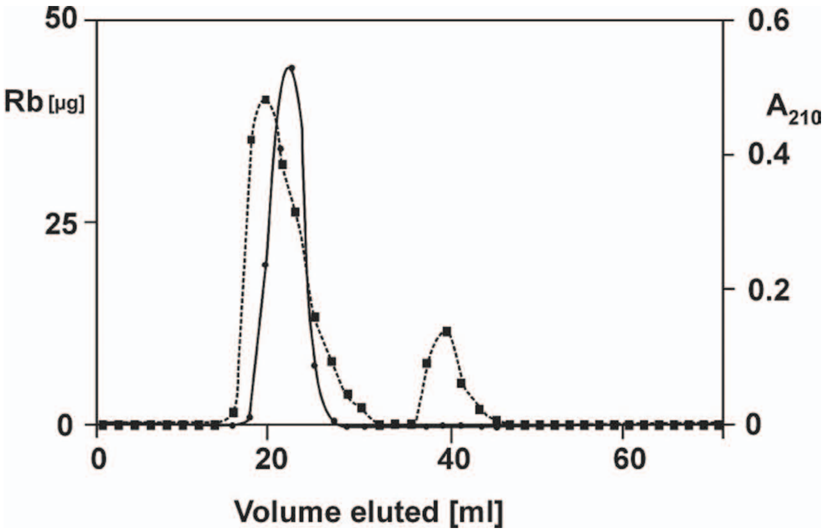
4 Formation and Stability of a RbOH Polyethylene Glycol Complex

The genuine formation of a RbOH–PEG 400 complex was successfully demonstrated by gel-fil-trating a mixture of RbOH and PEG 400 through a Bio Gel P 2 column. It was clearly shown that the Rb^+ ions remained firmly bound in the polyethylene glycol fractions. The stability of the *in situ*-generated crown ether type complex must have been surprisingly high to have survived such a long-range gel filtration (Figure 5). The major portion appears slightly shifted directly under the shoulder of the PEG 400 absorption at $A_{210\ nm}$. Absolutely no dissociated Rb^+ ions were detected in front of or after the PEG 400 absorption band, supporting the conclusion of the high stability of the complex.

The use of Rb^+ was of special importance as at a later stage the radioactive ^{86}Rb ion was used to study possible migration into the lower paint layers. Thus, this cleansing regime in the presence of Rb^+ was documented in more detail (Figure 6).Varnish removal using this regime is slower compared to that using aqueous or alcoholic solutions of the same concentration. Fortunately, this PEG mixture is restricted to the varnish surface. Varnish removal is especially slow if the PEG 400 solution is not disturbed once applied to the surface of the painting. The high viscosity, as well as the large M_r, reduces diffusion and convection rates of varnish hydrolysis products. Accordingly, the restorer can determine the rate of varnish removal by gentle movement of the reaction solution (e.g. with a cotton swab or a polypropylene spatula). Oil varnish cleavage products dissolve in PEG 400, colouring it orange brown.

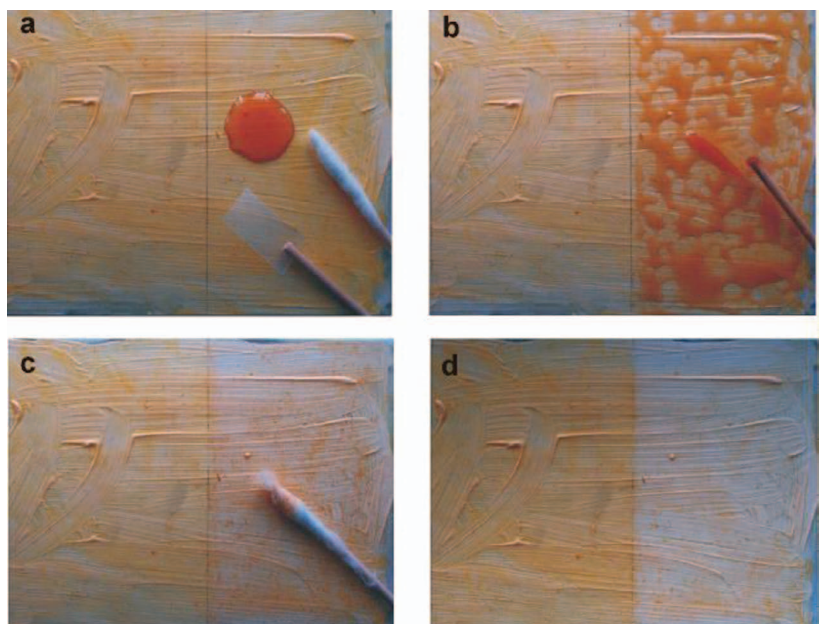
Removal of this solution terminates the reaction when the desired degree of cleansing has been achieved. The residual reaction solution is removed by subsequent stepwise washes. The advantage of this varnish removal technique over conventional methods is that varnish is hydrolysed only at its surface. At the same time, carboxylic acid residues are freed from the paint ground. As such, the effect of this technique resembles that of a ‘chemical plane’. Varnish can be removed or thinned even if the varnish and base are chemically similar (for example, oil varnish on an oil paint).

After the cleansing process no detectable abra-



Slika 5. **Gelska kromatografija *in situ* tvorjenega kompleksa tipa RbOH PEG 400 kronskega etra. -□-A210 nm; •• O •• Rb(I). 10 ml zmesi 1 mol/l RbOH in 28-kratnega presežka PEG 400 je potovalo skozi kolono Bio Gel P 2. Zaznati ni bilo nobene disociacije RbOH PEG 400 kompleksa, kar potrjuje zaključek o visoki stabilnosti tega kompleksa.**

Figure 5. Gel chromatography of *in situ* formed RbOH PEG 400 crown ether type complex. -□-A210 nm; •• O •• Rb(I). 10 ml of a mixture of 1 mol/l RbOH and a 28 fold excess of PEG 400 were passed through Bio Gel P 2 column. No detectable dissociation of the RbOH PEG 400 complex was seen, supporting the conclusion of a high stability of this complex.



Slika 6. **Podrobni koraki odstranjevanja laka z RbOH PEG kronskim etrom.**
Testna površina je suha barvna plast, sestavljena iz lanenega olja s svinčevim belilom. Barvna plast je pokrita s posušeno, približno sedem let staro plastjo laka iz posebnega lanenega olja (linseed stand oil). a: RbOH PEG čistilo nanesemo na površino s previdnimi potezami z bombažno blazinico ali polipropilensko lopatico. b: Rjavkasta barva RbOH PEG kronskega etra se po dveminutni inkubaciji postopoma intenzivira. c: Čistilo, ki vsebuje raztopljene komponente laka, mehansko odstranimo. Čiščeno površino v nadaljevanju nevtraliziramo s poliakrilno kislino PEG 400, sledi obdelava z uporabo topila z visoko Mr padajoče polarnosti. V zadnjem koraku površino obdelamo s Shellsol T in pustimo, da izhlapi. d: Po uspešnem odstranjevanju porumenelega laka je očiščena površina opazno svetlejša.
Pomembno opozorilo: **Po tem postopku nismo na površini slike zaznali nobenih mikroskopsko vidnih razjed.**

Figure 6. Detailed steps of RbOH–PEG crown ether varnish removal. The test surface is a dried paint layer consisting of lead white in linseed oil. The paint layer is covered with a dried, approximately 7 year-old varnish layer of linseed stand oil. a) The RbOH–PEG cleanser is applied by gingerly moving a cotton swab or a polypropylene spatula over the surface. b) The brownish colour of the RbOH–PEG crown ether is progressively intensified after an incubation of 2 minutes. c) The cleanser containing dissolved varnish components is removed mechanically. The cleaned surface is subsequently neutralised with polyacrylic acid PEG 400, followed by consecutive treatments using large Mr solvents of decreasing polarity. In the final step, the surface is treated with Shellsol T, which is allowed to evaporate. d) Following the successful removal of the yellowed varnish, the cleaned surface is noticeably lighter.
Note: No detectable abrasion of the paint surface is seen by microscopic examination after this treatment.

poznega 17. in iz 18. stoletja. V obeh primerih je bil lak na slikah temno rjave barve.

Sveže pripravljeno RbOH–PEG 400 čistilo smo nanesli na površino laka, na katerem ni bilo krakelir, in reagent malce premešali s polipropilensko lopatico. Oba laka sta zelo verjetno imela poliestrsko strukturo, saj je njuno odstranjevanje gladko uspelo. Po 3 do 4 minutah smo postopek ustavili z odstranitvijo odvečnega RbOH–PEG 400 z uporabo suhega bombažnega tampona. Očiščene površine smo naknadno nevtralizirali s poliakrilno kislino–PEG 400 in večkrat zapored sprali s topili z veliko M_r in padajočo polarnostjo. Na koncu postopka so bile površine, s katerih je bil lak odstranjen, izjemne kakovosti (sliki 7 in 8). Na nobenem vzorcu, očiščenem na ta način, nismo z mikroskopom zasledili razjed površin slike.

6 Ugotavljanje morebitne absorpcije RbOH-PEG 400 kronskega etra na površini slike in poliakrilat

Morebitno absorpcijo Rb^+ ionov v postopku alkalijskega odstranjevanja laka smo skušali ugotoviti s čistilno raztopino, obogateno z ^{86}Rb. Ta radioaktivni izotop je bil izbran zaradi kratkega razpolovnega časa, 18,6 dni, s čimer bi se izognili možnemu poškodovanju podsnove zaradi nenadzorovanega sevanja. Učinkovitost raztopine RbOH–PEG 400 kronskega etra smo primerjali z uporabo vodne in etanolne raztopine Rb(^{86}Rb)OH. Že samo z mehanskim brisanjem ostane na površini slike le 2,5 % ^{86}Rb. V nadaljnjem postopku odstranjevanje čistila Rb–PEG 400 s poliakrilno kislino v PEG 400 zniža koncentracijo rubidijevih ionov na površini na 0,8 % njihove začetne vrednosti. Nasprotno smo pri postopku z etanolno raztopino Rb(^{86}Rb)OH opazili 30-krat višjo ^{86}Rb radioaktivnost (23,3 %). Uporaba vodnega Rb(^{86}Rb)OH je povzročila skoraj 40-krat višjo ^{86}Rb radioaktivnost (30,1 %) kot pri postopku s kronskim etrom (tabela 1).

sion or levelling off of the paint surface was noticed either visually or upon microscopic examination. Detailed steps of varnish removal with the RbOH–PEG crown ether method are depicted in Figure 6.

5 Application of RbOH–PEG 400 Crown Ether for Varnish Removal on Old Master Paintings

The new method was demonstrated on two fragments of Old Master paintings. Canvas fragments of two oil paintings, dating from the late 17^{th} century and the 18^{th} century, were cleaned during a workshop at the Courtauld Institute of the History of Art, London. In both cases, the picture varnish was of a deep brown colour.

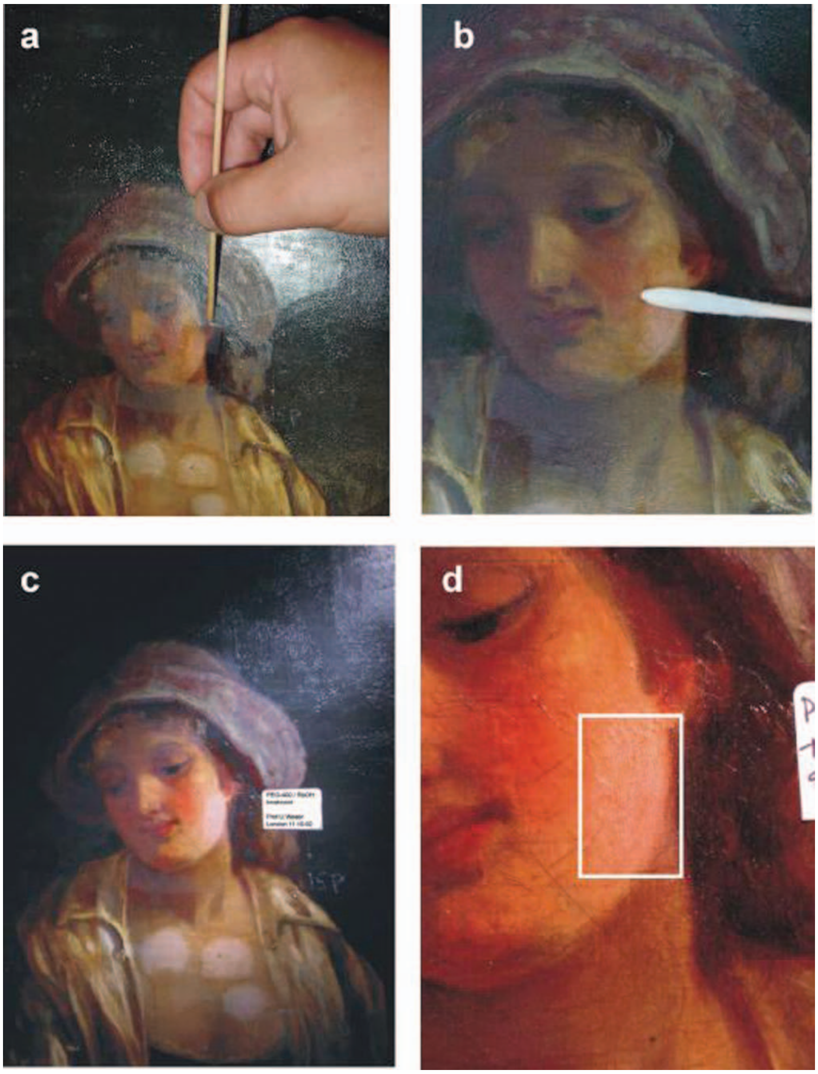
The freshly prepared RbOH–PEG 400 cleaning reagent was applied to the varnish surfaces, in areas without craquelure, slightly agitating the reagent using a polypropylene spatula. Both varnishes very possibly had a polyester structure as their removal succeeded in a smooth manner. After 3 to 4 minutes the treatment was terminated by the removal of excessive RbOH–PEG 400 using dry cotton swabs. The cleansed surfaces were subsequently neutralised with polyacrylic acid–PEG 400 and repeatedly washed with large M_r solvents of decreasing polarity. At the end of the whole treatment the de-varnished areas were of exceptional quality (Figures 7 and 8). No detectable abrasion of the paint surface could be seen by microscopic examination in either cleaned paint fragment after this treatment.

6 Possible Absorption of RbOH–PEG 400 Crown Ether onto the Paint Surface and Polyacrylate

In order to locate possible absorption of Rb^+ ions in the course of alkaline varnish removal, the cleansing solution was enriched with ^{86}Rb. This radioactive isotope was chosen for its short half life of 18.6 days, thereby avoiding possible damage to the paint ground due to un-

Slika 7. Praktična uporaba RbOH / PEG-400 na oljnih slikah iz poznega 17. stoletja. Nova metoda je bila predstavljena na delavnici na Courtauld Institute of the History of Art v Londonu. a: Po uspešnem odstranjevanju porumenelega laka. b: Detajl.

Figure 7. Practical application of RbOH–PEG-400 on a late 17th-century oil painting. The new method was demonstrated during a workshop at the Courtauld Institute of the History of Art, London. a) After the successful removal of the yellowed varnish. b) Detail.



Slika 8. **Odstranjevanje laka z oljne slike iz 18. stoletja z uporabo RbOH PEG 400. Neznani umetnik, olje na platnu. Slika je bila prekrita z lakom Mastix. Delavnica na Courtauld Institute of the History of Art v Londonu.**
a: Nanašanje čistila RbOH / PEG 400. Učinek čiščenja smo izboljšali tako, da smo raztopino rahlo premešali s polipropilensko lopatico.
b: Po odstranitvi laka smo čistilo odstranili s suho bombažno blazinico.
c: Očiščeno površino smo nato nevtralizirali s poliakrilno kislino / PEG-400 in večkrat spirali s topili z visoko M_r padajoče polarnosti (glej tabelo 2 v eksperimentalnem delu).
d: Po uspešni odstranitvi porumenelega laka je očiščena površina opazno svetlejša. Po tem postopku nismo na površini slike ugotovili nobenih mikroskopsko vidnih razjed.

Figure 8. Varnish removal on an 18th-century oil painting (Unknown Artist, oil on canvas, Courtauld Institute, London), using RbOH–PEG 400. The painting was covered with a mastic varnish. Workshop at the Courtauld Institute of the History of Art, London. a) Application of the RbOH–PEG 400 cleanser. The solution was agitated slightly with a polypropylene spatula to improve the cleansing action. b) After varnish removal, the cleanser was removed with dry cotton swabs. c) The cleaned surface is subsequently neutralised with polyacrylic acid–PEG-400, followed by consecutive treatments using large M_r solvents of decreasing polarity (see Table 2 in the experimental section). d) Following the successful removal of the yellowed varnish, the cleaned surface is noticeably lighter. No detectable abrasion of the paint surface is seen by microscopic examination after this treatment.

Pri poskusih nevtralizacije s ^{14}C poliakrilno kislino, s čimer naj bi ugotovili morebitno površinsko absorpcijo ^{14}C poliakrilata, so bili izvedeni nadaljnji postopki čiščenja, opisani pod Metodami. Po čiščenju niso ugotovili ^{14}C poliakrilata, to pa pomeni, da ni prišlo do absorpcije te viskozne polikisline na površini slike.

controlled irradiation. In order to compare the efficacy of the RbOH–PEG 400 crown ether, cleansing solutions of both ethanolic and aqueous Rb(^{86}Rb)OH were applied. Already with mere mechanical wiping only 2.5% of ^{86}Rb is left on the paint surface. In the follow up treatment, the Rb–PEG 400 cleanser and its removal with polyacrylic acid in PEG 400 reduces the surface concentration of rubidium ion to 0.8% of its initial amount. By way of contrast, a thirty fold higher ^{86}Rb radioactivity (23.3%) was seen after the ethanolic Rb(^{86}Rb)OH treatment. The use of aqueous Rb(^{86}Rb)OH resulted in an almost 40 times higher residual ^{86}Rb radioactivity (30.1%) compared to the crown ether treatment (Table 1).

$Rb(^{86}Rb^{+})$-applied [2.4 $\mu mol/cm^2$] = 900 cpm	radioactivity [cpm]	$Rb(^{86}Rb^{+})$ [$\mu mol/cm^2$]	Residual $Rb(^{86}Rb^{+})$ [%]
$Rb(^{86}Rb^{+})$-PEG-crownether *wiping off*	23	0.06	**2.5**
$Rb(^{86}Rb)$-PEG-crownether *post-cleansing*	8	0.02	**0.8**
$Rb(^{86}Rb^{+})$-ethanol *wiping off*	850	2.23	**94.5**
$Rb(^{86}Rb^{+})$-ethanol *post-cleansing*	210	0.55	**23.3**
aqueous $Rb(^{86}Rb^{+})OH$ *wiping off*	380	0.99	**41.9**
aqueous $Rb(^{86}Rb^{+})OH$ *post-cleansing*	280	0.73	**30.9**

Tabela 1. **Ostanki rubidijevih ionov na površini slike. Že po mehanskem brisanju ostanejo na površini slike le majhne količine ^{86}Rb (2,5 %). Nasprotno večina čistil na bazi alkohola izhlapi že na površini laka. Praktično ves uporabljeni rubidij ostane na površini (94,5 %) preostale reaktivnosti. Tudi po spiranju z vodo smo še vedno izmerili nekaj 86Rb na površini slike (42 %).**

Table 1. Residual rubidium ions on paint surface. Mere mechanical wiping already leaves only a small amount of ^{86}Rb (2.5%) on the paint surface. By way of contrast, most of the alcohol-based cleanser evaporated on the varnish surface. Consequently, practically all of the applied rubidium remains on the surface leaving 94.5% of residual reactivity. Some 42% of 86Rb could still be measured on the surface after a water-based cleaning process.

