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A new family of high viscosity polymeric dispersions for cleaning easel paintings

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ABSTRACT

The procedures for making and applying a new family of high viscosity aqueous polymeric dispersions based on poly(vinyl alcohol)-borax (PVA-borax) matrices are presented. A specific system of this type has been used to remove an oxidized varnish coating from the surface of “Coronation of the Virgin with Saints”, a 15th century egg tempera painting on wood by Neri di Bicci (Florence, 1418–1492). FTIR spectra showed that the oxidized varnish was constituted of highly aged shellac resin. Good cleaning performance was attained when the liquid portion of the dispersion consisted of a mixture of water and acetone. Rheological investigations indicate that the acetone content does not affect the mechanical properties of the polymeric dispersion. Those mechanical properties permit easy removal of the cleaning agent simply by peeling it from the surface by means of a forceps or spatula once it has carried out its cleaning function. Optical microscopic and FTIR investigations show that the cleaning agent is able to remove the oxidized varnish coating from the surface of the Neri di Bicci painting without leaving detectable residues.

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1. Introduction

During the conservation of the surface of a work of art, the cleaning process is, perhaps, the most important and delicate because it is an irreversible operation and, if improperly performed, it can be invasive and potentially lead to undesired effects. The direct application of organic solvents for cleaning canvas and wood paintings is still a widely used technique for the removal of foreign deteriorating coatings. Unfortunately, this approach sometimes causes some damage if the liquids penetrate into the painting layers and swell them. The swelling of natural polymeric organic materials (most of which have a structural function for the painting) in organic solvents can be evaluated (e.g., for oil paintings [1–3]) and discussed in relationship to the implications for the cleaning action.

During the last 15 years, several cleaning procedures for works of art, employing new cleaning agents, have been developed using as a guiding principle that they would be very selective [4]. Most involve the use of highly viscous cleaning agents [5], such as gels, in order to minimize the negative effects related to the penetra-

tion of the liquid phase into the painting matrix. However, it is not always possible to ensure complete removal of the gelling polymer after its application [6,7]. For example, Burnstock and Kieslich demonstrated that residues of a poly(acrylic acid)-based gelator can remain after the application of its gels onto and removal from a painted surface [8]. Thus, new methods that ensure greater efficiency of removal of all of the gel components are needed.

A possible approach that minimizes the deleterious aspects of gel removal from a painted surface might utilize high viscosity polymeric dispersions with mechanical properties characterized by a high elastic modulus (i.e., that make them rigid systems). Such systems could be peeled from the surface onto which they were applied by means of a benign mechanical action and without addition of a second liquid component (Fig. 1). In principle, such a cleaning system and removal procedure would reduce the amount of the polymeric residues from the dispersion on the painting surface to a greater extent [7] than gels that must be removed by more conventional means [9,10].

Solutions of poly(vinyl alcohol) (PVA), in the presence of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) as cross-linker, are known to form aqueous dispersions with high elastic modulus [11–16]. The borate ester cross-links result in very strong interactions between PVA chains [17]. Furthermore, the elasticity and, more generally, all the rheological properties of these systems can be tuned by changing either the ratio of PVA to borax or their total concentration [18]. Another important characteristic of the PVA-based high viscosity systems is

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Fig. 1. Removal of a PVA/borax/water-based dispersion after it was in contact with a gilded surface for the minimum time necessary to soften the outermost surface layer. The gel was peeled easily from the surface by forceps.

their chemical versatility: recently, it has been shown that thermodynamically stable aqueous PVA–borax dispersions can be prepared with some organic liquids as cosolvents [19]. This discovery is particularly important to the use of these systems to clean painting surfaces because both the polarity of the continuous phase and the mechanical properties of the dispersions can be modulated; specific polarities of the liquid component enhance the extracting power of the cleaning system [20]. Objectives of this work are to learn how to modulate the behaviour of these PVA/borate/cosolvent systems and to test their efficacy as new cleaning agents for easel paintings as assessed by their ability to clean coatings from painting surfaces and to be removed easily from them while leaving minimal residues.