Zaključki

Odstranjevanje lakov poliestrskega tipa z RbOH-PEG 400 kronskim etrom je obetavna nova metoda pri ohranjanju kulturne dediščine. Kljub temu moramo biti pri uporabi te metode zelo previdni. Alkalijsko odstranjevanje lakov poliestrskega tipa bi moralo biti omejeno na močno postarane lake in oljne slike. V vsakem primeru je treba učinek najprej preveriti na manjšem obrobnem področju, preden ga lahko z gotovostjo uporabimo. S to metodo ne bi smeli popolnoma odstraniti oljnih lakov, ki prekrivajo zelo tanko plast oljne barve, ali barvnih lakov; v takem primeru bi se bilo bolje odločiti za tanjšanje površine laka. Priporočeno naj bi bilo odstranjevanje in/ali tanjšanje kasnejših preslikav, temelječih na lanenem olju. Seveda bodo potrebne obsežne dodatne mikroskopske in elektronske mikrografske kontrole. Rezultat uporabe nove tehnike na originalih je bil obetaven. Vsekakor je potrebno nadaljnje dolgotrajno spremljanje učinkov tega postopka čiščenja, da bi ugotovili morebitne skrite poškodbe, ki se lahko pojavijo naknadno. Alkalijske tehnike odstranjevanja ne bi smeli uporabiti v primerih

In the case of ^{14}C polyacrylic acid neutralisation experiments aiming to detect possible surface absorption of ^{14}C polyacrylate during the post-cleansing process was carried out as described above under Methods. No 14C polyacrylate was detected at the end of the cleansing process, indicating that no absorption of this viscous poly-acid onto the paint surface was noticed.

Conclusion

The RbOH–PEG 400 crown ether induced removal of varnishes of polyester type is a promising new method in the conservation of cultural heritage. Nevertheless, the application of this method should be performed with great care. Alkaline removal of polyester-type varnish should, consequently, be restricted to severely aged varnishes and oil paintings. In any case, preliminary tests must be conducted on an unobtrusive area to confirm applicability. Oil varnishes covering very thin layers of oil paint or paint varnishes should not be removed completely by this method: varnish thinning

globokih krakelir ali v primerih, ko se barvna plast lušči in odkriva podsnovo. Alkalna raztopina namreč lahko polzi pod površino in napada ali razgrajuje plasti podsnove, ki vsebujejo pigmente.

Eksperiment

1 Materiali

Kemikalije: radioaktivni rubidij 86 (razpolovni čas 18,7 dni; tip razpada ß -; ß- energija (maks.): 0,69 MeV (8,8 %) / 1,77 MeV (91,2 %); vir γ sevanja 1,077 MeV (8,8 %) je bila vodna raztopina rubidijevega klorida (Amersham Pharmacia Biotech, code RGS.2). Radioaktivnost je bila 37–185 MBq/mL ali 1–5 mCi/mL. ^{14}C poliakrilno kislino je doniral dr. Eugen Barbu, School of Pharmacy and Biomedical Sciences, University of Portsmouth iz Hampshira v Veliki Britaniji. Vsi drugi reagenti, vključno z rubidijevim hidroksidom, so bili največje možne čistosti, pridobljeni od Sigme Aldrich iz Steinheima v Nemčiji.

***Steklene plošče:* okenske steklene plošče, dolžine 18 cm; širine 10 cm, debeline 3 mm, dobavitelj: Glaserei Härle, Tübingen, Nemčija.**

***Slike:* Oljna slika iz 18. stoletja in avtentični fragment oljne slike iz poznega 17. stoletja na platnu sta bila čiščena z metodo s kronskim etrom v londonskem Courtauld Institute of the History of Art. Delno čiščenje fragmenta oljne slike na platnu iz 19. stoletja je bilo izvedeno v Institut für Restaurierungs und Konservierungswissenschaften v Kölnu.**

2 Postopek

***Lak:* Tip 1: Sveže, hladno stiskano laneno olje (Kremer, Aichstetten) za neposredno uporabo kot lak. Tip 2: Pospešeno sušen (v prisotnosti svinčevega oksida) lak iz lanenega olja. 0,5 g PbO je bilo suspendiranega v 100 mL svežega lanenega olja. Suspenzija je bila za 2 do 3 ure segrevana do 220° C v dušikovi atmosferi ob stalnem mešanju. Temno rjav lak je bil po ohladitvi oddekantiran in shranjen v dušikovi atmosferi. Tekoč lak se v tanki plasti nanese na očiščeno stekleno ploščo (0,2 do 0,5 mL na 100 cm^2). Plošče se nato sušijo pri 25° C. Hitrost sušenja lahko pospešimo s povišano temperaturo v prostoru za sušenje do največ 40° C. Da bi dosegli popolno otrditev in vsaj minimalno podobnosti s starimi laki, so lakirane plošče naknadno shranili za sedem let. Čas, potreben, da se lak posuši toliko, da je suh na dotik, je odvisen od tipa laka. Povprečen**

should be preferred as the method of choice. Removal and/or thinning of later overpaint based on linseed oil may be recommended. Of course, extensive controls by optical and scanning electron microscopy will be necessary. The result of the application of this new technique on genuine paintings was promising. However, long term observations of this cleaning process are still necessary to see whether or not any hidden damages may emerge. The alkaline removal technique should not be applied in cases of deep craquelures or when the paint layer is peeling off, consequently uncovering the ground. In such cases alkaline solutions could creep under the surface attacking or separating the pigment containing ground.

Experimental

1 Materials

Chemicals: Radioactive rubidium 86 (half life: 18.7 days; type of decay: ß-; ß- energy (max.): 0.69 MeV (8.8%) / 1.77 MeV (91.2%); γ radiation 1.077 MeV (8.8%)) was delivered as an aqueous rubidium chloride solution from Amersham Pharmacia Biotech, code RGS.2. The radioactivity was 37–185 MBq/ml or 1–5 mCi/ml. ^{14}C polyacrylic acid was generously donated by Dr Eugen Barbu, School of Pharmacy and Biomedical Sciences, University of Portsmouth, Hampshire, UK. All other reagents including rubidium hydroxide were of the highest purity available and obtained from Sigma Aldrich, Steinheim, Germany.

Glass plates: Window glass plates, length 18 cm, width 10 cm and thickness 3 mm, were obtained from Glaserei Härle, Tübingen, Germany.

Paintings: An 18th-century oil painting and an authentic fragment of a late 17th-century oil painting on canvas were cleaned employing the crown ether method at the Courtauld Institute of the History of Art, London. The partial cleaning of a fragment of a 19th century oil painting on canvas was performed at the Institut für Restaurierungs und Konservierungswissenschaften, Cologne.

2 Procedures

Varnish: Type 1: Fresh cold-pressed linseed oil (Kremer, Aichstetten) for direct use as a varnish. Type 2: Linseed oil varnish with accelerated drying in the presence of lead oxide: 0.5 g PbO are suspended in 100 ml fresh linseed oil. The suspension was heated to 220 °C for 2 to 3 hours under nitrogen while stirring was maintained. The dark brown varnish was decanted after cooling and stored under nitrogen. Liquid varnishes are applied in a thin layer to cleaned glass plates (0.2 to 0.5

čas pri 25° C, potreben za posušitev različnih lakov, je: čisto laneno olje: 2–3 tedne pospešenega sušenja, lak iz lanenega olja ob prisotnosti PbO: 3 do 4 dni.

Vzorci površin oljnih slik: **Ustrezne pigmente (Kremer, Aichstetten) zmešamo z lanenim oljem do zasičenosti. Nastalo barvo nanesemo na natančno očiščeno stekleno ploščo in sušimo pri 25° C. Ko popolnoma otrdi (3 do 7 dni), plast barve prelakiramo, kot je opisano zgoraj. Plošče nato shranimo za več let.**

PEG 400 kronski eter z alkalijskimi ioni ali z ioni alkalijskih kovin **1 g rubidijevega hidroksida raztopimo v 10 ml PEG 400 pri 60 do 70° C. Alkalne raztopine PEG zaradi oksidacije postopoma porjavijo. Zaradi tega morajo biti shranjene v prostoru brez kisika. RbOH v PEG 400 je uporaben v primerih debelih plasti umazanije. Kakorkoli že, površina ne sme biti niti porozna niti ne sme imeti krakelir. Lak se raztopi v obliki oranžne barve in ga lahko odstranimo z bombažno blazinico. Da izboljšamo čistilni učinek, moramo raztopino rahlo premešati s polipropilensko lopatico.**

Tanjšanje laka moramo nenehno nadzirati. Iz varnostnih razlogov moramo vedno pustiti, da sliko prekriva tanka plast laka. Če je potrebno, lahko alkalno čistilno raztopino hitro nevtraliziramo z dodatkom poliakrilne kisline v PEG 400. Če bi bila površina slike onesnažena s solmi majhnih kationov, bi bila potrebna predhodna obdelava s kislim kationskim izmenjevalcem ali poliakrilno kislino v PEG 400. Površino moramo potem očistiti s čistim PEG 400. Po odstranjevanju ali tanjšanju laka moramo čistilno sredstvo odstraniti s suho bombažno blazinico. Površina mora biti nato očiščena s PEG 400. Gel poliakrilne kisline v PEG 400 bi morali nanesti in pustiti učinkovati 1 do 5 minut za nevtralizacijo možnih alkalnih preostankov. Ko gel poliakrilne kisline odstranimo s tamponom, moramo površino slike zaporedoma očistiti z naslednjimi raztopinami: PEG 400 / dodekanol 1:1, poli-1,2-propandiol 1000 in nato PEG 4000. Polarnost topila se zmanjša do točke, pri kateri lahko nehlapne polietre popolnoma odstranimo z več čiščenji z izo dodekanom (Shellsol T.). Površino slike lahko potem pustimo, da se posuši z evaporacijo dodekana.

3 Analizne metode

Retitracija starih lakov: **tri mesece stare plasti sušenega laka iz lanenega olja postrgamo s steklenih površin s sklapelom. Vsebino karboksilne kisline v laku določamo z maceracijo 50 do 150 mg laka v 10 ml natrijevega hidroksida (50 mM) za 1 uro v ultrazvočni kopeli pri 25° C. Po tej obdelavi je raztopina rumenkasto oranžna in rahlo motna. Raztopino retitriramo z uporabo 25 mM žveplove kisline. Količina natrijevega**

ml per 100 cm^2). The plates are then dried at 25 °C. The drying rate may be increased by raising the temperature of the drying cabinet to a maximum of 40 °C. To achieve complete and thorough hardening, as well as a minimum of similarity to aged varnishes, the varnish plates are subsequently stored for up to seven years. The time required for non-stick drying depends upon the type of varnish. Average times required for non-stick drying of the various varnishes at 25 °C are: pure linseed oil: 2 to 3 weeks accelerated drying; linseed oil varnish in the presence of PbO: 3 to 4 days.

Model oil paint surfaces: The corresponding pigments (Kremer, Aichstetten) are mixed with linseed oil until smooth. The resulting paint is applied to the meticulously cleaned glass plates and dried at 25 °C. When thoroughly hardened (3 to 7 days), the paint layer is varnished as described above. The plates are stored for several years.

Alkali ion PEG 400 crown ether: One gram of rubidium hydroxide is dissolved in 10 ml PEG 400 at 60–70 °C. Alkaline solutions of PEG gradually turn brown due to oxidation. They should consequently be stored with oxygen excluded. RbOH in PEG 400 is applicable in cases of thick layers of grime. However, the surface should be neither porous nor contain craquelures. The varnish dissolves with an orange brown colour and can be removed with cotton swabs. The solution should be agitated slightly to improve the cleansing action by using a polypropylene spatula.

The thinning of varnish must be monitored continuously. For safety purposes, a thin varnish layer should be left covering the paint. If required, the alkaline cleansing solution may be neutralised rapidly by the addition of polyacrylic acid in PEG 400. Should the picture surface be soiled with the salts of small cations, a pre treatment with an acidic cation exchanger or polyacrylic acid in PEG 400 is required. The surface should then be cleaned with pure PEG 400. After varnish removal or thinning, the cleaning agent should be removed with dry cotton swabs. The surface should then be cleaned with PEG 400. A gel containing polyacrylic acid in PEG 400 should be applied and incubated for 1 to 5 min to neutralise possible alkaline remnants. Once the polyacrylic acid gel is removed, the surface of the painting should be treated step by step with the following solutions: PEG 400 / dodecanol 1:1, poly(1,2-propanediol) 1000 and then PEG 4000. The solvent polarity will be reduced to the point at which the non-volatile polyethers can be removed completely in a final step by several treatments with iso-dodecane (Shellsol T). The surface of the painting is then allowed to dry by iso-dodecane evaporation.

hidroksida, ki se porabi pri saponifikaciji (umiljenju) je razlika med teoretično količino žveplove kisline in količino dejansko porabljene kisline pri titraciji.

Rezultate titracije svežega lanenega olja kot kontrole in laka iz sušenega lanenega olja primerjamo, da bi preverili oz. potrdili, da prvi ne vsebuje prostih karboksilnih skupin in da glicerolni estri drugega še niso hidrolizirani z natrijevim hidroksidom pri 25° C. Pokažemo lahko, da niti sveže laneno olje (tip 1) niti lak na osnovi lanenega olja s svinčevim sikativom (sušilo) (tip 2) ne vsebuje pomembne količine prostih karboksilnih kislin ali estrskih skupin, ki lahko hidrolizirajo pri 25° C.

***Infrardeča spektrometrija:* FTIR spektrometrija različnih vzorcev lanenega olja je bila izvršena na Beckman Acculab 4 Spektrometru. Sveže in staro laneno olje je bilo pred merjenji vključeno v KBr pilule.**

***Gelska kromatografija:* Gelska kromatografija RbOH PEG 400 kompleksa je bila izvedena z uporabo Bio Gel P 2 (100 do 200 mešov) iz Bio Rad Laboratories iz Richmonda v Kaliforniji.**

10 ml zmesi 1 mol/l RbOH in 28-kratni presežek PEG 400 je potovalo skozi kolono 1,3 x 43 cm. Kvantifikacijo Rb ionov so izvedli z uporabo atomske emisijske spektroskopije pri 780,023 nm na enoti Zeiss M4 Q III, opremljeni z detektorjem PM QII.

***Absorpcijske študije na površini slike z uporabo ^{86}Rb-PEG 400 kronskega etra in ^{14}C poliakrilata:* zato da bi v postopku alkalnega odstranjevanja laka locirali Rb^{+} ione, je bila čistilna raztopina obogatena z ^{86}Rb. Na ta način bi namreč lahko določali možne preostanke rubidijevih ionov na površini slike. ^{86}Rb raztopina je bila razredčena z vodo v razmerju 1 : 1 in uporabljena v naslednjih eksperimentih (standardna raztopina). ^{86}Rb standardna raztopina (50 µl) je bila razredčena s 500 µl zmesi, ki je vsebovala 1 % tritona X 100, 19 % metanola in 80 % vode. Alikvot (200 µl) te označene raztopine je bil uporabljen na lakirani plošči in enakomerno razporejen na pravokotni površini 50 cm^2 z uporabo finega čopiča iz umetnih vlaken. Med sušenjem je bilo z uporabo samodejnega TLC linearnega analizatorja LB 2821 (Berthold Technologies, Bad Wildbad, Nemčija) determinirano možno ß-sevanje na površini laka.**

Naprava omogoča merjenja vzdolž segmenta površine z ustvarjanjem emisijskih profilov testne plošče od točke do točke. Emisijska gostota kalibracijske površine, kot je bila določena z detektorjem, je bila 900 $\pm$100 cpm (št. impulzov v minuti; merjeno: 4500 $\pm$450 impulzov v 5 min.). Standardna deviacija 10% rezultatov od neenakomerne porazdelitve kalibracijske raztopine. Kot pri eksperimentih s kronskim etrom ^{86}Rb PEG 400 je bila v fazi nevtralizacije dodana ^{14}C poliakrilna kislina, ogljik 14 pa je bil kontroliran z upo-

3 Analytical Techniques

Back titration of aged varnish: Three month-aged layers of dried linseed oil varnish are scraped off glass plates with a scalpel. The carboxylic acid content of the varnish is determined by maceration of 50 to 150 mg varnish in 10 ml sodium hydroxide (50mM) for 1 hour in an ultrasonic bath at 25 °C. Upon this treatment, the sample solution becomes yellowish orange and slightly turbid. This solution is back-titrated using 25mM sulphuric acid. The amount of sodium hydroxide consumed by saponification is the difference between the amounts of sulphuric acid theoretically and actually required for titration.

The titration results of fresh linseed oil, used as a control, and dried linseed oil varnish are compared to ascertain that the former does not contain free carboxylic groups and that the glycerol esters of the latter are not already hydrolysed by sodium hydroxide at 25 °C. It could be shown that neither fresh linseed oil (type 1) nor linseed oil varnish with a lead siccative (type 2) contain significant amounts of free carboxylic acid or ester groups that can be hydrolysed at 25°C.

Infrared spectrometry: FTIR spectrometry of different linseed oil samples was performed using a Beckman Acculab 4 Spectrometer. Both fresh and aged linseed oil were incorporated into KBr discs prior to the measurements.

Gel chromatography: Gel chromatography of RbOH–PEG 400 complex was carried out using Bio Gel P 2 (100 to 200 mesh) from Bio-Rad Laboratories, Richmond, California. 10 ml of a mixture of 1 mol/l RbOH and a 28 fold excess of PEG 400 were passed through a column 1.3 x 43 cm. Quantification of Rb ions was performed using atomic emission spectroscopy at 780.023 nm on a Zeiss M4 Q III unit equipped with a PM QII detector.

Absorption studies on the paint surface using ^{86}Rb–PEG 400 crown ether and ^{14}C polyacrylate: In order to locate Rb^{+} ions in the course of alkaline varnish removal, the cleansing solution was enriched with ^{86}Rb. Possible rubidium ions remaining on the paint surface could be determined in this way. The ^{86}Rb solution was diluted 1:1 with water (stock solution) and applied in the following experiments. The ^{86}Rb stock solution (50 µl) was diluted with 500 µl of a mixture containing 1% Triton X 100, 19% methanol and 80% water. An aliquot (200 µl) of this labelled solution was applied to a varnish plate and distributed evenly on a rectangular area of 50 cm^2 using a fine haired, plastic brush. When dry, possible ß-radiation at the varnish surface was determined using an automatic TLC Linear Analyzer LB 2821, Berthold Technologies, Bad Wildbad, Germany. This apparatus allows measurements along a segment of the surface creating point-to-point radioactive emission profiles of the test plate. The emission density of the calibration surface as determined by the detector was 900 $\pm$ 100 cpm (counts

rabo enakega eksperimentalnega postopka, kot je opisan v poglavju Analizne metode (*Kronski eter PEG 400 z alkalijskimi ioni*).

RbOH PEG alkalno čistilno sredstvo; obe raztopini, ekvimolarna raztopina RbOH v etanolu in vodna raztopina RbOH v vodi, sta bili označeni z enako količino ^{86}Rb (50µl ^{86}Rb – standardna raztopina in 500 µl testirane raztopine) in sta imeli enako končno koncentracijo ^{86}Rb, kot je bila v kalibracijski raztopini. Volumen teh označenih raztopin (200 µl) kakor tudi površine (50 cm^2), na katerih so bile uporabljene, so bili identični tistim, ki so bili uporabljeni za kalibracijo. Koncentracija rubidija v vseh treh raztopinah je bila identična. Uporaba 200 µl na površini 50 cm^2 je povzročila gostoto rubidija 2,36 µmol/cm^2 ali 900 cpm, kot je bilo določeno v fazi kalibracije. Po 3 minutah sta bili obe Rb(^{86}Rb) raztopini obrisani in osušeni z uporabo analitsko čistega celuloznega filtrirnega papirja. Nadaljnja obdelava površine slike s čistilom kronskega etra Rb(^{86}Rb) PEG je bila opravljena po korakih s poliakrilatom in dvema spiranjema s PEG 400. Rb(^{86}Rb) obdelavi z etanolom sta sledili dve pranji z etanolom. Po vodni Rb(^{86}Rb)OH obdelavi je bila površina slike dvakrat sprana z vodo. Pri poskusu nevtralizacije s ^{14}C poliakrilno kislino, katere namen je ugotavljanje možne absorpcije ^{14}C poliakrilata na površino, je bil proces po čiščenju izveden, kot je opisano zgoraj.

Zahvala

Zahvaljujemo se: Landesbanki Baden Württemberg, Stiftung Kunst und Kultur v Nemčiji, 'Firnisuntersuchung an Gemälden' File No.: 200 1040129, za velikodušno podporo; dr. Avivi Burnstock s Courtauld Institute of the History of Art v Londonu za originalne fragmente slik iz 17. in 18. stoletja; dr. Hansu Jürgenu Hartmannu, dr. Albrechtu Jungu, dr. Yoki Kaupu, dr. Haroldu Taylorju in dr. Christianu Heinrichu Wunderlichu za spodbujanje razprav; ter dr. Eugenu Barbuju s School of Pharmacy and Biomedical Sciences, University of Portsmouth, Hampshire, Velika Britanija, za donacijo ^{14}C poliakrilne kisline.

per minute; measured 4500 $\pm$ 450 counts in 5 min). The standard deviation of 10% results from a non-uniform distribution of the calibration solution. As with the ^{86}Rb–PEG 400 crown ether experiments, ^{14}C polyacrylic acid was added to the polyacrylate neutralisation step and carbon 14 was monitored using the same experimental setup described above in the Methods section.

Alkaline RbOH–PEG cleanser, an equimolar solution of RbOH in ethanol and an aqueous solution of RbOH in water were each labelled with the same amount of ^{86}Rb (50µl ^{86}Rb stock solution and 500 µl of the solution to be tested), resulting in the same final concentration of ^{86}Rb as in the calibration solution. The volume of these labelled solutions (200 µl), as well as the types and surface areas (50 cm^2) to which they were applied, were identical to those used for calibration. The rubidium concentration in all three solutions was identical. The application of 200 µl to a 50 cm^2 surface results in a rubidium density of 2.36 µmol/cm^2 or 900 cpm as determined in the calibration step. After 3 minutes each Rb(^{86}Rb) solution was wiped off using an analytical grade cellulose filter paper. Post-treatment of the paint surface following the Rb(^{86}Rb)–PEG crown ether cleansing was carried out stepwise with polyacrylate and two washes of PEG 400. Rb(^{86}Rb) ethanol treatment was followed by two ethanol washes. After the aqueous Rb(^{86}Rb)OH treatment the paint surface was rinsed twice with water. In the case of ^{14}C polyacrylic acid neutralisation experiments aiming at possible surface absorption of ^{14}C polyacrylate the post-cleansing process was carried out as described above.

Acknowledgements

The generous support of the Landesbank Baden Württemberg, Stiftung Kunst und Kultur, Germany, 'Firnisuntersuchung an Gemälden' File No.: 200 1040129 is gratefully appreciated. Dr. Aviva Burnstock, Courtauld Institute of the History of Art, London, is thanked for kindly providing authentic fragments of 17th- and 18th-century paintings.
Thanks go to Dres. Hans Jürgen Hartmann, Albrecht Jung, Yoka Kaup, Harold Taylor and Christian Heinrich Wunderlich for stimulating discussions. The generous donation of ^{14}C polyacrylic acid by Dr. Eugen Barbu, School of Pharmacy and Biomedical Sciences, University of Portsmouth, Hampshire, UK, is gratefully acknowledged.

Viri

[1] Berger, E. (1912) *Quellen und Technik der Fresko, Oel und Tempera Malerei des Mittelalters, von der byzantinischen Zeit bis einschließlich der Erfindung der Oelmalerei durch die Brüder van Eyck*, 3. Folge, München, 15-83.

[2] Wolbers, R. (1988) *Aspects of the Examination and Cleaning of Two Portraits by Richard and William Jennys,* Preprints of Papers presented at the sixteenth annual meeting (Ur. Roenberg, S.Z.), New Orleans, Louisiana, June 1–5, 1988, American Institute for Conservation, Washington, 251-280.

[3] Wolbers, R.C., Sterman, N.T. in Stavroudis, D. (1990) *Notes for a Workshop on New Methods in the Cleaning of Paintings*, Getty Conservation Institute, Los Angeles.

[4] Weser, U. in Wunderlich, C.H. (1996) *Removal of aged oil films by lipase: A placebo phenomenon*, Zeitschrift für Kunsttechnologie und Konservierung 1, ICCROM, 147-152.

[5] Lazzari, M. in Chiantare, O. (1999) *Drying and oxidative degradation of linseed oil,* PolymeDegradation and Stability 65/2, Elsevier Science, Oxford, 303-313.

[6] Koller, J. (1990) *Cleaning of a Nineteenth Century Painting with Deoxycholate Soap: Mechanism and Residue Studies*, Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture (Ur. Mills J.S. in Smith P.), Preprints of the Contributions to the IIC Brussels Congress, 3–7 September 1990, International Institute for Conservation, London, 106–110.

[7] Von Gilsa, B. (1993) *Harzseifen zur Firnisabnahme,* Zeitschrift für Kunsttechnologie und Konservierung, 1, ICCROM, 184-218.

[8] Illuminati, G., Mandolini, L. in Masci, B. (1983) *Template Effects 4*, Journal of the American Chemical Society 105, American Chemical Society, Washington, 555-563.

[9] Mandolini, L. in Masci, B. (1984) *Template Effects 6*, Journal of the American Chemical Society 106, American Chemical Society, Washington, 168-174.

[10] Vitali, C. A. in Masci, B. (1989) *Template Effects 8*,

References

[1] Berger, E. (1912) *Quellen und Technik der Fresk, Oel und Tempera Malerei des Mittelalters, von der byzantinischen Zeit bis einschließlich der Erfindung der Oelmalerei durch die Brüder van Eyck*, 3. Folge, München, 15-83.

[2] Wolbers, R. (1988) *Aspects of the Examination and Cleaning of Two Portraits by Richard and William Jennys*, Preprints of Papers presented at the sixteenth annual meeting (Edit. Roenberg, S.Z.), New Orleans, Louisiana, June 1–5, 1988, American Institute for Conservation, Washington, 251-280.

[3] Wolbers, R.C., Sterman, N.T. in Stavroudis, D. (1990) *Notes for a Workshop on New Methods in the Cleaning of Paintings*, Getty Conservation Institute, Los Angeles.

[4] Weser, U. and Wunderlich, C.H. (1996) *Removal of aged oil films by lipase: A placebo phenomenon*, Zeitschrift für Kunsttechnologie und Konservierung 1, ICCROM, 147-152.

[5] Lazzari, M. and Chiantare, O. (1999) *Drying and oxidative degradation of linseed oil*, PolymeDegradation and Stability 65/2, Elsevier Science, Oxford, 303-313.

[6] Koller, J. (1990) *Cleaning of a Nineteenth Century Painting with Deoxycholate Soap: Mechanism and Residue Studies*, Cleaning, Retouching and Coatings: Technology and Practice for Easel Paintings and Polychrome Sculpture (Edit. Mills J.S. and Smith P.), Preprints of the Contributions to the IIC Brussels Congress, 3–7 September 1990, International Institute for Conservation, London, 106–110.

[7] Von Gilsa, B. (1993) *Harzseifen zur Firnisabnahme*, Zeitschrift für Kunsttechnologie und Konservierung, 1, ICCROM, 184-218.

[8] Illuminati, G., Mandolini, L. And Masci, B. (1983) *Template Effects 4*, Journal of the American Chemical Society 105, American Chemical Society, Washington, 555-563.

[9] Mandolini, L. and Masci, B. (1984) *Template Effects 6*, Journal of the American Chemical Society 106, American Chemical Society, Washington, 168-174.

[10] Vitali, C. A. and Masci, B. (1989) *Template Effects 8*,

Tetrahedron Letters 45/7, Elsevier, Oxford, ROYAUME-UNI , 2213-2222.

[11] Chun, S., Dzyuba, S.V., in Bartsch, R.A. (2001) *Influence of Structural Variations in Room Temperature Ionic Liquids on the Selectivity and Efficiency of Competitive Alkali Metal Salt Extraction by a Crown Ether*, Analytical Chemistry 73, American Chemical Society, Washington, 3737-3741.

[12] Da Silva, J.J.R.F. in Williams, R.J.P. (1991) *The Biological Chemistry of the Elements*: *The Inorganic Chemistry of Lif*e, Oxford University Press, 39.

Tetrahedron Letters 45/7, Elsevier, Oxford, ROYAUME-UNI , 2213-2222.

[11] Chun, S., Dzyuba, S.V. and Bartsch, R.A. (2001) *Influence of Structural Variations in Room Temperature Ionic Liquids on the Selectivity and Efficiency of Competitive Alkali Metal Salt Extraction by a Crown Ether*, Analytical Chemistry 73, American Chemical Society, Washington, 3737-3741.

[12] Da Silva, J.J.R.F. and Williams, R.J.P. (1991) *The Biological Chemistry of the Elements*: *The Inorganic Chemistry of Life,* Oxford University Press, 39.

Uporaba encimov pri čiščenju oljnih in tempera slik

Application of Enzymes in the Cleaning of Oil and Tempera Paintings

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Ključne besede:
encim;
amilaza;
proteaza;
lipaza;
olje;
cerkev Sv. Jakoba, Čiovo;
kazein;
krog Paola Veneziana, ***Madona z detetom*****,**
cerkev Marijinega vnebovzetja, Crikvenica;
višnjev gumi;
Hans Georg Geiger, triptih, Zagrebška stolnica.

Keywords:
enzyme;
amylase;
protease;
lipase;
oil;
St Jacob's Church, Čiovo;
casein;
circle of Paolo Veneziano, *Madonna and Child*,
Church of the Assumption, Crikvenica;
cherry-tree Gum;
Hans Georg Geiger, triptych, Zagreb Cathedral.

POVZETEK: Encimi so beljakovine in njihova uporaba za odstranjevanje nečistoč s slikovne površine ni niti konvencionalna niti preprosta. Encime uporabljamo za kataliziranje razpada molekulskih vezi neželenih organskih materialov, in sicer če bolj konvencionalne metode ne dajo zadovoljivih rezultatov. Ne smemo jih imeti za alternativo drugim metodam, temveč za sredstva, ki druge metode dopolnjujejo. Prispevek predstavlja tri primere, pri katerih smo uspešno uporabili encime, potem ko druge metode in sredstva niso dali primerljivo kakovostnih rezultatov. Prvi primer je odstranitev petdeset let stare oljne preslikave s premaza, ki vsebuje smolo. Drugi primer je odstranitev kazeinske preslikave s plasti, ki vsebuje emulzijsko jajčno tempero. Tretji primer je odstranitev razbarvane plasti višnjevega gumija, onesnažene z olji in smolami pri predhodnih restavratorskih posegih.

ABSTRACT: Enzymes are proteins and their use is not a conventional or easy method for the removal of impurities from a painted surface. They are used to catalyse the disintegration of molecular bonds of unwanted organic materials. They can be used if more conventional methods do not yield satisfactory results. They should not be regarded as an alternative to other methods, but as the agents that supplement them. Three examples where enzymes were used successfully, while other methods and agents did not yield results of comparable quality, are presented in this work. The first example is the removal of 50-year old oil overpaint, executed over a resin-containing glaze. The second example is the removal of casein overpaint; overpaint was executed over an egg tempera emulsion layer. The third example is the removal of a discoloured, aged, cherry-tree gum layer, contaminated with oils and resins during previous restorations.

Primernost encimov za čiščenje slikovne površine

Encimi so beljakovine. Njihova uporaba za odstranjevanje nečistoč s slikane površine ni niti običajna niti preprosta. Uporabimo jih lahko, če bolj konvencionalne metode (suho mehansko čiščenje, kelati, uporaba vode s spremenjeno pH vrednostjo, tenzidi in topila) ne dajo zadovoljivih rezultatov. Pri ocenjevanju primernosti encimov za čiščenje slikanih površin je treba upoštevati, katero nečistočo je treba odstraniti, tj. katere so njene prevladujoče vezne sile (adhezijske ali kohezijske); kaj je vezivo plasti, ki se ne sme poškodovati; in razpad katerih vezi katalizira določeni encim.

Suitability of Enzymes in the Cleaning of Painted Surfaces

Enzymes are proteins and they do not provide a conventional or easy method for the removal of impurities from a painted surface. They can be used if conventional methods (dry mechanical methods; chelating agents; the use of water of modified pH; tensides [surfactants]; solvents) do not yield satisfactory results. To evaluate the suitability of enzymes in cleaning painted surfaces, the following factors should be taken into consideration: the impurity to be removed, that is, its dominant bonding forces (in adhesion and cohesion); the binder of the layer that must not be damaged; the disintegration of which bonds is catalysed by a specific enzyme.

Kaj je nečistoča na sliki?

Nečistočo lahko opredelimo kot snov na napačnem mestu. Nečistoče na slikah motijo percepcijo umetniških stvaritev. Po tej opredelitvi se nečistoča lahko nanaša na vse snovi, ki motijo percepcijo umetnine, na primer nezaželene ali naknadno dodane snovi, kot so prah, maščoba, madeži, neprimerna lepila, neprimerna polnila in neprimerne ali razbarvane retuše ali preslikave s predhodnih restavriranj. Nečistoča je lahko tudi posledica sprememb originalnih materialov, na primer nesprejemljivo razbarvan lak in produkti korozije.

Snov, ki pomeni nečistočo, se veže na sliko z določenimi silami. Čiščenje lahko razumemo kot razmerje med adhezijskimi silami delcev nečistoče na predmet in kohezijskimi silami molekul predmeta, ki se pri čiščenju ne sme poškodovati. Adhezijske sile so električne sile, kapilarne sile, elektrostatične sile in tri (med)molekulske sile: sile polarnosti, sile vodikovih vezi in predvsem disperzijske sile.

Med adhezijskimi in kohezijskimi silami raznih tipov nečistoč obstajajo razlike, zato je bistveno, da se čiščenja lotimo plast za plastjo oziroma tip za tipom. Neka metoda je lahko primerna za odstranjevanje nečistoč, ki se prenašajo po zraku, druga je lahko primerna za odstranjevanje razbarvanega laka itn.

What is an Impurity on the Painting?

An impurity can be defined as a material in the wrong place. The impurities on paintings disturb the perception of artistic creation; thus an impurity as defined can refer to all the material that disturbs the perception of artistic creation, for example, foreign material, including dust, grease, spots, inappropriate glues, inappropriate fills, and inappropriate or discoloured retouchings or overpaints resulting from previous restorations. An impurity can also result from the alteration of original materials, such as unacceptably discoloured varnish and corrosion products.

The material of the impurity is bound to the painting by certain forces. Cleaning can be regarded as the ratio between the adhesion forces of impurity particles on an object and the cohesion forces of the molecules of the object that must not be damaged by cleaning. Adhesion forces include electrical forces, capillary forces, electrostatic forces and three (inter)molecular forces: forces of polarity, forces of hydrogen bonds and, primarily, dispersion forces.

There are differences between the adhesion and cohesion forces of various types of impurity; therefore, it is essential to approach the cleaning layer by layer, or type by type. One method would be suitable for the removal of airborne impurities; another method would be suitable for the removal of discoloured varnish, and so on.

Encimi

Encimi so beljakovine, najdemo jih v vseh živih celicah, kjer uravnavajo metabolične procese. Katalizirajo razpad organskih snovi v preprostejše spojine, s čimer omogočajo ali pospešujejo kemične procese. Po

Enzymes

Enzymes are proteins that can be found in all living cells where they regulate metabolic processes. They catalyse the disintegration of organic materials into simpler compounds, thus enabling or accelerating chemical

končani reakciji encimi ostanejo nespremenjeni, vendar je njihova doba uporabnosti omejena, zato encime, ki se uporabljajo pri čiščenju, običajno uporabimo le enkrat. Teoretično naj bi vsak tip encima kataliziral razpad le enega tipa snovi. V nekaterih primerih je njihova aktivnost omejena na določene vezi.

Encimi so zelo specifični glede na okolje, v katerem delujejo. Vsak encim je aktiven katalizator le, če sta zagotovljena optimalna pH in temperatura. Pri komercialnih encimih dajejo podatke o optimalni aktivnosti proizvajalci v dokumentaciji, ki spremlja proizvod, ali pa jih lahko poiščemo v kateri izmed relevantnih baz podatkov na spletu. V neugodnih razmerah encimi ne delujejo.

Testi z dostopnimi encimi, opravljeni na Hrvaškem restavratorskem zavodu, so potrdili sklepe, do katerih je predhodno leta 1983 prišla Pia DeSantis [1]: za uspešno uporabo encimov ni nujno strogo vzdrževati optimalne temperature in optimalnega pH-ja (striktno je treba upoštevati le enega od obeh dejavnikov). Poleg tega se je povišanje temperature, da bi dosegli optimalno aktivnost, izkazalo za kontraproduktivno, saj se je naneseni gel prehitro izsušil, toplota in voda pa bi potencialno lahko negativno delovali na barvno plast. Temperaturni razpon, v katerem so encimski kompleksi aktivni, je 20–40° C, običajno 35° C. Za termostabilne encime je razpon temperature, pri kateri so aktivni, 50–80° C, običajno 70° C.

Za čiščenje slikovnih površin je mogoče uporabljati encime, ki jih proizvajajo za industrijo detergentov. Razvrstimo jih lahko v štiri osnovne skupine: amilaze, celulaze, lipaze in proteaze. Vendar je to le groba razdelitev, saj imajo nekateri encimi lastnosti več skupin. Amilaze se uporabljajo predvsem za razgradnjo molekulskih vezi polisaharidov, kot so rastlinski gumiji in škrob. Lipaze katalizirajo razgradnjo molekulskih vezi maščob in olj. Proteaze katalizirajo razpad molekulskih vezi beljakovin, nekatere pa lahko celo zelo selektivno razgrajujejo kazeinske tempere. Celulaze katalizirajo razpad molekulskih vezi v celulozi ali pomagajo odstranjevati nečistoče iz celuloze.

Deaktivaciji encimov je tudi treba posvetiti dovolj pozornosti. Encime je mogoče začasno deaktivirati z nenadno spremembo pH-ja in temperature, tako da ni izpolnjen noben pogoj za njihovo delovanje. Deaktivirati jih je mogoče tudi s toploto in z organskimi topili, s katerimi jih je mogoče bolj popolno fizično odstraniti s slike. Veliko pozornosti vzbuja možnost spontane reaktivacije encimov, ki ostanejo v barvni plasti poslikave. Ta možnost pogosto prevlada pri osebnem presojanju o ustreznosti encimov za čiščenje slik. V vsakem primeru pa velja: encimi so beljakovine, ki imajo omejeno dobo uporabnosti.

processes. Once the reaction is completed, the enzyme remains unchanged. However, the shelf life of enzymes is limited, and enzymes that are used for cleaning purposes are usually used only once. Theoretically, each type of enzyme should catalyse disintegration of only one specific type of material. In some cases, they limit their action to specific bonds.

Enzymes are also very specific with respect to the environment in which they act. Each enzyme is an active catalyst only if its optimal pH and temperature are achieved. In the case of commercial enzymes, the information about their optimal activity is given by the manufacturer in the documentation for the product, or this information can be found in one of the relevant Internet databases. Enzymes are not active in adverse conditions.

However, tests conducted in the Croatian Conservation Institute with the enzymes available confirmed the conclusions reached by Pia DeSantis in 1983 [1]: it is not necessary that both the optimal temperature and the optimal pH should be strictly maintained for a successful use of enzymes; only one of them has to be strictly maintained. Moreover, raising the temperatures to achieve optimal activity was shown to be counterproductive as the applied gel dried too fast and potentially the heat and water could have negative effects on the paint layer. The temperature range of activity for enzyme complexes is 20–40 °C, usually 35 °C. For thermostable enzymes, the temperature activity range is 50–80 °C, usually 70 °C.