As a test, PVA–borax based mixtures containing up to 6% (w/w) of acetone as a cosolvent were used to remove a dark coating composed of highly oxidized varnishes from the surface of “*Coronation of the Virgin with Saints*”, a wood panel by Neri di Bicci (1418–1492). The degree of success of those cleaning processes has been assessed visually (i.e., an aesthetic effect) and by comparing the results with those obtained with traditional methods. Results from those tests have been correlated with the viscoelastic properties (i.e., the elastic modulus [G'] and the loss modulus [G'']) of the PVA-based aqueous systems.

2. Materials and methods

PVA (99+ % hydrolyzed, [Mw] 124,000–186,000, Aldrich), sodium tetraborate decahydrate (99.5%, Merck), acetone (99.5%, Merck), ethanol (95.5%, Merck) and KBr (Merck, 99.98%) were used as received. Shellac resin was purchased from Zecchi (Florence, Italy) and its infrared spectrum was used as a standard in subsequent work. Water was purified by a Millipore Organex system ($R \geq 18 \text{ M}\Omega \text{ cm}$).

2.1. Preparation and application of the polymeric dispersions

Aqueous dispersions with 2 wt% of PVA and 0.4 wt% of sodium tetraborate decahydrate were prepared by dissolving the salt in water. Then, the PVA was added and dissolved by stirring and heating the mixture at 90 °C for 3 hours in hermetically closed vials (to prevent evaporation of water). Finally, the samples were cooled slowly to room temperature. Unless stated otherwise, all samples contain 2 wt% of PVA and 0.4 wt% of sodium tetraborate decahydrate.

Once a rigid material was obtained, an amount of cosolvent was added and the mixture was shaken by means of a vortex stirrer for 10 minutes. About 48 hours after their preparation, the cleaning systems were applied directly onto the painting surface by means of a spatula and left there for a maximum of 5 minutes. The cleaning agent was peeled from the painting surface by means of a forceps or a spatula as shown in Fig. 1, without adding any additional liquid component to the remaining polymeric dispersion or on the painting surface after the peeling process. The application of the dispersions on microscope slides was carried out as above. Fluorescence images (under a Wood lamp; emission maximum 364 nm) were collected from the microscope slides after various treatments (*vide infra*).

2.2. Accelerated photochemical aging

The FTIR spectra of three KBr pellets were recorded and then a few drops of a solution of shellac resin in ethanol were placed on each. Then the pellets were dried for 48 hours in the atmosphere and for 48 hours in a drier at room temperature to produce very thin films of shellac on one side of the pellets. An FTIR spectrum of one pellet (not aged shellac) was recorded and the other two pellets were irradiated (and “aged”) under a Xe lamp ($\lambda > 305 \text{ nm}$; 500 W/m^2) for 120 and 240 hours, respectively. Thereafter, their FTIR spectra were recorded.

2.3. Evaporation measurements of acetone-containing dispersions

A 2 g sample of dispersion was placed on a microscope slide so that it covered ca. $2 \times 2 \text{ cm}^2$ and left in contact with the atmosphere for 1 hour, during which time the weight decrease was measured on a Sartorius CP225D model analytical balance. The contribution due to the evaporation of water was determined from experiments with PVA systems that did not contain any acetone. To estimate the loss of acetone alone, the weight loss of a totally aqueous dispersion (same amount and same area exposure) was subtracted from the loss noted for the corresponding system containing acetone. Each point is the average of four measurements.

2.4. Instrumentation

Mid-infrared spectra were acquired from 4000 to 800 cm^{-1} with a Nexus 870-FTIR (Thermo-Nicolet) and a FT-IR Continuum microscope in the reflectance mode (beam splitter: KBr; detector: MCT) with a resolution of 4 cm^{-1} and 512 scans. Rotational and oscillatory shear measurements were carried out at $25.0 \pm 0.1 \text{ }^\circ\text{C}$ (Peltier temperature control system) on a Paar Physica UDS 200 rheometer using a 2° cone and plate geometry (25 mm diameter) and working at controlled shear stress. After their loading, samples were equilibrated for 1 hour at 25 °C prior to carrying out the experiments. Rotational tests were carried out at constant PVA concentration (2 wt%) and varying the borax amount from 0 to 0.4 wt%; at each composition, a viscosity versus shear stress curve was established. The intrinsic viscosity (η_0) values plotted versus borax concentration were deduced from the plateau of the curves in the low shear rate regime (low Newtonian region) [20]. G' and G'' were measured over the frequency range 0.005–15 Hz. The values of the stress amplitude were checked by means of amplitude sweep tests in order to ensure that all measurements were performed within the linear viscoelastic region. For all the frequency sweep measurements, the stress amplitude chosen was 2%. Optical micrographs were recorded on a USB Scalar portable microscope (model M2) and a Heerbrugg Wild M5A long focal microscope equipped with 6x, 12x, 25x, and 50x objectives. The USB portable microscope collects images by illuminating the region to be magnified

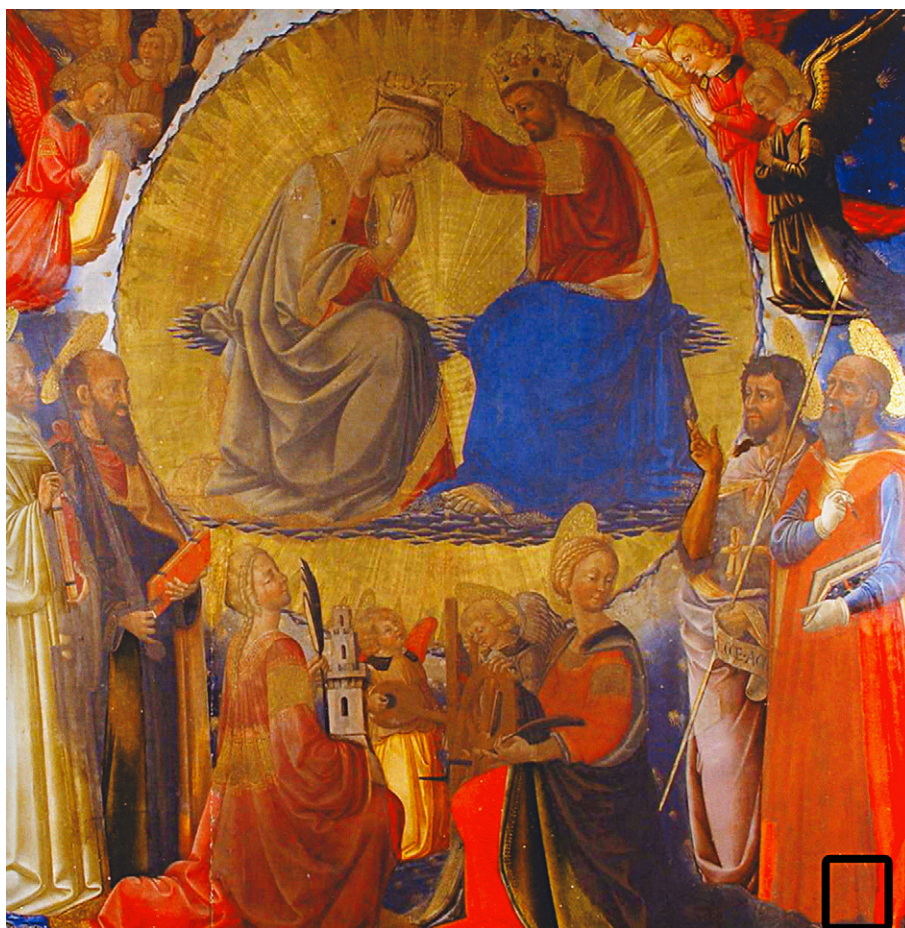


Fig. 2. “Coronation of the Virgin with Saints”, a 15th century egg tempera wood panel by Neri di Bicci, Galleria degli Uffizi, Florence, Italy. The black box indicates the region where the cleaning tests using PVA-based dispersions were carried out.

with its own light source; the resulting micrographs were in false colours.