Enzymes produced for the detergent industry can be used for the cleaning of painted surfaces. They can be classified into four basic groups: amylases, cellulases, lipases and proteases. However, this is only a rough classification since some enzymes can have the properties of more than one group. Amylases are used primarily for the disintegration of molecular bonds of polysaccharides, such as starch. Lipases catalyse the disintegration of molecular bonds of fats and oils. Proteases catalyse the disintegration of protein molecular bonds, and some can even disintegrate casein tempera very selectively. Cellulases catalyse the disintegration of molecular bonds in cellulose, or aid the removal of impurities from cellulose.

Deactivation of enzymes is an issue that requires due attention. Enzymes can be temporarily deactivated by a sudden change in pH and temperature so that neither condition for their activity is met. They can also be deactivated by heat or by organic solvents, which can assist in their more complete physical removal from the painting. A possible spontaneous reactivation of enzymes remaining in the paint layer is a topic receiving a great deal of attention. This topic often prevails in the personal evaluation of the suitability of enzymes for the cleaning of paintings. In any case, however, enzymes are proteins with a limited shelf life.

Pri čiščenju slik je ustrezen encim lahko učinkovito in selektivno sredstvo za odstranjevanje nečistoč, ki imajo močne molekulske vezi. Za uspešno uporabo encimov morata biti izpolnjena dva pogoja. Prvi je laboratorij za analize, s katerimi konservator-restavrator dobi zanesljive podatke o tem, katere vrste veziv obstajajo v plasti, ki jo je treba odstraniti, in v plasti pod njo, ki se ne sme poškodovati. Logično bi bilo uporabiti encime, ki katalizirajo razgradnjo molekulskih vezi snovi, ki jo je treba odstraniti, in ki ne delujejo na snov, ki jo je treba ohraniti. Vendar to ni vedno tako preprosto. Kot bomo videli pozneje, lahko nekateri empirični testi pripeljejo do nepričakovanih spoznanj. Drugi pogoj in največji problem pri uporabi encimov za čiščenje slikovnih površin je, da bi morali imeti v hladilniku na zalogi sveže aktivne encime, tj. razne lipaze, proteaze, celulaze, ki imajo vsi svojo ceno in omejen rok uporabe. Pri naročanju encimov bi se morali zavedati, da bodo uporabljeni za teste, od katerih bodo le nekateri pozitivni (če sploh kateri!). Če se neki encim izkaže učinkovit, je treba zagotoviti količino, ki je potrebna za vso nalogo, ali pa imeti možnost sprotne, nemotene nabave. To utegne biti v primeru nekomercialnih laboratorijskih vzorcev težavno.

Odstranjevanje nečistoč s slik in uporaba encimov

Poudariti moramo, da encimi niso alternativa drugim postopkom, temveč sredstvo, ki druge metode dopolnjuje. Predstavili bomo nekaj primerov uspešne uporabe encimov, ko druge metode in sredstva niso dali primerljivo kakovostnih rezultatov.

1 Odstranjevanje oljne preslikave s smolnega laka ali premaza

Encimi so se izkazali za zelo koristno selektivne pri odstranjevanju preslikave, ki vsebuje olje, z laka ali premaza, ki vsebuje smolo, če preslikava le ni prestara ali preveč polarna. Teoretično ni parametra pH-ja ali topnosti organskega topila, ki bi nakazoval, da bi topilo lahko uporabili za odstranjevanje oljne preslikave z laka, ki vsebuje smolo, ne da bi se ta poškodoval, saj je območje topnosti olja v trikotniku Teas znotraj območja topnosti smole. Naš primer je odstranjevanje preslikave, ki vsebuje olje, z retabla na stranskem oltarju cerkve sv. Jakoba na otoku Čiovo. Preslikava s komercialnimi olji, nanesena sredi 20. stoletja, prekriva plast marmoriranja, naslikanega z oljno-smolnimi premazi.

In cleaning paintings the appropriate enzyme can be an efficient and selective agent for the removal of impurities that have strong molecular bonds. There are two prerequisites for the successful use of enzymes. Firstly, it is necessary to have an analytical laboratory providing reliable information to the conservator-restorer about the type of binder(s) present, that is, the binder of the layer to be removed and that of the underlying layer that should not be damaged. It would be logical to use the enzymes that catalyse disintegration of the molecular bonds of the material to be removed and that exert no action on the material to be preserved. However, this is not always that simple: some empirical tests can result in unexpected findings as discussed later. Secondly, the greatest problem in the use of enzymes for cleaning painted surfaces is that one should have stocks of fresh, active enzymes in a refrigerator, that is, the various lipases, proteases and cellulases, all of which have their price and a limited shelf life. When ordering the enzymes, one should be aware of the fact that they will be used for tests, a few of which – if any! – will be positive. When a particular enzyme proves to be efficient, the quantity necessary for the entire job or the possibility of its continued availability for purchase should be ensured. This may not be easy in the case of non-commercial laboratory samples.

Removal of Impurities from Paintings and the Use of Enzymes

When we talk about enzymes, we have to emphasise that they should not be regarded as an alternative to other methods, but as agents that supplement them. We shall provide a few examples where enzymes were successfully used, while other methods and agents did not yield results of comparable quality.

1 Removal of Oil Overpaint from a Resin Varnish or Glaze

Enzymes have proved to be very usefully selective in the removal of oil-containing overpaint from a resin-containing varnish or glaze, as long as the overpaint is not too old or too polar. In theory, there is no pH or solubility parameter of an organic solvent that suggests that the solvent can be used for the removal of oil overpaint from a resin-containing varnish without damaging it, since the oil solubility zone in the Teas triangle is within the resin solubility zone. The example we have is the removal of oil-containing overpaint from the retable of the lateral altar of St Jacob's Church on the island of Čiovo. The

Na sliki 1 lahko vidimo, da poskusi odstranjevanja preslikave s hidrolizo, z uporabo detergentov ali z organskimi topili načenjajo premaze ali pa uporabljene snovi preslikave ne napnejo dovolj.

Na sliki 2 lahko vidimo poskuse mehčanja ali odstranjevanja preslikave na oljni osnovi z A) puferiranim gelom, ki smo ga pustili delovati 20 minut in potem čistili s skalpelom; B) suhim čiščenjem (s skalpelom); in C) čiščenjem s skalpelom, potem ko je bila preslikava omehčana s puferiranim gelom in dodanim encimom. Preizkus je pokazal, da dodatek lipaze v resnici omogoči tanko in mehko lupljenje preslikave s skalpelom, ne da bi se poškodoval smolni premaz. V tem primeru je bila uspešno uporabljena lipaza Lipase 0763 Tip XXI (Sigma), raztopljena v gelu, ki je bil narejen iz Aqua purificata (destilirana voda; Magdis) in 5% Klucela G (Hercules). Lipaza je bila raztopljena v razmerju 1 g lipaze / 1 dl puferiranega gela. Gel je bil puferiran na pH 7,7 s TRIS-om (Tris(hidroksimetil)aminoetan ali 2-amino-2-hidroksimetil-1,3-propanediol; Kemika), pustili pa smo ga delovati na preslikavo 20 minut pri sobni temperaturi.

2 Odstranjevanje kazeinskih preslikav s plasti jajčne tempere ali emulzijske tempere

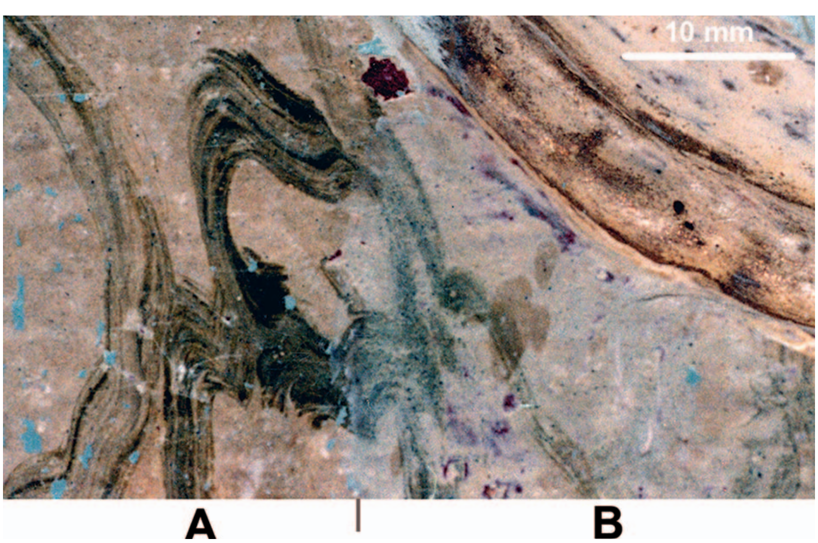
Naslednja uporaba, pri kateri je težko najti alternativo za encime, je odstranjevanje kazeinskih preslikav s plasti jajčne tempere ali emulzijske tempere. Ko poskušamo preslikavo previdno odstraniti s skalpelom, pogosto odpadejo koščki barve, ker je jajčna tempera mehkejša od kazeinske tempere. Če pa preslikavo

commercial oil overpaint applied in the mid-20th century covers the layer of marbling painted with oil-resin glazes. It can be seen in Figure 1 that the attempts to remove the overpaint by hydrolysis or with organic solvents damage the glazes, or the materials used do not swell the overpaint sufficiently.

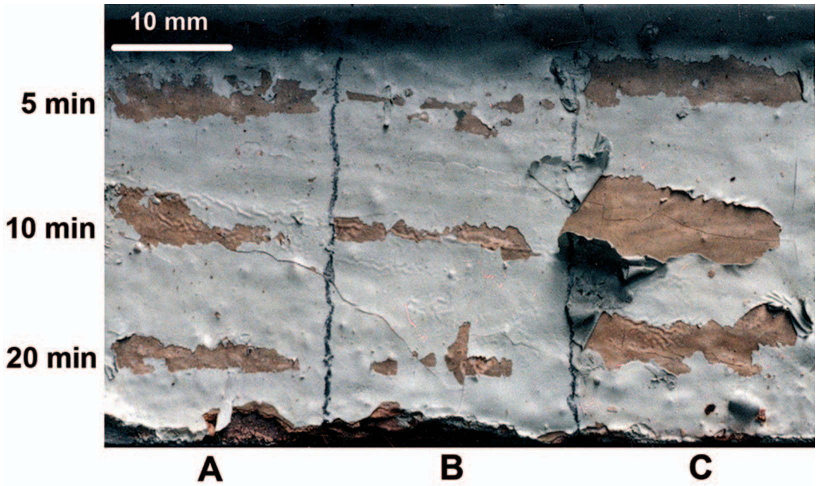
Figure 2 shows the tests of softening or removing the oil-based overpaint with A) buffered gel, left on for 20 minutes, and scalpel cleaning; B) dry cleaning (scalpel); and C) cleaning with a scalpel after softening the overpaint with buffered gel and the added enzyme. The test shows that the addition of lipase does enable a fine peeling of the softened overpaint with a scalpel, without damaging the resin glaze. In this case, Lipase 0763 Type XII (Sigma) dissolved in a gel made of Aqua purificata[1] (Magdis) and 5% of Klucel G (Hercules) was used successfully. The lipase was dissolved in the ratio of 1 g lipase/1 dl buffered gel. The gel was buffered to pH 7.7 with TRIS (Tris(hydroxymethyl)aminoethane or 2-amino-2-hydroxymethyl-1,3-propanediol; Kemika), and left on the overpaint for 20 minutes at room temperature.

2 Removal of Casein Overpaints from Egg Tempera or Emulsion Tempera Layers

Another use where it is hard to find an alternative to enzymes is the removal of casein overpaints from egg tempera or emulsion tempera layers. In an attempt to remove the overpaint carefully with a scalpel, the colour often flakes off because egg tempera is softer than casein tempera. After softening the overpaint with the appropriate protease, the casein overpaint can be peeled off



Slika 1.
Figure 1.



Slika 2.
Figure 2.

zmehčamo z ustrezno proteazo, lahko kazeinsko preslikavo nežno odluščimo, ne da bi poškodovali jajčno tempero. Naš primer je slika *Madona z detetom*, ki jo pripisujejo krogu Paola Veneziana in ki je v lasti župne cerkve Marijinega vnebovzetja v Crikvenici. Slika je bila že trikrat "restavrirana". Pri prvem restavriranju je bila podoba preslikana s kazeinsko tempero. Originalno barvno površino je prekrivala mreža drobnih razpok; kazeinska preslikava nima razpok, poleg tega je veliko debelejša od originalne barve in vsebuje veliko bolj grobe pigmente. Plast kazeinske tempere je izvirna plast retabla, ki je delo Paulusa Riedla iz leta 1776.

Pri drugem restavriranju je bila podoba preslikana s polkritnimi oljnimi barvami in zlatom v prahu, vezivo pa je bilo damarjev lak. Restavrator, ki je sliko retuširal z oljno barvo, je poskušal najprej odstraniti kazeinsko preslikavo, vendar z zelo slabimi rezultati. Kazeinska tempera je delno ostala, originalna slika pa je bila pretirano očiščena.

V tem občutljivem primeru smo najprej odstranili plast nečistoč, ki se prenašajo po zraku, in potem še oljno retušo. Potem ko smo odstranili oljno retušo z organskimi topili, smo uspešno nanesli proteazo Esperase® 8.0 L (Novozymes). Encim smo raztopili v koncentraciji 10 % v gelu, narejenem iz destilirane vode Aqua purificata (Magdis) in 5 % Klucela G (Hercules), pufeINRanem do pH 9 s TRIS-om (Kemika), in ga pustili delovati pri sobni temperaturi (19° C) 20 minut. Kazeinska tempera se je zmehčala, da jo je bilo lažje mehansko odstranjevati, na jajčno tempero pa encimski gel ni deloval (slika 3). A zaradi močne poškodovanosti izvirne poslikave smo odstranili kazeinsko plast le na

gently without damaging the egg tempera. The example is the painting of the *Madonna and Child*, attributed to the circle of Paolo Veneziano and owned by the Parish Church of the Assumption in Crikvenica. The painting had already been 'restored' three times. The first restoration consisted of overpainting the image with casein tempera. The original paint surface was covered with a fine network of craquelures; the casein overpaint has no craquelure and it is also much thicker and contains much coarser pigments than the original. The casein tempera layer is the original paint layer of the retable, which was designed by Paulus Riedl in 1776.

The second restoration consisted of overpainting the image with semi-covering oil colours and powdered gold bound in dammar varnish. The restorer who retouched the painting with oil colour tried to remove the casein overpaint beforehand; the results were very poor, however. The casein tempera partly remained and the original painting was badly overcleaned.

In this delicate case, the layer of airborne impurities was first removed, and then the oil retouching. After the removal of the oil retouching with organic solvents, the protease Esperase® 8.0 L (Novozymes) was applied successfully. The enzyme was dissolved at a concentration of 10% in a gel made of Aqua purificata (Magdis) with 5% of Klucel G (Hercules), buffered to pH 9.0 with TRIS (Kemika), and exposed at room temperature for 20 minutes. The casein tempera was softened for easy mechanical removing, while the egg tempera remained unaffected by the enzyme gel (Figure 3). However, only a small area of the casein overpaint was removed to reveal the original, because the original was so badly damaged majhni površini, da se je pokazala izvirna plast; večino kazeinske preslikave smo pustili, ker povezuje retabel v celoto.

3 Odstranjevanje razbarvane plasti starega višnjevega gumija, onesnaženega pri predhodnem restavriranju z olji in smolami

Tretji primer, ki ga bomo predstavili, je odprl več vprašanj in spodbudil naknadno analizo. Gre za sliki Hansa Georga Geigerja s triptiha iz zakristije zagrebške katedrale.

Umazanijo s površine slik smo odstranili s 3% vodno raztopino triamonijevega citrata (Aldrich). Lak in retušo iz prejšnjih restavratorskih posegov smo odstranili s ksilenom, toluenom in etanolom. Koprena, ki je bila moteča že pri starem laku, je zdaj še bolj motila percepcijo slik, saj ni bilo več učinka omočenja.

Kopreno smo poskusili mehansko odstraniti pod mikroskopom pri 40-kratni povečavi. Pokazalo se je, da je izjemno trdno vezana na barvno plast. Ob praskanju je barvna plast pod pritiskom skalpela prepogosto počila, ni pa popustila vez med kopreno in barvo. Táko mehansko odstranjevanje koprene bi bilo zelo dolgotrajno, rezultat pa kakovostno nezadovoljiv. Poleg tega je bila koprena odporna proti vsem konvencionalnim kemijskim sredstvom, ki smo jih preizkusili; ali na kopreno niso delovala ali pa so poškodovala barvno

and the casein overpaint at least provided some unity to the retable as a whole.

3 Removal of a Discoloured Aged Cherry Gum Layer Contaminated with Oil and Resin in Previous Restorations

The third example to be presented has opened several questions and encouraged some subsequent analyses. These are the paintings of Hans Georg Geiger from the triptych of the sacristy of Zagreb cathedral.

The dirt from the surface of the paintings was removed with a 3% aqueous solution of triammonium citrate (Aldrich). The varnish and the retouching from the previous restoration operations were removed with xylene, toluene and ethanol. The haze that had interfered with the perception of the paintings while they were varnished with the old varnish was now an even greater obstacle to the perception of the paintings, because the effect of wetting was now gone.

A trial of the mechanical removal of the haze was carried out with the help of a microscope at a magnification of 40x. It could be seen that the haze was extremely tightly bound to the paint layer. Scraping broke the paint layer under the pressure of the scalpel all too frequently, but the bond between paint and haze did not break. And so the removal of the haze in a mechanical manner would last interminably, with a result that would not be

Slika 3.
Figure 3.

plast. Poskuse smo izvajali na majhnih, diskretnih delih slik. Vključevali so dolgotrajno delovanje vode (do 120 minut), kislinsko hidrolizo do pH 3, hidrolizo z amonijevim hidroksidom pri različnih koncentracijah in časih delovanja, kelate, tenzide in organska topila.

Naravoslovna analiza, ki nam jo je posredoval laboratorij Hrvaškega restavratorskega zavoda s sodelavci, je razkrila, da je koprena sestavljena večinoma iz višnjevega gumija, majhne količine kleja in neidentificirane snovi, topne v kloroformu (približno 3 %), barvna plast pa je emulzija proteinske tempere. Potem ko so vse preizkušene konvencionalne metode za odstranjevanje koprene odpovedale, smo preizkusili encime. Najprej smo preizkusili tri različne amilaze: prva je bila testirana BAN 480 L® (Novozymes), sledila je amilaza v prahu, ki jo prodaja italijansko podjetje Phase (Phase enzima amilasi lotto 01511), in nazadnje amilaza (tehnične čistosti), ki smo jo dobili iz laboratorija farmacevtske družbe Pliva Zagreb. Vsi poskusi so dali negativen rezultat. Enako nezadovoljiv rezultat smo dobili z amilazo BAN 480 L® (Novozymes) pri vzdrževanju za delovanje optimalnega pH-ja in temperature (70° C). Sonda je bila nameščena poleg termometra, temperaturo pa je vzdrževal majhen infrardeč grelec 20 minut. Tudi rezultati, ki smo jih dobili po številnih modifikacijah površinske napetosti, metod aplikacije, koncentracije encimov in intervalov izpostavljanja, so bili podobno neugodni.

Potem smo preizkusili vrsto drugih encimov (celulaz, proteaz in lipaz). Teoretično naj ti ne bi delovali na polisaharide v višnjevem gumiju; naš namen pa je bil, da preizkusimo njihov medsebojni učinek, sinergijski učinek s tenzidi in sinergijski učinek z dodatno spremenjenim pH-jem (slika 4).

Alcalase 2.5 L® (Novozymes) in Esperase 8.0 L (Novozymes) sta proteazi. Najprej smo naredili preizkus na zelo majhnem delčku. Delovanje teh encimov ni poškodovalo barvne plasti na sliki, čeprav je naravoslovna analiza pokazala, da je bila za vezivo uporabljena proteinska tempera. CIPzyme® (Novozymes) in drugi preizkušeni encimi niso imeli nobenega učinka.