3. Results and discussion

Fig. 2 shows “Coronation of the Virgin with Saints”, an egg tempera wood panel (15th century, 150 × 150 cm) by Neri di Bicci housed at

the Galleria degli Uffizi in Florence, Italy, and presently on loan to the Civic Museum in Pescia (Pistoia), Italy. The original appearance of the work of art was modified by a highly degraded and yellowed brown varnish (Fig. 3). In the regions where the red vermillion pigment is present (N.B., the mantle of Saint-Caterina and Saint-Girolamo in the lower part of the painting), the aging effects were particularly pronounced. As shown in the two images of Fig. 3,

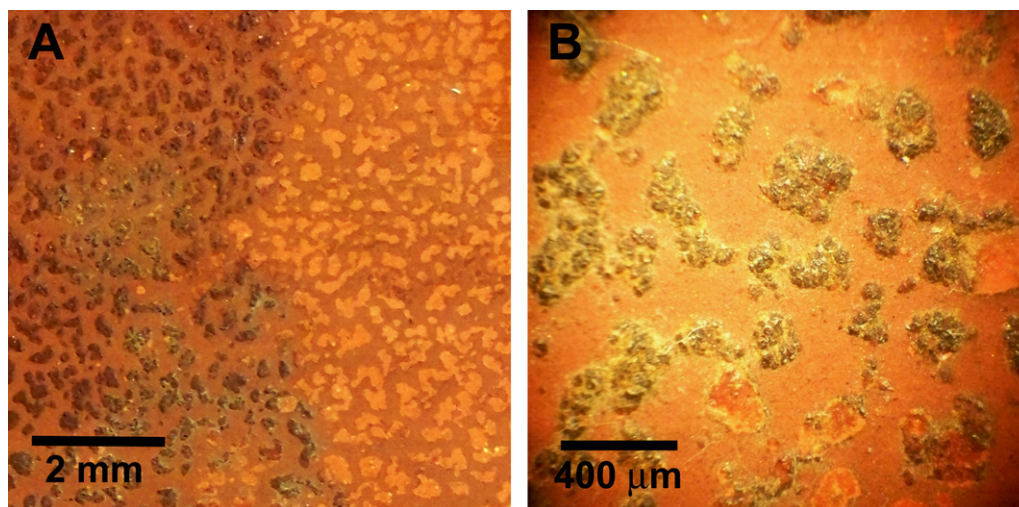


Fig. 3. Optical micrographs at two different magnifications of the region of the “Coronation of the Virgin with Saints” showing the morphology of the degraded varnish coatings to be removed. In A, the two features of the coatings are seen as brown clots (on the left) and a dark texture underneath (right). B shows the clots at higher magnification.

Table 1

Some spectral features associated with changes arising in FTIR spectra as a result of photochemical aging (see the *Materials and methods* section for details) [21].

	Photochemical aging time (h)			Brown coating from painting Natural aging
	0	120	240	
ν (cm ⁻¹) C–O stretch	1251	1249	1246	1245
$A_{1250}/A_{1141-1171}$	1.63	1.12	1.00	0.95
Resolution of peaks at 1141 and 1171 per centimetre	Yes	No	No	No
Shoulder at ~1245 per centimetre	Yes	Yes	No	No

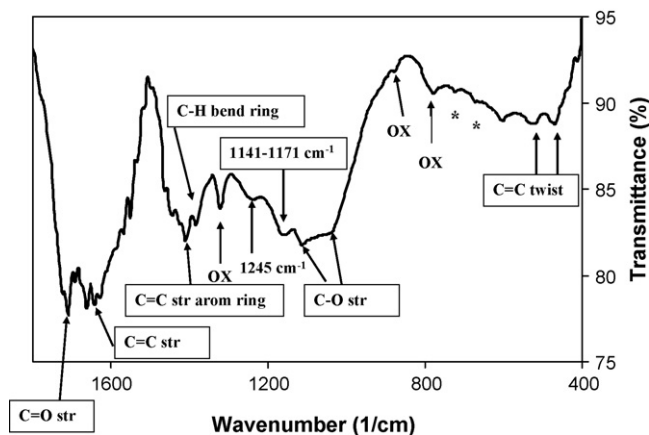


Fig. 4. FTIR spectrum in the 1800–400 cm⁻¹ range of the powdered brown surface coating present on the red painting layers of the “Coronation of the Virgin with Saints”. The assignment of the absorptions are based on [22]. The asterisks refer to peaks typical of naturally aged shellac but not assigned; OX means oxalates.

shrinkage induced by the oxidation of the varnish layer as a consequence of its aging was inhomogeneous and it was manifested in two superimposed layers. The first was characterised by the presence of brown, rough clots, while the second one by a dark texture underneath that was bound strongly to the paint layer. Accordingly, the first step in the conservation protocol devised by the conservators was to remove selectively both varnish coatings without damaging the red pigment layer underneath. Insights about the chemical nature of the brown coatings were derived from comparisons between FTIR spectra of the artificially aged (photochemically oxidized) standard shellac varnish and a micro-sample from the surface brown coating of the painting (Table 1). Preliminary investigation by FTIR had shown that the brown coating was not composed of varnishes usually employed in past conservation treatments (i.e. dammar, mastic, copal, or sandarac). Instead, the FTIR spectrum of the brown coating clot sample presented some, but not all, features matching those of shellac. In order to ascertain whether the brown coating was attributable to shellac, and to investigate the discrepancies between the FTIR spectrum of the brown coating and that of the standard shellac resin, FTIR spectra of the two photochemically-aged samples were recorded also and compared with the features of the Neri di Bicci sample. Table 1 summarises the results: the spectrum of the brown coating sample from the Neri di Bicci panel is extremely similar to those of the extremely aged shellac varnish.

Photo-oxidation from natural or artificial aging results in:

- a slight shift of the band associated with the C–O stretching;
- an inversion of the reciprocal absorbance of the peaks at 1250 cm⁻¹ and that in the range 1147–1171 cm⁻¹;
- a loss of resolution of the two peaks at 1147 and 1171 cm⁻¹;
- disappearance of the shoulder at ca. 1245 cm⁻¹.

Interestingly, inversion of the reciprocal absorbance of the band at 1250 and that in the range 1147–1171 cm⁻¹ has been recently reported for the shellac varnish coating the canvas painting, “*Virgin of Sorrows*”. [22] The spectrum of the sample of the powdered

brown coating from the red mantle of the Neri di Bicci panel is reported in Fig. 4. Apart from the peaks labelled with the assignment or asterisks (that match those of a naturally aged shellac varnish [22]), we observe three additional peaks typical of oxalates whose presence can be attributed to photo-oxidation. Table 2 reports all the peak wavenumbers with the corresponding – when known – vibrational modes assignment. From the Table 2, it is possible to deduce that the part of the spectrum not reported (in the range 4000–1800 cm⁻¹) did not show particular features apart the broad peak centered at 3429 cm⁻¹ and the two absorptions relative to the C–H stretching at 2929 and 2856 cm⁻¹ in perfect agreement with the spectrum of shellac. Despite the comparison of our spectra with those reported in the cited work [22] and with the ones made on artificially aged shellac [21] gave clear indication on the presence of aged shellac, nevertheless, the spectrum of our sample (Fig. 4) evidenced a fine structure in the 1600–1750 cm⁻¹ region not compatible with shellac (see also IRUG database at <http://www.irug.org>). In particular, the two strong and medium absorptions at 1653 and 1540 cm⁻¹ attributable to C=O amide I and II stretching mode (Table 2) associated with the presence of the peaks of oxalates infer that the brown coating could not be constituted only by shellac, but possibly by some other coatings with white egg based varnishes widely diffused in the conservation practice. Finally, because the dark texture of the undercoating (second) layer had the same spectral characteristics as the outer layer, we conclude that the two have one origin (i.e., oxidized shellac) and, therefore, the underlayer is not an older, possibly original glaze.