Lipex 100 L® (Novozymes) je lipaza, ki doseže optimalno aktivnost pri pH vrednosti 7 in temperaturi 30°C. Za preizkus smo v 8 ml Aqua purificata (Magdis), puferirane s TRIS-om (Kemika) na pH 7, dodali 2 ml Lipexa 100 L. Košček vpojnega papirja smo položili na diskretno mesto na sliki in ga do zasičenosti namočili z raztopino encima. Potem smo ga pustili na sliki 20 minut. Preizkus je bil narejen pri sobni temperaturi (25° C) in 63 % relativni vlažnosti (izmerjeni z merilcem Testostor 171).

Nepričakovano se je uporaba lipaze Lipex 100 L® v tem primeru izkazala za učinkovito. Lipex je omehčal

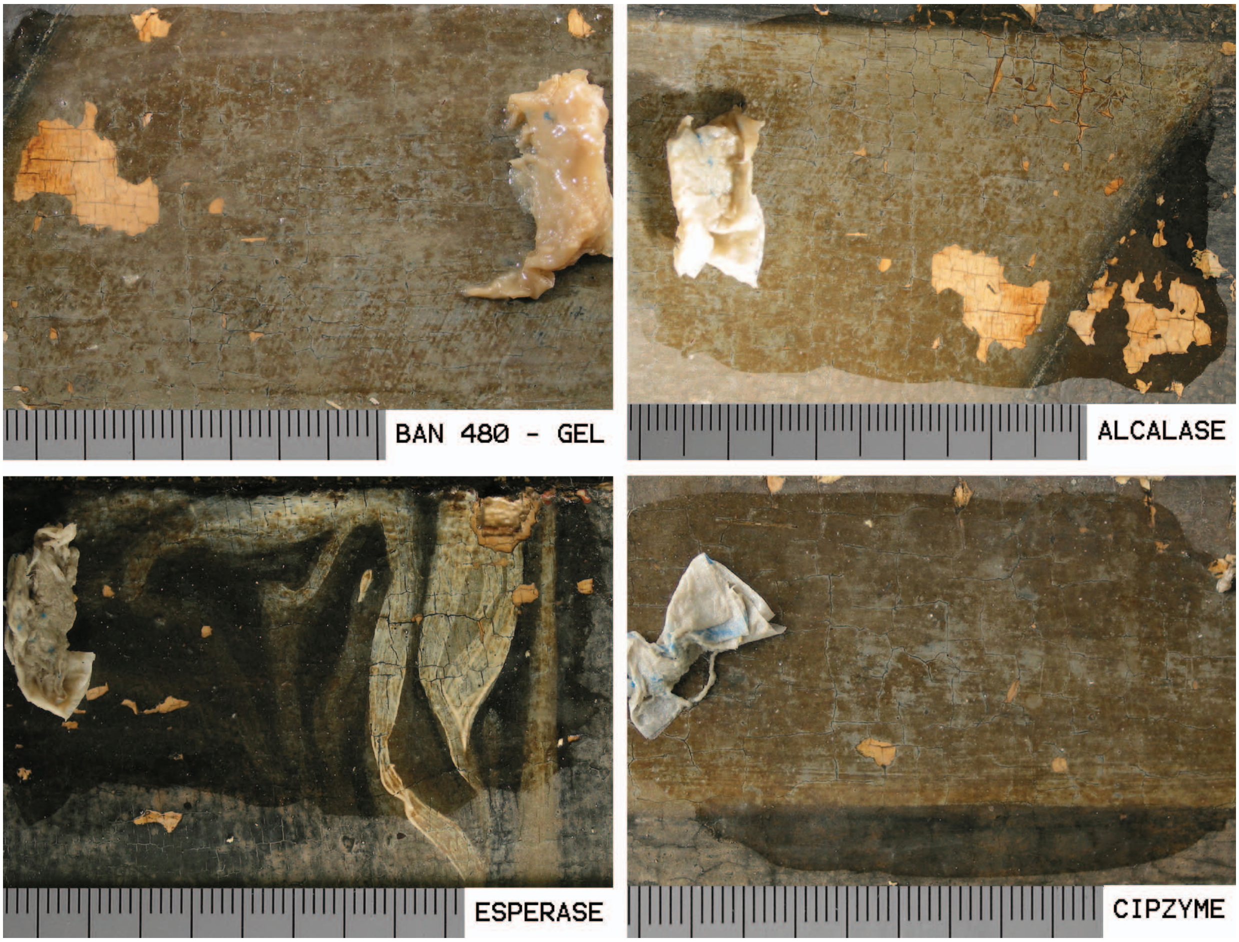
of a sufficiently high quality. In addition, the haze proved to be resistant to all the conventional chemical means that were tried, which either did nothing to the haze, or damaged the paint layer. Trials were carried out on small discrete areas of the paintings. These included the prolonged action of water (up to 120 minutes); hydrolysis with acid up to pH 3.0; hydrolysis with ammonium hydroxide at different concentrations and exposure times; the use of chelating agents; tensides and organic solvents.

The scientific analysis obtained from the laboratory of the Croatian Conservation Institute and collaborators revealed that the haze consisted mainly of cherry-tree gum, a small amount of animal glue and an unidentified chloroform-soluble component (about 3%), while the paint layer itself was a protein tempera emulsion. After the failure of all the conventional methods tested for the removal of the haze, enzymes were tested. First, three different amylases were tested: first BAN 480 L® (Novozymes); then a powdery amylase sold by the Italian company Phase (Phase enzima amilasi lotto 01511); and finally an amylase (technical grade) obtained from the laboratory of the pharmaceutical company Pliva Zagreb. A negative result was obtained. An equally unsatisfactory result was obtained using BAN 480 L® (Novozymes) while maintaining both the optimal pH of activity and the optimal temperature at 70 °C. The probe was placed next to the thermometer and the temperature was maintained with a small infrared electrical heater for 20 minutes. The results obtained after many modifications of the surface tension, the methods of application, the concentration of enzymes, and the exposure times were similarly poor.

After that, a series of other enzymes (cellulases, proteases and lipases) were tested. Theoretically, these should not have acted on the polysaccharides of cherry-tree gum; however, the intention was to test their synergetic effect, the synergetic effect with tensides and that with the pH modified in addition (Figure 4).

Alcalase 2.5 L® (Novozymes) and Esperase 8.0 L (Novozymes) are proteases. First, very small tests were made. The paint layer on the painting was not damaged by the action of these enzymes, although scientific analyses showed that protein tempera was used as the binder. CIPzyme® (Novozymes) and the other enzymes tested were ineffective.

Lipex 100 L® (Novozymes) is a lipase that reaches optimal activity at pH 7.0 and the temperature of 30 °C. For the test 2 ml of Lipex 100 L were added to 8 ml of Aqua purificata (Magdis) buffered with TRIS (Kemika) to pH 7.0. A small piece of absorbing paper was placed on a discrete area of the painting and soaked to saturation with the enzyme solution. It was allowed to remain on the painting for 20 minutes. The test was made at room temperature (25 °C) and a relative humidity of 63% (mea-



Slika 4.
Figure 4.

in želiral koprenasto plast na površini slike, tako da jo je bilo ponekod mogoče odstraniti s previdnim drgnjenjem z namočenim tamponom. Na mestih, kjer je bila bolj gumijasta in lepljiva in kjer je bila barvna plast bolj hrapava, jo je bilo mogoče dobro odstraniti s ščetko iz steklenih vlaken. Barvna plast je po delovanju Lipexa ostala nepoškodovana, vendar je treba krtačiti previdno, saj voda zmehča barvno plast. Opisano metodo čiščenja z Lipexom smo preizkusili na različnih barvah, preden smo jo uporabili na osrednjih delih in figurah. Rezultat je bil nadvse zadovoljiv (sliki 5, 6).

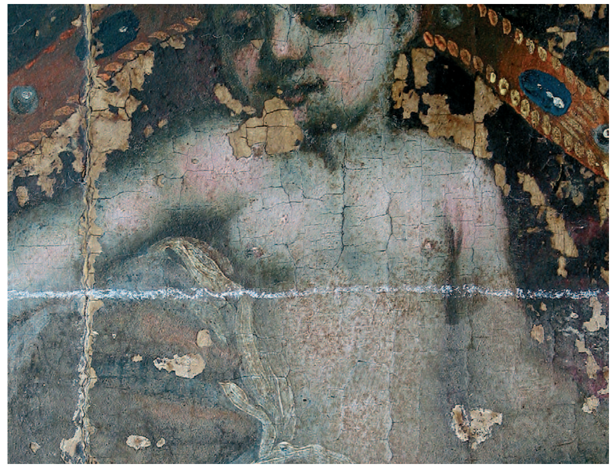
Pozitivni rezultat z Lipexom je sprožil novo vprašanje: ali lipaza Lipex 100 L® (Novozymes) delno deluje kot amilaza? Preizkus z drugo lipazo, L 0763 Type XII® (Sigma), je bil v tem konkretnem primeru negativen. Nadaljnji preizkusi na vzorcih raznih gumijev so

sured by Testostor 171).

Unexpectedly, the application of lipase Lipex 100 L® was successful in this case. Lipex softened and gelled the haze layer on the paint surface so that in some places it could be removed by careful rubbing with a wet cotton swab. In places where it was more rubbery and sticky and where the paint layer was rougher it could be removed well with a fibreglass brush. The paint layer remained undamaged under the action of Lipex. However, the rubbing with a fibreglass brush should be carefully controlled as the paint layer is softened by water. The cleaning method with Lipex described was tested on other colours before it was applied on the central parts and figures. The result was very good (Figures 5, 6).

A positive result with Lipex opened a new question: does the lipase Lipex 100 L® (Novozymes) exert a

Slika 5.
Figure 5.



Slika 6.
Figure 6.

pokazali, da Lipex 100 L ni deloval kot amilaza. Čeprav je znano, da nekatere lipaze lahko delujejo kot amilaze, se zdi, da v tem primeru ni bilo tako. Preizkusi raztapljanja češnjevega, višnjevega, slivovega in orehovega gumija niso pokazali, da bi vodni (!) encimi lahko raztapljali gumije hitreje kot gel brez dodatka encimov. Gumiji so se napeli zaradi vode v puferiranem encimskem gelu. Voda v gelu povzroča tudi napihovanje kleja, katerega obstoj v majhni količini v kopreni je pokazala znanstvena analiza. Zdi se, da je Lipex 100 L® deloval na tisto neidentificirano in v kloroformu topno snov, ki sestavlja približno 3 % plasti koprene. Zaradi teh 3 % lahko koprena postane hidrofobna ali pa se zaradi njih spremeni topnostni parameter višnjevega gumija.

Sklepi

Encime lahko uporabljamo kot katalizatorje razpada molekulskih vezi neželenih organskih materialov. Uporabo encimov v konservatorstvu-restavratorstvu raziskujemo v primerih, ko bolj konvencionalne metode ne dajejo zadovoljivih selektivnih rezultatov.
Delo z encimi v konservatorstvu-restavratorstvu (posebno še naš tretji primer) dokazuje, da za pozitiven rezultat poleg vseh znanstvenih analiz potrebujemo še kanček sreče. Zelo veliko raziskav in precej napredka bo še potrebnih, preden bomo pri uporabi encimov za selektivne postopke razgradnje lahko tako popolni kot narava.

partial amylase activity? Another lipase tested, L 0763 Type XII® (Sigma), gave negative results in this particular case. Subsequent tests on samples of various gums showed that Lipex 100 L did not exert amylase-type activity. Although it is known that some lipases can have amylase activity, it seems that this was not the case in this particular example. Tests to dissolve the gums of cherry, sour cherry, plum and walnut did not show that an aqueous(!) enzyme gel could dissolve gums faster than the gel without the addition of enzymes. The gums swelled due to the water from the buffered enzyme gel. The water from the gel also causes swelling of the animal skin glue that was detected in the haze layer by scientific analysis to a smaller extent. It seems that Lipex 100 L® acted on the approximately 3% of the haze layer that could not be identified but is soluble in chloroform. This 3% could render the haze hydrophobic or change the solubility parameters of the cherry-tree gum.

Conclusions

Enzymes can be used to catalyse the disintegration of molecular bonds of unwanted organic materials. Their use in conservation-restoration should be investigated in the cases where more conventional methods do not yield satisfactory selective results.
Work with enzymes in conservation-restoration (especially in our third example) proves that with all scientific analyses one must in addition have a bit of good luck to

V vseh treh specifičnih primerih je odstranitev površinskih nečistoč z raztopino triamonijevega citrata (3 % v destilirani vodi Aqua purificata) omogočila poznejše omočenje površine. Ko se je površina po taki "predpripravi" povsem posušila, smo lahko uporabili encimski gel, ne da bi morali pri pripravi gela uporabiti tenzide za omočenje površine. Tenzidi nižajo površinsko napetost vode, kar je nasprotno od želiranja vode. Gel mora biti dovolj gost, da njegova tekoča komponenta čim manj prodira v razpoke v barvni plasti, ob tem pa mora biti tudi dovolj šibak, da se lahko encimi enakomerno porazdelijo.

Obstajata dve metodi izdelovanja pufreriranega encimskega gela. Po prvi metodi zmešamo puferirano vodo z encimi, nato pa pripravimo gel z magnetnim mešalnikom. Pri drugi metodi uporabimo že pripravljen puferiran gel, kateremu dodamo encime (magnetni mešalnik v tem primeru ni potreben, razen če je gel prešibak). Vrednost pH-ja gela se čez dan ali dva ustali, kar je verjetno posledica bolj popolne raztopitve in porazdelitve TRIS-a po vsem gelu. Porazdelitev sestavin je bolj enakomerna pri prvi metodi, ugotovili pa smo, da je učinkovita le druga metoda. Več raziskav bo potrebnih, če hočemo dokazati to, kar je nakazal ta posamični primer.

Videti je, da bi bilo treba za uravnavanje pH-ja gela uporabljati čim manj kislin ali se jim sploh povsem izogniti. Manj kislin in baz v mešanici pomeni manjšo prevodnost. V študiji primera, predstavljeni v prvem opisu, je puferirana mešanica z visoko prevodnostjo dala negativen rezultat. To opažanje se razlikuje od nekaterih opažanj v biokemiji živih celic.

Vse tri študije primera so pokazale, da encimi lahko delujejo kot učinkoviti katalizatorji, tudi če zagotovimo le enega od optimalnih pogojev za delovanje. Seveda, veliko bolj praktično je zagotoviti optimalni pH kot doseči in vzdrževati optimalno toploto. Poleg tega smo dobili boljše rezultate, če smo se izognili postopku segrevanja in posledicam, ki sta jih na barvni plasti povzročili segrevanje in pospešeno hlapenje gela. V vseh treh študijah primera je bila toplota okolja 20° C.

Ne smemo pozabiti, da se pH nepuferiranega ali šibko puferiranega encimskega gela ob nanosu na površino barvne plasti spremeni zaradi njenega delovanja. Ugotovili smo, da ta problem najbolj zmanjšamo s predhodno pripravo s triamonijevim citratom (pH 7), tako da močno puferiranje raztopine encimskega gela ni potrebno.

get positive results. Much, much more investigation and development has to be done to become as perfect as nature in its use of enzymes for selective disintegration processes.

In all three specific cases described, the removal of surface impurities with triammonium citrate solution (3% in Aqua purificata) enabled the later wetting of the surface. After complete drying of such a ‘pretreatment,’ the enzyme gel could be used and no tensides (surfactants) were necessary in the gel preparation to ensure surface wetting. Tensides lower the surface tension of the water and that is the opposite of gelling the water. The enzyme gel should be hard enough to minimise spilling of the liquid medium in the fissures of the paint film and at the same time weak enough to enable equal distribution of enzymes.

There are two methods to make a buffered enzyme gel. The first method is to mix buffered water with enzymes and then gel the preparation using a magnetic stirrer; the second method is to take prepared buffered gel and then to add enzymes (the magnetic stirrer is not helpful in this case unless the gel is too weak). The pH value of the gel becomes stable after a day or two, probably due to a more complete dissolution and distribution of TRIS throughout the gel. In the first method, the distribution of the ingredients is more uniform, but we observed that only the second method gave a positive result. More investigation is needed to prove this ‘one case indication’.

It looks as if the use of acids should be minimised or avoided in the balancing of the pH of the gel. Less acid and base in the mixture results in less conductivity. In the case study presented in example 1, the result was negative in the buffered mixture of higher conductivity. This observation differs from some observations on the biochemistry of living cells.

All three case studies indicated that enzymes can function as efficient catalysts even if only one of their optimal activity conditions is met. Of course, it is much more practical to achieve the optimal pH than to achieve and maintain a uniform and stable warm temperature. Moreover, better results were obtained by avoiding the heating process and its consequences to the paint layer arising from heating and accelerated gel evaporation. In all three case studies, the ambient temperature was over 20 °C.

It must not be forgotten that the pH of the unbuffered or weakly buffered enzyme gel is going to differ when applied to the surface of the paint layer due to the influence of this paint layer. We observed that triammonium citrate pretreatment (pH 7.0) can minimise this problem and that strong buffering of the enzyme gel solution is not necessary.

Zahvale

Uspešno čiščenje so omogočili Istvan Laszlo (Novozymes – Dunaj), Štefanija Šimunić (Kutrilin – kemijski laboratorij), Smilja Britvić-Budicin (Institut Ruđer Bošković), Dragica Krstić (Prirodoslovni laboratorij Hrvatskog restauratorskog zavoda), Đurđa Vasić-Rački (Fakultet kemijskog inženjerstva i tehnologije, Zagreb), Ivan Marković (Pliva – razvojni laboratorij) in Stjepan Bogdan (Pliva – razvojni laboratorij).

Acknowledgements

The successful cleanings were made possible by Istvan Laszlo (Novozymes – Vienna), Štefanija Šimunić (Kutrilin Chemical Laboratory), Smilja Britvić-Budicin (Ruđer Bošković Institute), Dragica Krstić (Science Laboratory, Croatian Conservation Institute), Đurđa Vasić-Rački (Chemical Engineering and Technology Faculty, Zagreb), Ivan Marković (Pliva – Development Laboratory) and Stjepan Bogdan (Pliva – Development Laboratory).

Viri

[1] DeSantis, P. (1983) *Some observations on the use of enzymes in paper conservation,* Journal of the American Institute for Conservation 23, American Institute for Conservation, Washington, 7–27.

Opomba

1 Aqua purificata, ki jo proizvaja Magdis ustreza standardu Eu. Ph. 2000 za farmakološko in medicinsko uporabo.

References

[1] DeSantis, P. (1983) *Some observations on the use of enzymes in paper conservation*, Journal of the American Institute for Conservation 23, American Institute for Conservation, Washington, 7–27.

Note

1 Aqua purificata by Magdis meets the Standard Eur. Ph. 2000 for the use in pharmacology and medicine.

Biokorozija poslikav

Biocorrosion Studies on Painted Surfaces

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Ključne besede:
biorazgradnja;
celulozna vlakna;
pasteli;
oljne slike.

Key words:
biodeterioration;
cellulose fibres;
pastels;
oil paintings.

POVZETEK: **Biokorozija na različnih umetniških delih je naraven pojav, pri katerem mikroorganizmi v svojem življenjskem ciklusu razgrajujejo različne organske snovi, kot so celuloza in naravna veziva. Delovanje mikrobnih encimov spreminja te snovi v organske in amino kisline, ki skupaj z encimskim delovanjem predstavljajo osrednji del biokorozije. Predstavljene raziskave obravnavajo mehanizem delovanja biokorozije na papirnem in platnenem temeljniku in možnosti restavracije in konservacije likovnih del na tej osnovi.**

ABSTRACT: The influence of filamentous fungal metabolism, indicated by the joint action of various organic acids and the activities of fungal enzymes recognized as the cause of biocorrosive action on pastels and on the ground of oil paintings on canvas supports was studied. The study included the influence of the temperature and humidity of the environment on biodeterioration. Differences in the mechanisms of filamentous fungal growth and the influence of fungal metabolites on pastels and oil paintings were shown. Preservation and conservation procedures using benzisothiazolone in ethanol (1:4) were used effectively.

Uvod

Rast mikrobne biomase in aktivnosti različnih encimov, njen metabolizem pretvarjanja različnih organskih komponent veziv, naravnih polimerov, celuloznih vlaken ali organskih nečistoč v različne organske in amino kisline ter njihovo korozivno delovanje, kar vse lahko označimo kot biološko korozijo temeljnikov ali biokorozijo, so lahko resen problem za konservatorje-restavratorje. Biokorozija je specifičen problem, ki v restavriranju in konserviranju različnih umetniških del zavzema posebno mesto. Organske kisline in aminokisline skupaj z encimi hidrolizirajo celulozna vlakna v strukturi papirnega ali tkanega temeljnika. Zunanji dejavniki, kot so temperatura od 20 do 30° C, pH od 5 do 7 in relativna vlažnost nad 65 % pospešujejo rast nitastih gliv, plesni in pravih gob iz vrst basidiomicetes. V večini primerov sta običajen postopek reševanja problemov biokorozije in konservacije restavriranih poslikav mehansko čiščenje in odstranjevanje plesni brez kakršnegakoli predhodnega postopka denaturacije ali sterilizacije poslikane površine, brez uporabe učinkovitih konservansov ali ob uporabi nesmiselnih in neuporabnih snovi.

Introduction

The presence of the different stages in the life circle of various microorganisms growing on various art monuments could represent a serious problem for the restorer. Biocorrosion of art monuments is defined as a natural phenomenon where a microorganism in its life circle is causing the deterioration of various organic substances as well as natural resins or cellulose fibres. In this process, microbial enzymes decompose organic compounds, such as carbohydrate, fibres, proteins or other kinds of natural polymers into various metabolites, including organic acids and amino acids. These products, together with cellulytic enzymes released mostly from various filamentous fungi, accelerate further hydrolysis of cellulose fibres from paper or a canvas support. A pH from 5 to 7 and high relative humidity, together with a temperature from 20 to 30 °C, significantly encourage this process. In most cases in restoration, microbial infection is simply mechanically removed from the infected surface without any denaturation of the remaining fungal spores and mycelia or thorough cleaning and further preservation of the ground.

Materiali in metode

V vseh izvedenih primerih je bil kot sterilizacijsko sredstvo za vegetativno mikrobno biomaso spor plesni in gliv uporabljen plinasti formaldehid. Postopek sterilizacije je bil uporabljen na obeh straneh poslikave, in tudi pri okvirju, podokvirju in krovnem steklu. Čas ekspozicije je bil 12 ur.
Kot konservacijsko sredstvo je bila uporabljena raztopina (1 : 4) benz-isotiazolona v etanolu. Dodatek 10 promilov v agarju je pokazal učinkovitost benz-isotiazolona pri preprečevanju rasti plesni.

Pri preučevanju okuženih površin smo za kontrolo uporabili optično mikroskopijo z mikroskopom Wild 1.25X in stereo mikroskopom Wild - M 20, Švica, ter vrstičnim elektronskim mikroskopom JEOL JSM-T220, Japonska pri pospeševalni napetosti 20 KV.

Materials and Methods

For denaturation of fungal mycelia and spores from the picture area, from both the front and reverse surfaces, the frame and the stretcher, sterilisation by gaseous formaldehyde was used. The exposure time was 12 hours.

For conservation of the surfaces of the works of art, benzisothiazolone in ethanol (1:4) was used. The addition of 10 ppm to agar was found to be the optimal concentration.

A JEOL JSM-T220 scanning electron microscope (Japan), using an acceleration voltage of 20 KV, was used in the study. Organic compounds relating to fungal spores and filamentous fungal biomass on the surface of pastel and oil painting grounds and supports were checked by X-ray diffraction analysis. For optical observation a Wild - M 20 stereomicroscope and a Wild optical microscope 1.25X (Switzerland) were used.

Rezultati in razprava

1 Pastelne poslikave

Pri pastelnih slikah gre običajno za poslikavo na papirnem temeljniku, ki je kaširan s škrobnim lepilom na kartonasto ali včasih tudi lesonitno ozadje. Do

Results and Discussion

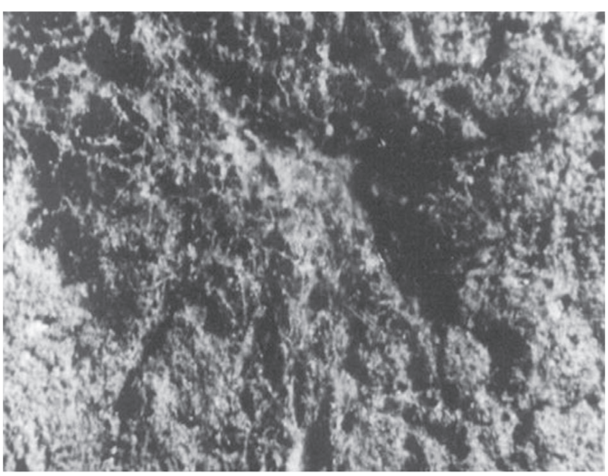
1 Pastel Support

The pastel support or ground is often represented by cardboard or a starch-pasted rough paper on a cardboard support. In this case fungal infection develops

okužbe s plesnimi ali nitastimi glivami pride v primernem okolju vlažnosti in temperature od 20 do 30° C, ob relativni vlažnost nad 65 % in pH od 5 do 7, saj razmere pospešujejo rast nitastih gliv, plesni in pravih gob. Glavni vzrok za rast in razvoj mikrobne biomase je škrob ali lahko razgradljivo organsko vezivo. Vlažnost pod 60 %, temperatura 20° C in kroženje zraka v razstavnih prostorih preprečujejo razvoj in rast mikroorganizmov na poslikani površini. Relativna vlažnost nad 60 % ob temperaturi od 20 do 30° C pa precej pospešuje širjenje glivne infekcije po vsej površini in globini temeljnika. Prisotnost nekaterih pigmentov na osnovi bakrovih, svinčevih in kositrovih oksidov preprečuje širjenje infekcije na teh površinah, drugi pigmenti pa so pri tem nevtralni.

Metabolizem nitastih gliv in plesni temelji na porabi glukoze, ki jo mikroorganizem sprošča z encimsko hidrolizo škroba, celuloze ali traganta - veziva pastelnega pigmenta.

V prisotnosti mikro vlage se rast mikroorganizma v smeri iskanja hrane poglablja v trdni matriks temeljnika in pri tem izrablja vezivo in celulozna vlakna. Ko gliva porabi vezivo, del biomase odmre in pusti za seboj svoje mikrobne spore, drugi del biomase, ki je sposoben razgrajevanja celuloznih vlaken, pa nadaljuje rast biomase in izkoriščanje celuloze. Ob tem se sproščajo organske in amino kisline, ki skupaj z encimi pospešeno razgrajujejo strukturo temeljnika.



Slika 1. Micelij *Mucor michei* na površini pastelne slike (stereo mikroskop 25-kratna povečava).

Figure 1. Mucor *michei mycelia* on the surface of a pastel. Photographed using Wild stereomicroscope, 25x magnification.

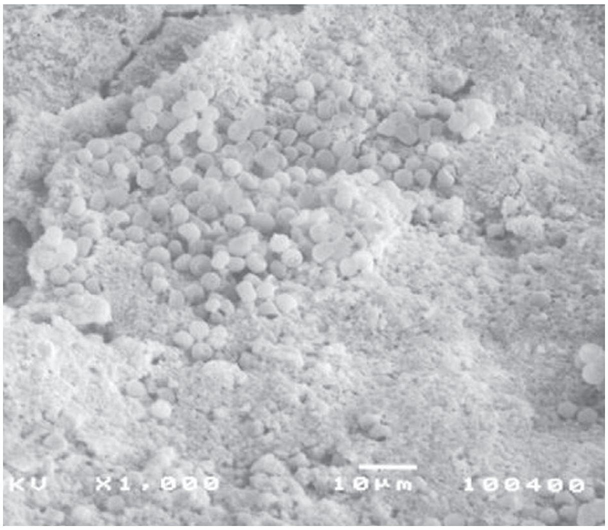
on the pigment-covered, porous painted surface. The main source of fungal growth is represented by starch paste and some organic waste on the painted surface derived from various fixatives. A dry atmosphere and air circulation in exhibition halls inhibit the growth of fungal mycelia, acting as natural protectors. On the other hand, a relative humidity of over 60% together with a temperature ranging from 20 to 30 °C strongly promote the development of fungal infection. The presence of some pigments based on copper, tin and lead oxides and salts usually blocks local infection, while the other pigments play a neutral role.

Fungal mycelia on the pastel surface exploit glucose formed by hydrolysis from a starch paste or gum tragacanth, or other polysaccharides used as an adhesive for the pastel pigment. In the presence of the minute amounts of water contained in a solid matrix, microbial growth develops as a function of time and temperature. In a very dry climate, and after exhausting all the substrate and water sources, microbial growth stops and the fungal spores must wait patiently for the next suitable opportunity.

This process also includes the presence of various metabolic products and the results of their activities that remain on the painted surface. Various organic acids, mostly citric, oxalic, malic or fumaric acids secreted in the metabolic tricarboxylic acid (TCA) cycle, could react with a vulnerable pastel pigment, transforming it to salts of the acids, decolourising it and changing its optical appearance. The effect of the secreted organic acids on the paper fibres of drawings or the printed pages of graphic arts or books stored in humid and non-aerated depositories is often manifested as brownish circles and spots of carbonised cellulose fibres. This effect on the coloured surface of the pastel results in the formation of various funnel-shaped forms, usually filled with fungal mycelia. If microbial infection is linked with wet starch-containing underlayers, its further progress increases much more rapidly.

To prevent this process, rapid measures have to be taken. The first essential step consists of drying the whole painted surface and its support in the drying chamber. A further step consists of the mechanical cleaning of the fungal mycelia from the painted surface, followed by sterilisation of the whole picture using gaseous formaldehyde to denature the fungal mycelia and spores. Sterilisation with gases is the most effective method as gases are able to enter the painted surface and porous layers.

For conservation of the restored pastel surfaces benzisothiazolone in ethanol, at a concentration of one part benzisothiazolone to four parts ethanol, was found to be optimal. The emulsion was sprayed on the inner



Slika 2. Spore plesni na površini pastelne slike (vrstični elektronski mikroskop, 1000-kratna povečava).

Figure 2. Filamentous fungal spores on the pastel surface. Scanning electron microscope image, 1000x magnification.

Prisotnost različnih metabolitov, še posebej citronske, jabolčne, oksalne, fumarne in mlečne kisline, in drugih produktov TCA cikla organskih kislin deluje na snovne lastnosti pigmenta in podlage, pri čemer pride do karbonizacije in temnenja papirja. Ob tem nastajajo koncentrični predeli rasti mikroorganizma in rast na površini in v globini poslikave. Povišana vlaga v prostoru precej pospešuje nadaljevanje tega procesa.

Za zaustavitev rasti mikroorganizma je potrebno hitro ukrepanje. Prvi korak je razstavljenje slike na okvir, sliko in steklo, temu sledita sušenje vseh segmentov v sušilni komori in čiščenje stekla s 70-odstotnim alkoholom, nato pa še mehansko čiščenje plesni s površine slike in sterilizacija vseh delov slike s plinastim formaldehidom. Sterilizacija s plinom omogoča tudi globinski poseg.

Za konservacijo površine slike je primerna posredna metoda razpršitve raztopine benz-isotiazolona v etanolu (1 : 4), ki jo nanesemo na notranjo stran krovnega stekla. Površina pastela je tako v posrednem stiku s konservansom, katerega pare oblivajo površino in preprečujejo nadaljnjo rast plesni na pastelu.

side of the protecting glass. A thin layer of this preservative enables the indirect contact between its vapours and the pastel surface at a distance of a few millimetres.

2 Oil Paintings on Canvas

By contrast, in the case of linen canvas supports fungal infection starts from the back of an oil painting. It actually starts as a result of a microcondensation of water, usually as a result of the microtransport of water from outside walls towards the inner side of the walls of exhibition halls.

With increased spring or autumn humidity and temperatures of 20 to 30 °C fungal infection of canvas impregnated with glue on the reverse side of the picture starts. After consuming the available organic compounds from the surface of glue-containing areas, fungal growth penetrates into a glue-chalk ground (where present) where fungal hyphae are growing from the back of the painting towards the front surface. The increasing amount of fungal biomass and the activity of fungal metabolic products, enzymes and organic acids results in stretching of the painted surface. This problem finally results in cracking and flaking of the paint. This action is followed by the entrance of fungal biomass, from the reverse surface towards its outlet, the painted surface, and finally colonies of fungal mycelia growing on the painted surface.

A part of the growth of fungal mycelia usually stops when organic compounds from the glue-containing ground are exhausted, but a part of the infection represented by cellulose-degrading fungi is still in progress. This part represents the most problematic and dangerous part of biodeterioration as this group of fungi could hydrolyse cellulose fibres from the linen canvas. Under the attack of fungal xylanases and organic acids, cellulose fibres start to crumble and whole parts of the canvas background finally disappear. The rest of the painted surface and the chalk-glue ground remain without a support, so the paint layers break at the first mechanical stroke and holes in the pictures finally appear.

Restoration and conservation of such a case start with mechanical cleaning of fungal mycelia from the painted surface, related to sterilisation of the whole picture including the frame, the stretcher and the unframed picture with gaseous formaldehyde: this enables denaturation of fungal mycelia and spores.

After this step the lining of the canvas on the vacuum table and covering the holes with wax mass start. The next step is related to classical restoration procedures. A 1 : 4 emulsion of benzisothiazolone in ethanol was very effectively applied in all the experiments.

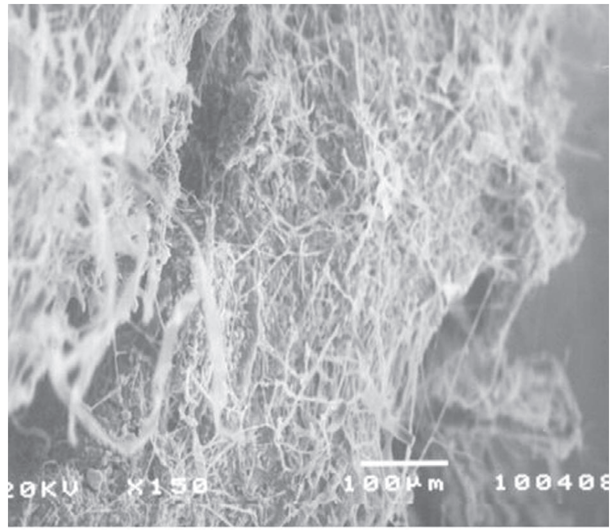
2 Olje na platnu

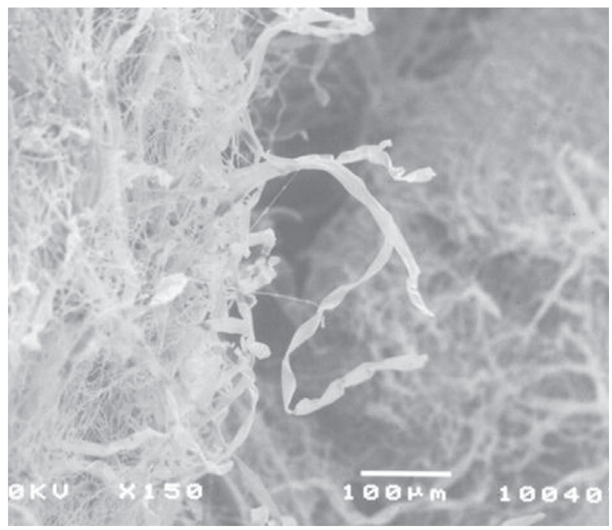
V nasprotju s pastelom, kjer pride do okužbe s plesnimi na površini slike in se širi v globino, se okužba oljne slike začne na neposlikanem hrbtu platna in se od tod širi proti površini poslikave. Infekcija se začne ob primerni vlagi in temperaturi, običajno na prehodu v pomlad ali jesen, kjer so temperature 20 do 30° C. K temu procesu pripomore še mikrokondenz vlage v prostoru med sliko in steno. Ko mikroorganizem raste, porablja klej, sprošča encime in proizvaja organske kisline. Organske kisline razkrajajo kredno podlogo in hidrolizirajo klejno vezivo.

Oslabela struktura slike je tako izpostavljena še mehanskim pritiskom biomase, ki prodira proti površini. Struktura oljne poslikave je načelno elastična, vendar se ta lastnost s starostjo manjša in poslikava postaja krhka. Ko mikrobna biomasa naraste, se površina poslikave napenja in podmehurja. Ta proces se nadaljuje, dokler ne pride do pokanja in luščenja površine in prodora biomase na površino oljne poslikave. Tu se lahko plesen razraste po površini in se prehranjuje tudi z oljnim slojem, ki ga razkraja s pomočjo proteolitičnih encimov in izločenih organskih kislin.

Del biomase ob porabi veziva in oljnih plasti odmre, drugi del pa začne z razkrajanjem lanenih vlaken. Ta faza pomeni najnevarnejši del biokorozije, saj se ob delovanju ksilanaz in organskih kislin lanena vlakna uprašijo in poslikava nima več trdne opore.

Prvi korak pomeni razstavljenje slike na okvir, podokvir in sliko na platnu. Temu sledi sušenje vseh segmentov v sušilni komori in mehansko čiščenje plesni s površine oljne poslikave s 70-odstotnim alkoholom. Sledi sterilizacija vseh delov slike s plinastim formaldehidom, ki omogoča tudi globinski poseg. Temu sledijo utrjevanje oslabelega tkanega temeljnika in klasični postopki restavriranja. Kot konservans je priporočljiva uporaba raztopine benz–isotiazolona v etanolu v razmerju (1 : 4).





Sliki 3 in 4. Rast celulitičnih nitastih gliv *Trichoderma viridae* (a) in *Aspergillus niger* (b) na lanenih vlaknih (vrstični elektronski mikroskop pri 1000-kratni povečavi).

Figures 3 and 4. Filamentous fungi *Trichoderma viridae* (a) and *Aspergillus niger* (b) on canvas fibres. Scanning electron microscope image, 1000x magnification.

Viri

Bader, F. G. (1986) *Sterilisation: prevention of contamination*, Manual of Industrial Microbiology and Biotechnology (ur. Demain, A.L. in Solomon, N. A.), American Soc. Microbiology, Washington, 345–361.

Cruger, W. in Cruger, A. (1982) *Biotechnology: A Textbook of Industrial Microbiology*, Sinauer Assoc. Inc. Press, Sunderland, Madison, 84-86.

Larpent-Gourgaud, M. in Sanglier, J. J. (1992) *Biotechnologies, principes et methodes*, Doin Editeurs, Paris.

Richards, J. W. (1968) *Introduction to industrial sterilisation*, Academic Press, London.

Wallhäusser, K. H. (1982) *Securité programmée lors la filtration sterilisante*, Inf. Chim. 230, 201–216. [Membrane filter specification]

Wallhäusser, K. H. (1985) *Sterilisation*, 2. zvezek (ur. Rehm, H-J. in Reed, G.), 700-716, VCH Weinheim.

References

Bader, F.G. (1986) *Sterilisation: prevention of contamination*, Manual of Industrial Microbiology and Biotechnology (Edit. Demain, A.L. and Solomon, N.A.), American Society for Microbiology, Washington, 345–361.

Crueger, W. and Crueger, A. (1984) *Biotechnology: A Textbook of Industrial Microbiology,* Sinauer Associates Inc.Press., Sunderland, Madison, 84–86.

Larpent-Gourgaud, M. and Sanglier, J.J. (1992) *Biotechnologies, principes et méthodes*, Doin Editeurs, Paris.

Richards, J.W. (1968) *Introduction to Industrial Sterilization*, Academic Press, London.