Some preliminary cleaning tests using Feller mixtures [20] were carried out on the dark coating on the red mantle (see black box of

Table 2

Band assignments for the FTIR spectrum.

Wavenumber (cm ⁻¹)	Intensity	Vibrational modes
3429	s (broad peak)	O–H str, N–H str
2929	s	C–H str
2856	m	C–H str methyl
1740	s (shoulder)	C=O str
1716	s	C=O str
1653 ^a	s	C=O amide I, C=C str aromatic rings
1540 ^a	m	C=O amide II
1457	m	C=C str aromatic rings, C–H bend
1385	w	C–H bend ring
1329	m	Oxalates
1245	w	C–O str
1171	w (broad not resolved)	C–O str, C–N str
1068	w (broad not resolved)	C–O str
781	w	Not assigned
726	w	Not assigned
943	w	Oxalates
875	w	Oxalates
517	w	C=C twist
463	w	C=C twist

s: strong; m: medium intensity; and w: weak.

^a The two absorptions at 1653 and 1540 cm⁻¹ cannot be attributed to aged shellac (see discussion in the text).

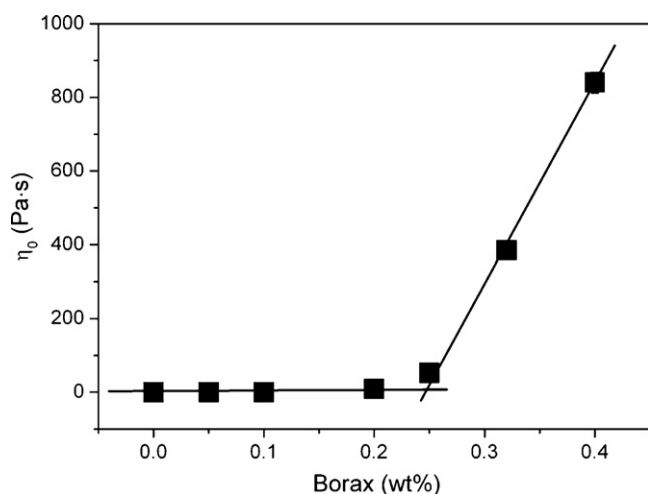


Fig. 5. Intrinsic viscosity η_0 of PVA (2 wt%)/borax H₂O systems as a function of borax concentration (wt%).

Fig. 2) of the painting surface. The results indicated that the best cleaning action was achieved by the mixture with a f_d value of 47 (i.e., corresponding to neat acetone). Although this solvent did not succeed in solubilising the dark coating, it did soften and swell the clots, making possible their removal by means of a soft mechanical action. Because the softening achieved by neat acetone was not optimal, additional mixtures were prepared by adding small amounts of other solvents in a rather empirical way. Thus, adding 10 wt% benzyl alcohol to neat acetone resulted in better softening of the clots. However, the texture beneath the clots (see right portion of Fig. 3A) was very difficult to remove: a previous attempt to remove this coating by means of cotton swabs impregnated with conventional organic solvents (acetone, benzyl alcohol, or mixtures of them) led to loss of stability of the red pigment layer due to the high sensitivity of vermilion-containing paints to aqueous and polar organic liquids. These results were quite unexpected since it is well known that acetone is not a good solvent for both aged and not aged shellac.

They and the FTIR characterisations of the shellac discussed above led us to examine the cleaning action of acetone incorporated within our aqueous PVA-borax systems. [23]. First, only acetone was added to the PVA/borax dispersion because systems with added acetone/benzyl alcohol mixtures or with pure benzyl alcohol were neither completely transparent nor stable over reasonable periods of time for cleaning purposes. Second, new PVA-based dispersions were made and characterized to be certain that they maintained their elasticity and easy removal from a painted surface (as had been demonstrated for aqueous PVA/borax systems with added 1-propanol [19]). Because the threshold concentration of PVA (C^*) is 1.54 wt% at ambient temperatures [13], 2 wt% was chosen to assure that the entanglements of PVA chains (that are requisite for formation of the 3D-networks that immobilize the liquid phase) were possible. High viscosity and 3D-networks reduce the rates of penetration of a liquid in a dispersion into the porous matrix of a painting. As indicated in Fig. 5, a borax content > 0.25 wt% is necessary to obtain highly viscous material at this PVA concentration: the intrinsic viscosity η_0 changed from 8.7 Pa·s to 860 Pa·s when the borax concentration was increased from 0.2 to 0.4 wt% (Fig. 5).