Wallhäusser, K.H. (1982) *Securité programmée lors la filtration sterilisante*, Inf. Chim. 230, 201–216. [Membrane filter specification]

Wallhäusser, K.H. (1985) *Sterilisation*, Vol.2 (Edit. Rehm, H-J. and Reed, G.), 700-716, VCH Weinheim.

Kemijsko čiščenje in izbira veziva za retušo, Stolna cerkev svetega Nikolaja v Ljubljani

Chemical Cleaning and the Selection of the Retouching Binder, The Cathedral of Saint Nicholas, Ljubljana

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POVZETEK: **Pri ugotavljanju stanja barvnih slojev stenske poslikave v notranjosti stolne cerkve Sv. Nikolaja v Ljubljani je bila ugotovljena sprememba kalcijevega karbonata v kalcijev sulfat. S selektivnim kemijskim čiščenjem nam je uspelo pretvoriti kalcijev sulfat v karbonat in površinsko odstraniti kazeinski premaz. Pri izbiri veziva za retušo smo raziskali vplive umetnega staranja na izbrane materiale ter kot vezivo za retušo določili Tylose MH.**

ABSTRACT: Due to significant darkening of Giulio Quaglio's mural paintings in the Cathedral of Saint Nicholas in Ljubljana, it was decided to clean the surface chemically. During research on the state of the colour layers of the mural paintings, the transformation of calcium carbonate to calcium sulphate was determined. Using selective chemical cleaning, the calcium sulphate was converted back to calcium carbonate and the casein layer that had been applied to the surface in one of the previous restoration procedures was removed. For the selection of the retouching binder the influence of accelerated ageing on several selected materials was investigated and Tylose MH was chosen for the purpose.

Ključne besede:
kalcijev sulfat;
kalcijev karbonat;
celulozni etri;
Klucel EF;
Tylose MH;
cinober;
zelena zemlja;
smalt.

Keywords:
Calcium Sulphate;
Calcium Carbonate;
Cellulose Ethers;
Klucel EF;
Tylose MH;
Vermilion;
Green Earth;
Smalt.

Uvod

Obnova stenske poslikave Giulia Quaglia (1705–1706) [1] na ladijskem oboku in zahodni steni stolne cerkve sv. Nikolaja v Ljubljani je bila eden najobsežnejših interdisciplinarnih posegov Restavratorskega centra v zadnjih letih. Dela so se začela leta 2002 in so trajala do leta 2006. V tem besedilu je predstavljen del, ki se nanaša na raziskave kemijskega čiščenja in izbiro veziva za retušo.

Na ladijskem oboku in zahodni steni so bili v preteklosti štirje večji restavratorski posegi (1859 [2], 1906 [3], 1944-1948 in 1961-1965). V objavljenih zapisih druge obnove je omenjen tudi nanos premaza čez celotno površino ladijskega oboka. Pred samim čiščenjem je bilo treba ugotoviti stanje barvnih slojev in izbrati najboljši reagent za čiščenje.

Raziskave

1 Stanje barvnih slojev pred čiščenjem

Z rentgensko praškovno difrakcijo je bila v površinskih slojih ugotovljena visoka vsebnost kalcijevega sulfata. Pri tem se je pojavilo vprašanje, ali je bil mavec dodan že v sam originalni sloj ali je posledica spremembe kalcijevega karbonata v kalcijev sulfat. Za kalcitne površine je to namreč značilna pretvorba [4,5] kot posledica prisotnosti žveplovega dioksida v zraku in visoke vlage na površini.

Z "mapping analizo" SEM / EDS je bilo preiskanih 20 vzorcev z različnih površin stenske poslikave in pri vseh je iz razporeditve žvepla razvidno, da je spreminjanje kalcijevega karbonata v kalcijev sulfat potekalo s površine proti notranjosti barvnih plasti. Ponekod je ta sprememba tako intenzivna, da je opazna tudi v ometu pod barvnim slojem. Slike od 1 do 4 prikazujejo skrajna primera: prvi: površinska sprememba in drugi: sprememba tudi v omet pod barvnim slojem.

Z analizo SEM / EDS so bili identificirani tudi pigmenti v originalnih barvnih plasteh in kasnejših preslikavah. Pigmenti v originalu: rumeni oker, rdeči železov oksid, smalt, zelena zemlja, caput mortum, umbra, svinčeva rdeča, cinober, ogljikova črna. Pigmenti v kasnejših restavratorskih posegih: prusko modra, barijev sulfat, cinkova bela, rdeči železov oksid, organski rdeči pigment, ultramarin, svinčev pigment (bela/rdeča). Našteti pigmenti so le najverjetnejše možnosti glede na kemijsko sestavo in morfologijo delcev. Za njihovo nedvoumno določitev bi bile potrebne nadaljnje raziskave z uporabo npr. ramanske spektroskopije.

Z uporabo FTIR mikroskopije in plinske kro-

Introduction

The renovation of the mural paintings on the nave vault and the west wall in the Cathedral of Saint Nicholas in Ljubljana, painted by Giulio Quaglio in 1705–1706 [1], was one of the most extensive interdisciplinary projects of the Restoration Centre in recent years, beginning in 2002 and lasting until 2006. There were four major restoration actions in the past, in 1859 [2], 1906 [3], 1944–1948 and 1961–1965. In the published records of the second renovation there are also notes about an application of a coat over the whole surface of the nave vault.

In the following text, the part of the research project that was important for the development of the chemical cleaning and the selection of the retouching binder is presented. Before the cleaning procedure, the actual condition of the colour layers had to be determined and the best cleaning method selected.

Research

1 The Condition of Colour Layers before Cleaning

A high concentration of calcium sulphate was determined in the surface layers using x-ray diffraction (XRD), and the question arose whether this was added to the original paint in the form of gypsum, or if it is a consequence of the transformation of calcium carbonate into calcium sulphate, a commonly known conversion of calcite in surfaces due to the presence of condensed water on the surface and sulphur dioxide in the air [4, 5].

Utilising scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) in the mapping mode, 20 samples taken from representative locations of the mural painting were investigated. The uneven distribution of sulphur in the surface colour layers suggested the transformation of calcium carbonate into the sulphate. In certain areas, examination of paint samples showed that the conversion even penetrated into the plaster below the colour layers. Figures 1 to 4 show two extreme examples, EDS mapping showing the distribution of sulphur in each case: the first, in a sample from the blue sky, shows the surface conversion; the second, in a sample taken from a violet region of the sky, shows the deep transformation.

The chemical elements composing the pigments in the original paint and in the colour layers applied in previous restoration actions were determined by SEM/EDS. Comparing the chemical composition and the morphology of the pigments, the presence of the following pigments in the original paint was suggested: yellow ochre, red iron oxide, smalt, green earth, caput mortuum, umber,

matografije – masne spektroskopije (GC – MS) je bila ugotovljena prisotnost kazeina na površini stenske poslikave.

2 Kemijsko čiščenje [6]

S čiščenjem smo hoteli doseči dvoje: pretvoriti kalcijev sulfat v karbonat in površinsko odstraniti kazeinski premaz. Pri tem je bilo treba določiti najboljši reagent, podporno sredstvo (absorber za reagent) in čas nanosa. Pri testiranju smo uporabili amonijev bikarbonat v celulozni pulpi, amonijev karbonat v celulozni pulpi in silikatnem absorberju in ionsko izmenjevalno smolo. Preiskanih je bilo 25 vzorcev, vzetih s testnih površin, in pokazalo se je, da sta najboljša reagenta nasičena raztopina amonijevega karbonata in/ali bikarbonata, podporno sredstvo pa celulozna pulpa in/ali kombinacija celulozne pulpe in silikatnega absorberja, ker se tako doseže najboljša oprijemljivost s površino. Čas nanosa je bil odvisen od globine pretvorbe, na najbolj problematičnih površinah pa je lahko znašal tudi 2 uri ali več. Po uporabi amonijevega bikarbonata in karbonata smo še preverili, ali je treba barvne sloje stabilizirati z barijevim hidroksidom, kar pa se je v našem primeru pokazalo kot neprimerno.

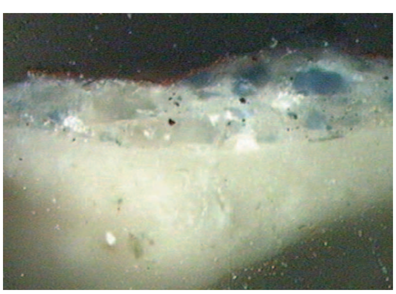
Z naslednjim primerom je prikazana uspešnost uporabe amonijevega bikarbonata v celulozni pulpi. Slika 5 prikazuje detajl stenske poslikave, kjer sta bila odvzeta vzorca št. 158 (pred čiščenjem) in št. 159 (po čiščenju).

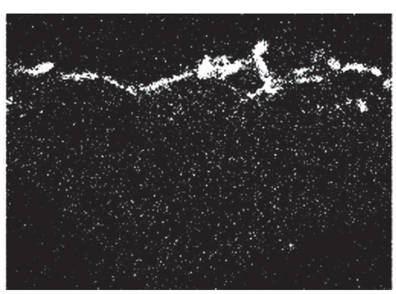
red lead, cinnabar (vermilion) and carbon black. Pigments used in previous restoration actions were suggested to be: Prussian blue, barium sulphate white, zinc white, red iron oxide, ultramarine, red lead, lead white and an organic red pigment. The pigments listed represent a very possible presence only; further research utilising, for example, Raman spectroscopy would be required for their unambiguous determination.

The presence of casein was determined in the coat applied to the whole surface of the mural painting in one of the previous restoration actions using Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectroscopy (GC–MS).

2 Chemical Cleaning [6]

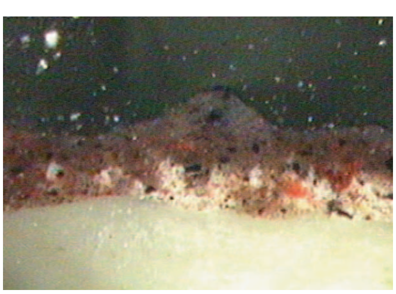
The darkened surface had to be treated by cleaning and it was required that two effects should be attained: to convert calcium sulphate back to the carbonate and to remove the casein layer from the surface of the mural painting. For that purpose it was necessary to establish the best reagent, the absorbent for the reagent and the time period necessary for the application. In the testing process, ammonium bicarbonate solution in a cellulose paste, ammonium carbonate solution in a cellulose paste and in a silicate absorbent, and an ion exchange resin were used. Samples from 25 treated surfaces were investigated, and it was established that the best treatment can be achieved using saturated solutions of ammonium carbonate and/or bicarbonate; the best at-

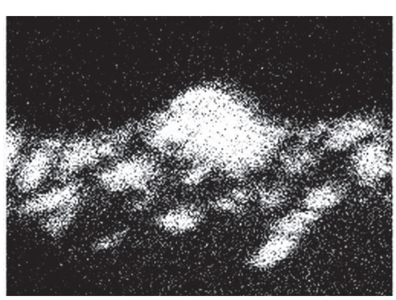




Slika 1. Posnetek preseka vzorca z optičnim mikroskopom. Vzorec je vzet z območja modrega neba.
Figure 1. Photomicrograph of cross section of sample taken from a blue area of the sky.

Slika 2. EDS razporeditev žvepla v vzorcu (primerjaj s sliko 1).
Figure 2. EDS-mapping distribution of sulphur in the surface paint layer (compare with Figure 1).





Slika 3. Posnetek preseka vzorca z optičnim mikroskopom. Vzorec je vzet s področja vijoličnega neba.
Figure 3. Photomicrograph of cross section of sample taken from a violet area of the sky.

Slika 4. EDS razporeditev žvepla v vzorcu (primerjaj s sliko 3).
Figure 4. EDS-mapping distribution of sulphur in the surface paint layer (compare with Photo 3).

Sliki 6 in 7 prikazujeta stanje barvnega sloja pred čiščenjem. Razporeditev žvepla (slika 7) kaže na zelo globoko pretvorbo kalcijevega karbonata v kalcijev sulfat, razširjeno tudi v omet pod barvnim slojem.

Sliki 8 in 9 prikazujeta stanje barvnega sloja po dveurni aplikaciji amonijevega bikarbonata v celulozni pulpi. Kot je razvidno iz slike 9, je masni delež žvepla v vzorcu padel z 2,87 % na 0,21 %. Pri reakciji nastali amonijev sulfat ni koncentriran v določenih predelih, temveč je bolj ali manj enakomerno porazdeljen po celotnem vzorcu, tako da ga z "mapping" analizo ni bilo mogoče slediti.

Pri pretvarjanju sulfata v karbonat z uporabo amonijevega karbonata in bikarbonata smo hkrati uspešno odstranili tudi kazeinski premaz, saj je kazein pri višjih pH vrednostih (nad 9) topen.

3 Izbira veziva za retušo [7]

Pri izbiri veziva za retušo smo želeli, da je vezivo stabilno dalj časa in da je retuša lahko odstranljiva. Pripravili smo čista veziva (Klucel EF, Tylose MH, amonijev kazeinat, Primal AC33 in Paraloid B72) na steklenih ploščicah in barvne sloje teh veziv v kombinaciji s pigmenti zelena zemlja, cinober in smalt na apnenem ometu. Vzorci so bili izpostavljeni pospešenim testom staranja v dveh klimatskih komorah.

V prvi komori sta temperatura in relativna vlaga oscilirali v treh ciklih (Tabela 1) na dan.

tachment at the surface can be achieved using cellulose paste and/or silicate absorbent. The time of application was dependent on the depth of transformation and in the most severe cases it was at least two hours or more. After the treatment using ammonium carbonate and bicarbonate, consolidation using barium hydroxide was tested, which in this case turned out to be inappropriate.

The following example shows the efficiency of the application of ammonium carbonate in a cellulose paste as an absorbent. Figure 5 illustrates a detail of one of the mural paintings, showing the location of two samples taken, one (no. 158) before cleaning and one (no. 159) after cleaning.

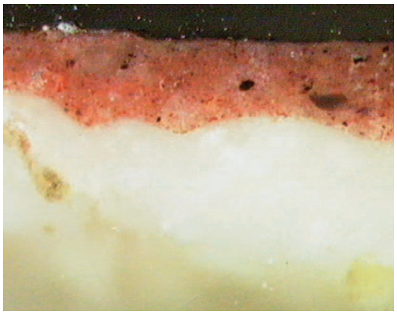
Figures 6 and 7 show the state of the colour layer before cleaning. The distribution of sulphur (Photo 7) shows a very deep penetration of the transformation of calcium carbonate into sulphate in the plaster below the colour layer.

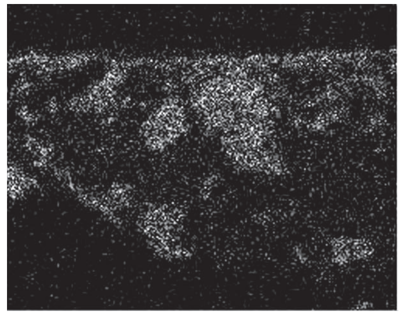
Figures 8 and 9 show the state of the colour layer after application of ammonium bicarbonate solution in a cellulose paste for two hours. As can be seen from Photo 9, the weight percent of sulphur in the sample falls from 2.87 to 0.21%. The ammonium sulphate that forms in the reaction is not concentrated in particular areas, but more or less evenly distributed throughout the whole sample, so it could not be traced by mapping analysis.

At the same time, by using ammonium carbonate and bicarbonate for the conversion of calcium sulphate to the carbonate, the casein layer was successfully re-

Slika 5. Detajl stenske poslikave z lokacijami vzorcev, vzetih za preiskave; št. 158: pred čiščenjem, št. 159: po čiščenju.

Figure 5. Detail of painting showing locations of samples taken for examination; 158: before cleaning, 159: after cleaning.





Slika 6. Posnetek preseka vzorca št. 158, vzetega pred čiščenjem.
Figure 6. Photomicrograph of cross-section of sample 158, taken before cleaning.

Slika 7. EDS razporeditev žvepla v vzorcu (primerjaj s sliko 6). W (masni odstotek) = 2,87 %.
Figure 7. EDS-mapping distribution of sulphur in the cross-section (compare with Figure 6). W (weight %) = 2.87 %.

Slika 8. Posnetek preseka vzorca št. 159, vzetega po čiščenju.
Figure 8. Photomicrograph of cross-section of sample 159, taken after cleaning.

Slika 9. EDS razporeditev žvepla v vzorcu (primerjaj s sliko 8). W (masni odstotek = 0,21 %.
Figure 9. EDS-mapping distribution of sulphur in the cross-section (compare with Figure 8). W (weight %) = 0.21 %.

Vzorci so bili v komori en mesec.

V drugi komori so bili vzorci en mesec izpostavljeni sevanju metalhalidne žarnice, ki ima UV-vidni (UV-Vis) spekter zelo podoben sončni svetlobi.

Analizirali smo vzorce pred pospešenim staranjem z uporabo optične, vrstične elektronske in mikroskopije FTIR ter po staranju.

a) Vizualni pregled staranih vzorcev

Slika 10 prikazuje vpliv pospešenega staranja na vodotopna celulozna etra Klucel EF in Tylose MH v kombinaciji s cinobrom. V komori, v kateri smo spreminjali relativno vlago in temperaturo, se je na površini nabral kondenz. Plošče so bile v komoro postavljene pod kotom 45° in barvni sloj Klucela EF s cinobrom je stekel, medtem ko se je sloj s Tylose MH le malenkost razmazal. Potemnitev barvnih slojev po izpostavitvi UV-Vis sevanju je posledica temnenja cinobra.

Slika 11 prikazuje vpliv pospešenega staranja na celulozna etra v kombinaciji s smaltom. Opazno je razbarvanje barvnega sloja s Klucelom EF kot vezivom v obeh komorah, medtem ko barvni sloj smalta v kombinaciji s Tylose MH ne kaže vidnih sprememb.

V kombinaciji z zeleno zemljo celulozna etra nista kazala vidnih sprememb staranja. Prav tako ni bilo

moved from the surface, since it became slightly soluble at the higher pH (above 9).

3 The Selection of the Retouching Binder [7]

The selection of the retouching binder was based on the general requirements for its long-term stability and reversibility. Selected samples of binders (Tylose MH, Klucel EF, ammonium caseinate, Primal AC 33, and Paraloid B-72), as well as some binder-pigment combinations, the pigments in the combinations being vermilion (cinnabar), green earth and smalt, were prepared on lime plaster and glass tiles. The samples were subjected to accelerated ageing tests in climatic chambers.

In the first chamber the temperature (T) and the relative humidity (RH) were oscillated daily for a period of one month.

There were three cycles per day. In the second chamber the samples were subjected to radiation from a metal halide lamp with a UV-visible (UV-Vis) spectrum very similar to that of sunlight.

The samples were analysed before and after the accelerated ageing, using optical and scanning electron microscopy and Fourier transform infrared spectroscopy.

a) Visual Examination of the Aged Samples

T (°C)	RH (%)
-20	/
0	/
20	50
50	90

Tabela 1. Pogoji enega cikla.
Table 1. Conditions of one cycle.

opaznih sprememb amonijevega kazeinata, Primala AC 33 in Paraloida B-72 z nobenim od izbranih pigmentov.

b) Raziskave spremembe kemijske strukture in mikrostrukture barvnih slojev

Obširni rezultati in razprava o raziskavah sprememb kemijske strukture in mikrostrukture barvnih slojev so bili objavljeni v publikaciji mednarodne konference 10th Euroseminar on Microscopy Applied to Building Materials [7]. Sledi kratek povzetek raziskav.

Klucel EF je v kombinaciji s pigmentoma cinober in smalt kazal vidne spremembe po staranju. Spremembe v mikrostrukturi barvnih slojev, ki so vsebovali Klucel EF in zeleno zemljo, so se pojavile po staranju v obeh komorah. Pojav novega absorpcijskega traku pri 1726 cm^{-1} v spektru FTIR Klucela EF po izpostavitvi UV-Vis sevanju nakazuje na spremembe v njegovi organski strukturi. Iz rezultatov analiz vzorca, ki je bil izpostavljen nihanju temperature in relativne vlage ter UV-Vis sevanju, lahko sklepamo, da povišana relativna vlaga zavira nastanek peroksidov.