Some experiments were conducted on a gilded surface to determine whether perceptible amounts of residues remain on a surface after its treatment with a PVA/borax cleaning system (Fig. 1). The gilded surface was selected to achieve maximum sensitivity with the FTIR micro-reflectance mode. The FTIR spectra of the surface (Fig. 6), collected before (black line, upper spectrum, part B) and

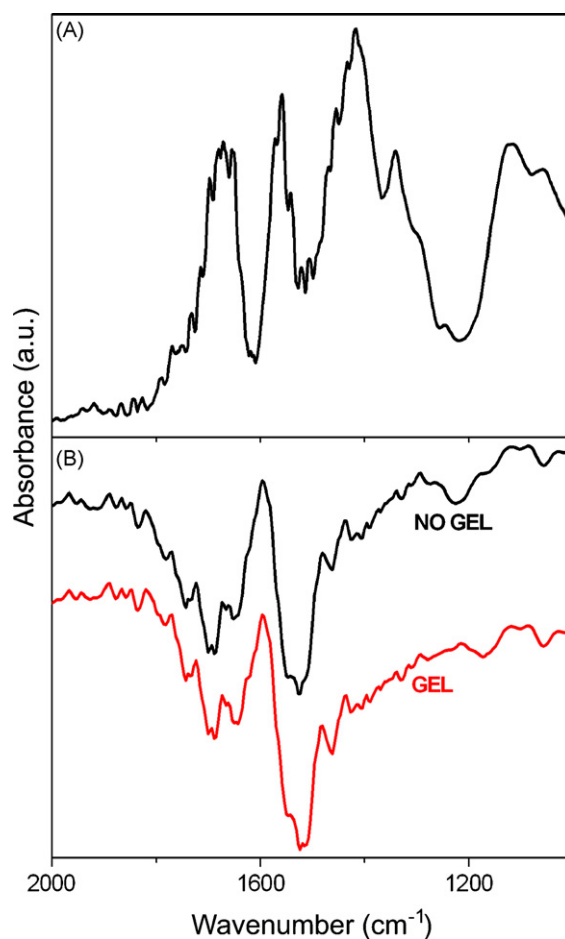


Fig. 6. (A) FTIR spectrum of the dried residue of a thin film of the PVA/borax aqueous dispersion. (B) Microreflectance FTIR spectra collected from the surface of a gilded wood support in a region where the PVA/borax aliquot was applied: before (black line, upper spectrum) and after the application (red line, lower spectrum). The contact time was 10 minutes.

after (red line, lower spectrum, part B) treatment with a PVA/borax dispersion for 10 minutes and removing it by peeling, are nearly identical in the fingerprint region. In particular, the region below 1400 cm⁻¹, where strong bands from PVA and borax are normally seen (Fig. 6A), was nearly without absorptions and lacked the characteristic pattern of either polymeric dispersion component; more than a very small trace of dispersion residue would have been detected. We note that it is not possible to conclude from these results that this cleaning agent is removed from gilding in the same way as from a painting surface; additional experimentation will be required to make that determination.

Based upon a recent theory concerning the solubilisation of hydrophobic substances by liquid hydrotropes in water [24], some water/cosolvent mixtures embedded into a high viscosity polymeric dispersion should be able to soften and/or swell many water-insoluble materials present in foreign coatings on easel painting surfaces. Thus, the approach taken in this work was to thicken a mixture of water containing some organic liquid that should be able to swell the oxidized varnish. The strength of the cleaning action would be modulated by varying the total amount of the organic cosolvent in the continuous phase of the dispersion. Acetone was chosen as the cosolvent because, as previously noted, it was able to soften the hard, highly degraded coating to be removed from the Neri di Bicci painting. Thus, PVA/borax systems containing from 5 to 15 wt% of acetone were prepared according to the procedure described in the *Materials and methods* section.