Tylose MH je v kombinaciji z vsemi tremi pigmenti kazal manjše vidne spremembe le v kombinaciji s cinobrom. V barvnem sloju zelene zemlje in Tylose MH ni bilo opaznih sprememb v mikrostrukturi. Analiza FTIR ni pokazala sprememb v organski strukturi Tylose MH po staranju. Manjše spremembe, ki so opazne v traku pri 1600 cm^{-1}, so verjetno nastale zaradi prisotnosti dodatkov v tem komercialnem produktu.

Amonijev kazeinat v kombinaciji z vsemi tremi pigmenti ni kazal vidnih sprememb po staranju. V barvnem sloju tega veziva v kombinaciji z zeleno zemljo so se pojavile razpoke v njegovi mikrostrukturi po izpostavitvi nihanjem temperature in relativne vlage.

Figure 10 shows the influence of accelerated ageing on colour layers of the cellulose ethers Klucel EF and Tylose MH in combination with vermilion (cinnabar). In the chamber in which temperature and relative humidity were oscillating, water condensed on the surface of the painted samples, which were placed in the chamber at an angle of 45°. Both Klucel EF and Tylose MH are water-soluble; the layer of vermilion bound with Klucel EF almost flowed away, in contrast to the colour layer containing Tylose MH as a binder. The darkening of colour layers after exposure to UV-Vis radiation appeared due to the darkening of vermilion.

Figure 11 shows the influence of the same accelerated ageing regimes on colour layers of both cellulose ethers in combination with smalt. Discoloration of the layer of smalt in combination with Klucel EF appeared after ageing in both chambers. The colour layers of Tylose MH in combination with smalt showed no visual changes.

Neither of the cellulose ethers showed any visual changes in combination with green earth. The colour layers of ammonium caseinate, Primal AC 33 and Paraloid B-72 mixed with any of the listed pigments showed no visual changes.

b) The Influence of Ageing on the Chemical and Microscopical Structure of Colour Layers

The extensive results and discussion of the influence of ageing on the chemical and microscopical structure of colour layers have been published in the Proceedings of the 10th Euroseminar on Microscopy Applied to Building Materials [7]. A short summary of the research is given here.

Klucel EF in combination with vermilion and smalt showed visual changes after ageing. There were changes in the microstructure of the paint layer comprising Klucel EF in combination with green earth after ageing in both chambers. The appearance of a new strong absorption band at 1726 cm^{-1} in the Klucel EF FTIR spectrum after exposure to UV-Vis radiation indicates changes in its organic structure. It was shown by the sample that was exposed to temperature and relative humidity fluctuations, as well as to UV-VIS radiation, that relative humidity had a repressive effect on peroxide formation.

Tylose MH in combination with the three pigments showed minor visual changes only in combination with vermilion (cinnabar). There were practically no changes in the microstructure of the layer of Tylose MH in combination with green earth. FTIR analyses showed no changes in the organic structure of Tylose MH after ageing. Some minor changes observed in the band at 1600 cm^{-1} are probably due to an additive in this commercial product.

Ammonium caseinate in combination with any of

Vsi starani vzorci so kazali spremembe v spektrih FTIR zaradi cepitve peptidne vezi.

Vzorci vseh izbranih pigmentov, vezanih s Primalom AC33 in Paraloidom B-72, niso kazali vidnih sprememb. Prav tako nobeno vezivo ni kazalo sprememb v spektrih FTIR. Razpoke, ki so se pojavile v njuni mikrostrukturi, so lahko posledica cepitve verig, ki je povzročila zmanjšanje molekulske teže. Verjetno Primal AC33 vsebuje dodatke, ki vplivajo na procese staranja.

Na podlagi teh raziskav smo izbrali Tylose MH za vezivo za retušo Quagliove stenske poslikave.

Zaključek

Barvni sloji istega pigmenta lahko v kombinaciji z različnimi vezivi kažejo različne vplive staranja. Glede na dobljene rezultate bi bilo treba testirati vse pomembne pigmente, ki se uporabljajo za retušo stenskih poslikav, v kombinaciji z različnimi vezivi. Na trgu je ogromno materialov, namenjenih za restavratorstvo, vendar niso vsi primerni. Predvsem je potrebna previdnost pri izbiri celuloznih etrov (razni Kluceli, Tylose, Metoceli ...) in če je le mogoče, jih je treba pred uporabo preizkusiti.

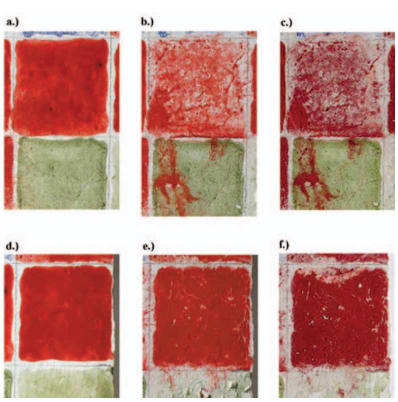
the pigments showed no visual changes after ageing in either of the chambers. The layer of this binder in combination with green earth showed cracks in its microstructure after being exposed to fluctuations of temperature and relative humidity. All aged samples showed differences in the FTIR spectra related to peptide bond breaking.

The samples of any of the selected pigments bound with Primal AC 33 and Paraloid B-72 showed no visual changes; nor did either binder show in its FTIR spectrum. The cracks that appeared in their microstructure could be a consequence of chain scission, resulting in a lowering of the molecular weight. It is possible that Primal AC 33 contains an additive that influences its ageing process.

On the basis of this research Tylose MH was selected as a retouching binder for the restoration of Quaglio's mural painting.

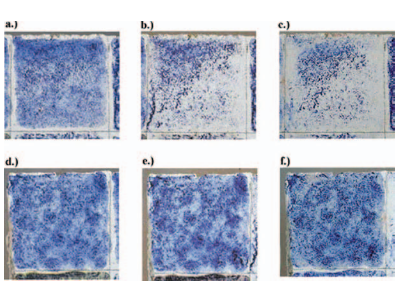
Conclusion

Different pigment-binder combinations can have variable effects on the durability of paint layers. According to the results already obtained, it is necessary to perform research on the ageing effects on all pigments



Slika 10. a) Klucel EF cinober pred staranjem; b) Klucel EF cinober po enem mesecu izpostavitve v T, RH komori; c) Klucel EF cinober po izpostavitvi v V-VIS komori; d) Tylose MH cinober pred staranjem; e) Tylose MH cinober po enem mesecu izpostavitve v T, RH komori; f) Tylose MH cinober po izpostavitvi v UV-VIS komori.

Figure 10. a) Klucel EF-vermilion (cinnabar) before ageing; b) Klucel EF-vermilion after one month's exposure in the temperature and relative humidity chamber; c) Klucel EF-vermilion after exposure in the UV-Vis chamber; d) Tylose MH-vermilion before ageing; e) Tylose MH-vermilion after one month's exposure in the temperature and relative humidity chamber; f) Tylose MH-vermilion after exposure in the UV-VIS chamber.



Slika 11. a) Klucel EF smalt pred staranjem; b) Klucel EF smalt po enem mesecu izpostavitve v T, RH komori; c) Klucel EF smalt po izpostavitvi v UV-VIS komori; d) Tylose MH smalt pred staranjem; e) Tylose MH smalt po enem mesecu izpostavitve v T, RH komori; f) Tylose MH smalt po izpostavitvi v UV-VIS komori.

Figure 11. a) Klucel EF-smalt before ageing; b) Klucel EF-smalt after one month's exposure in the temperature and relative humidity chamber; c) Klucel EF-smalt after exposure in the UV-Vis chamber; d) Tylose MH-smalt before ageing; e) Tylose MH-smalt after one month's exposure in the temperature and relative humidity chamber; f) Tylose MH-smalt after exposure in the UV-Vis chamber.

Viri

[1] Dolničar, J.G. (1882) *Historia Cathedralis Ecclesiae Labacensis* [manuscript Ljubljana 1706]; Lavrič, A. (2003) Janez Gregor Dolničar, *Zgodovina ljubljanske stolne cerkve*, Ljubljana 1701–1714, Založba ZRC, Ljubljana.

[2] Lavrič, A. (1996) *Goldensteinova kritika obnove ljubljanske stolnice*, Kronika 44, Ljubljana, 26–38.

[3] Steska, V. (1924) *Obnova ljubljanske stolnice ob dvestoletnici l. 1907*, Zbornik za umetnostno zgodovino IV, Ljubljana, 26–38.

[4] Elfving, P., Panas, I. in Lindqvist, O. (1994) *Model study of the first steps in deterioration of calcareous stone. I. Initial surface sulphite formation on calcite*, Applied Surface Science 74, 91–98.

[5] Zehnder, K. (1993) *New Aspects of Decay Caused By Crystallization of Gypsum,* Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress, 'Conservation of Stone and Other Materials: Research – Industry – Media (Ed. Thiel, M.J.), na UNESCO Headquarters, Paris, 1992, 2 vols (Spon, London), 107–114. (RILEM Proceedings, 21.)

[6] Ropret, P. in Bukovec P. (2005) *Chemical cleaning of Quaglio's mural painting in the Cathedral of Saint Nicholas in Ljubljana*, Scienza e beni culturali XXI: sulle pitture murali, riflessioni, conoscenze, interventi. Atti del convegno di studi, Bressanone, 12–15 luglio, 2005, Edizioni Arcadia Ricerdhe, Marghera, 283 - 291.

[7] Ropret, P., Zoubek, R., Sever Škapin, A. in Bukovec, P. (2005), *Effects of ageing on different binders for retouching and on some binder-pigment combinations used for restoration of wall paintings*, 10th Euroseminar on Microscopy Applied to Building Materials (ur. Hughes, J.J., Leslie, A.B. in Walsh, J.A.), University of Paisley, Scotland, June 21-25, 2005, University of Paisley, Paislay, 95-96.

that are important for the retouching of mural paintings in combination with different binders. There are many commercial products usable as binders on the market that are not supposed to be used in restoration. Precaution should be taken especially in the case of cellulose ethers – different types of Klucel, Tylose, Metocel and so forth: these should be tested before use.

References

[1] Dolničar, J.G. (1882) *Historia Cathedralis Ecclesiae Labacensis* [manuscript Ljubljana 1706]; Lavrič, A. (2003) Janez Gregor Dolničar, *Zgodovina ljubljanske stolne cerkve*, Ljubljana 1701–1714, Založba ZRC, Ljubljana.

[2] Lavrič, A. (1996) *Goldensteinova kritika obnove ljubljanske stolnice*, Kronika 44, Ljubljana, 26–38.

[3] Steska, V. (1924) *Obnova ljubljanske stolnice ob dvestoletnici l. 1907*, Zbornik za umetnostno zgodovino IV, Ljubljana, 26–38.

[4] Elfving, P., Panas, I. and Lindqvist, O. (1994) *Model study of the first steps in deterioration of calcareous stone. I. Initial surface sulphite formation on calcite,* Applied Surface Science 74, 91–98.

[5] Zehnder, K. (1993) *New Aspects of Decay Caused By Crystallization of Gypsum*, Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress, 'Conservation of Stone and Other Materials: Research – Industry – Media (Ed. Thiel, M.J.), held at UNESCO Headquarters, Paris, 1992, 2 vols (Spon, London), 107–114. (RILEM Proceedings, 21.)

[6] Ropret, P. and Bukovec P. (2005) *Chemical cleaning of Quaglio's mural painting in the Cathedral of Saint Nicholas in Ljubljana*, Scienza e beni culturali XXI: sulle pitture murali, riflessioni, conoscenze, interventi. Atti del convegno di studi, Bressanone, 12–15 luglio, 2005, Edizioni Arcadia Ricerdhe, Marghera, 283 - 291.

[7] Ropret, P., Zoubek, R., Sever Škapin, A. and Bukovec, P. (2005), *Effects of ageing on different binders for retouching and on some binder-pigment combinations used for restoration of wall paintings*, 10th Euroseminar on Microscopy Applied to Building Materials (Edit. Hughes, J.J., Leslie, A.B. and Walsh, J.A.), University of Paisley, Scotland, June 21-25, 2005, University of Paisley, Paislay, 95-96.

CHRISTOPHER HOLDEN

Med letoma 1961 in 1966 se je šolal na *Guildford School of Art* v Surreyju v Veliki Britaniji in pridobil državno diplomo iz umetnosti in oblikovanja – iz slikarstva in litografije. Od leta 1968 do 2003 je bil zaposlen kot konservator-restavrator, svetnik za tabelno slikarstvo v Tate Gallery v Londonu. S svojim več kot 35-letnim delom je vidno zaznamoval restavratorsko-konservatorsko stroko v tej ugledni ustanovi. Od leta 2003 je umetnik s polnim delovnim časom.

RACHEL BILLINGE

Leta 1984 je diplomirala iz strojništva na univerzi v Oxfordu Tri leta je delala kot strojna inženirka na Ministrstvu za obrambo, nato pa se je usmerila v konservatorstvo in leta 1990 naredila magisterij iz konservatorstva tabelnih slik na Politehniki v Newcastlu-upon-Tyne. Leta 1991 se je pridružila konservatorskemu oddelku londonske Narodne galerije, kjer je tesno sodelovala z dr. Lornom Campbellom pri tehničnih preiskavah slik, ki jih je preučeval za svoj katalog slik umetnikov nizozemskih šol 15. stoletja (*Fifteenth-Century Netherlandish Schools*). Je specialistka za infrardečo reflektografijo, s katero preučuje slike, nastale v obdobju od 13. do poznega 19. stoletja.

JO KIRBY

Študirala je kemijo in zoologijo na Exeter University ter zgodovino umetnosti na Birbeck College na londonski univerzi / *Courtauld Institute of Art*. Njeno delo v znanstvenem oddelku Narodne galerije v Londonu je posvečeno analizam pigmentov in preučevanju sestave barv. Posebno jo zanimajo pigmenti in barvila. Njen interes je prerasel v bolj splošno zanimanje za vpliv svetlobe in njen učinek na barve. Kot zgodovinarka je obširno raziskovala zgodovino zahodnoevropskih slikarskih materialov, od preučevanja receptov in navodil za pripravo in uporabo do dokumentarnih virov.

O avtorjih besedil

About the authors

Christopher Holden studied at the *Guildford School of Art* in Surrey, UK, between 1961 and 1966, where he obtained the National Diploma in Art &Design (NDD) – Painting and Lithography. From 1968 to 2003 he pursued a full-time career as a conservator-restorer, councillor for easel painting at the Tate Gallery, London. After working there for more than 35 years, he has left a visible mark on the restoration-conservation profession in this distinguished institution. Since 2003 he is a full-time artist.

Rachel Billinge graduated from Oxford University with a degree in Engineering Science in 1984. After three years as a mechanical engineer for the Ministry of Defence, she turned to conservation and in 1990 obtained her Master's degree in the conservation of easel paintings at the Newcastle-upon-Tyne Polytechnic. In 1991 she joined the Conservation Department of the National Gallery in London, where she worked closely with Dr. Lorne Campbell in the technical examination of paintings for his catalogue of paintings by artists of the *Fifteenth-Century Netherlandish Schools*. She is a specialist in infrared reflectography, which she uses to study paintings from the 13th to late 19th centuries.

Jo Kirby studied chemistry and zoology at Exeter University and art history at Birbeck College/ *Courtauld Institute of Art*, University of London. Her work in the Scientific Department of the National Gallery in London is devoted to pigment analysis and the examination of paint composition. She has a special interest in pigments and dyestuffs. This interest has developed into a more general concern with the influence of light and its effect on colours. As a historian, she has also extensively researched the history of western European painting materials, from the study of recipes and instructions for their production and use to documentary sources.

ULRICH WESER

Leta 1964 je doktoriral iz kemije na Tehniški univerzi v Münchnu. V letih 1965– 1971 je opravljal biokemijske raziskave kot docent na Univerzi Berkeley (ZDA) in v Londonu. Leta 1976 je bil redni profesor anorganske biokemije in molekularne arheologije na Univerzi v Tübingenu, med letoma 1982 in 1984 pa gostujoči profesor na Univerzi La Sapienza v Rimu ter od leta 2000 gostujoči profesor v Firencah. Od leta 1985 se posveča molekularni arheologiji in z encimskemu čiščenju slik, mumificiranim encimom in projektu Plinij o uporabi kovin v antični medicini.

DENIS VOKIĆ

Leta 2005 je magistriral na Akademiji za likovno umetnost in oblikovanje Univerze v Ljubljani na Oddelku za restavratorstvo. V letih 1998–2006 je bil vodja oddelka za konservatorstvo in restavratorstvo slik na lesu na Hrvaškem inštitutu za konservatorstvo in restavratorstvo v Zagrebu. Od leta 2006 je predavatelj na Oddelku za umetnost in restavratorstvo Univerze v Dubrovniku in direktor konservatorskega-restavratorskega podjetja K-R centar. Je predsednik Hrvaškega združenja konservatorjev in restavratorjev.

MARIN BEROVIČ

Diplomiral, magistriral in doktoriral je iz kemije in biokemije na Fakulteti za kemijo in kemijsko tehnologijo Univerze v Ljubljani. Izobraževal se je na Tehniški univerzi v Gradcu, v Delftu na Nizozemskem, v Nemčiji, na Danskem in v Veliki Britaniji. Zaposlen je kot profesor biotehnologije na Fakulteti za kemijo in kemijsko tehnologijo Univerze v Ljubljani. Opravil je tudi magisterij iz restavratorstva in konservatorstva na Akademiji za likovno umetnost in oblikovanje Univerze v Ljubljani, kjer je profesor na Oddelku za restavratorstvo.

POLONCA ROPRET

Polonca Ropret je diplomirala in doktorirala na Fakulteti za kemijo in kemijsko tehnologijo Univerze v Ljubljani. Tema doktorske disertacije je bila: Karakterizacija in stabilnost barvnih slojev umetniških predmetov. Od leta 2000 je zaposlena na Restavratorskem centru (danes Raziskovalnem inštitutu) Centra za konservatorstvo, Zavoda za varstvo kulturne dediščine Slovenije. Od leta 2004 mednarodno sodeluje z Department of Scientific Research, The Metropolitan Museum of Art, New York. Od leta 2006 je zunanja znanstvena sodelavka Museum Conservation Institute, Smithsonian Institution, Washington DC.

Ulrich Weser obtained a PhD in chemistry from the Technical University in Munich in 1964. Between 1965 and 1971, he was a biochemical research associate at Berkeley University (USA) and in London (UK). In 1976 he was full professor of inorganic biochemistry and molecular archaeology at the University of Tübingen, from 1982 to 1984 he was visiting professor at La Sapienza University in Rome, and since 2000 he is visiting professor in Florence. From 1985 onward, the focus of his studies has been on molecular archaeology, including enzymatic cleaning of paintings, mummified enzymes, and the Pliny project on the use of metal in ancient medicine.

Denis Vokić obtained his Master's degree in restoration from the Academy of Fine Arts and Design, University of Ljubljana. In the period from 1998-2006 he was Head of the Department for the Conservation and Restoration of Panel Paintings at the Croatian Institute of Conservation and Restoration in Zagreb. Since 2006 he is lecturer at the Department of Art and Restoration at the University of Dubrovnik, and director of a conservation-restoration company, K-R Centar. He is chairman of the Croatian Association of Conservators and Restorers.

Marin Berović holds B.Sc., M.Sc. and Ph.D. degrees in chemical and biochemical engineering from the Faculty of Chemistry and Chemical Engineering, University of Ljubljana. He pursued scientific training at the Technische Univesität in Graz, Austria, in Delft, The Netherlands, as well as in Germany, Denmark, and the UK. He is professor of biotechnology at the Faculty of Chemistry and Chemical Engineering, University of Ljubljana. He has also obtained a Master's degree in restoration and preservation at the Academy of Fine Arts in Ljubljana, where he works as professor at the Restoration and Preservation Department.

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LJUBLJANA 2013

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