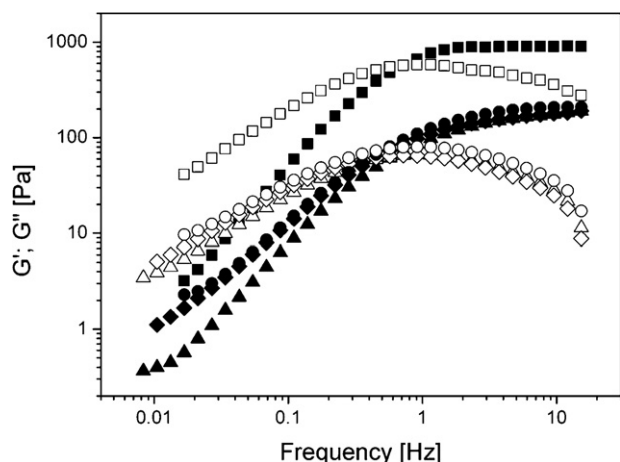


Fig. 7. Viscoelastic curves of PVA/borate dispersions at various acetone concentrations: elastic (storage) modulus G' (closed symbols) and loss modulus G'' (open symbols) at 0 (squares), 3 (triangles), 5 (diamonds) and 10 (circles) wt% of acetone.

Because the mechanical properties (especially the elastic modulus of the systems) are very important in determining the ease with which a cleaning system can remove a coating from the surface of a painting (Fig. 1), the viscoelastic natures of the PVA/borax dispersions with acetone were measured. In particular, the ease of removal of these systems from a surface after they have carried out their function is directly related to the density of the entanglements among the polymer chains of the 3D dispersion matrices: the higher is the entanglement density ρ [25], the higher is the intrinsic elasticity of the dispersion G_0 (measured as the G' asymptotic value [26]). Fig. 7 shows frequency sweep curves for aqueous PVA/borax systems at different acetone contents. A decrease of G_0 occurred for all of the acetone concentrations examined, and it was not dependent on the acetone concentration. As shown in Fig. 7, the three curves of the acetone systems are almost superimposable in the high frequency regime; the apparent relaxation time [27] of the dispersions, given by the crossover coordinates of the G' and G'' curves, was almost unchanged as well. Thus, the mechanical properties of the systems with acetone remained typical of viscoelastic polymeric solutions. This behaviour is probably related to the ability of acetone to act as a water-structure breaker [28]. Also, the crossover between the G' and the G'' values observed in Fig. 7 indicates that the mechanical behaviour of these systems is characteristic of high viscosity polymer solutions rather than true gels.

For purposes of using these dispersions as cleaning agents on works of art, the invariance of the rheological properties and, especially, of the elastic character as a function of acetone concentration, is very important – it allows easy removal of the cleaning agents by the so-called “peeling-off” technique [19]. However, because acetone decreased the elastic modulus of the aqueous dispersion, it was necessary to determine whether the ease of removal of the cleaning systems from a painting surface was also affected. Thus, acetone-containing dispersions were applied to and then removed from gilded surfaces similar to the one reported in Fig. 1. FTIR spectra again gave no evidence for residues on the areas treated with the polymeric dispersions after their removal.

Because acetone is quite volatile, its rate of evaporation from the aqueous dispersions may limit the utility of the aqueous PVA/borax systems in which it is a cosolvent, especially if the cleaning (contact) period is protracted. To determine the importance of this concern, the data in Fig. 8 were collected. They demonstrate that within the first 5 minutes, the maximum time that a cleaning system is expected to be in contact with the painting surface, the acetone weight loss from films of the aqueous dispersions is no more than 8%. On this basis, the cleaning ability of a dispersion, especially one

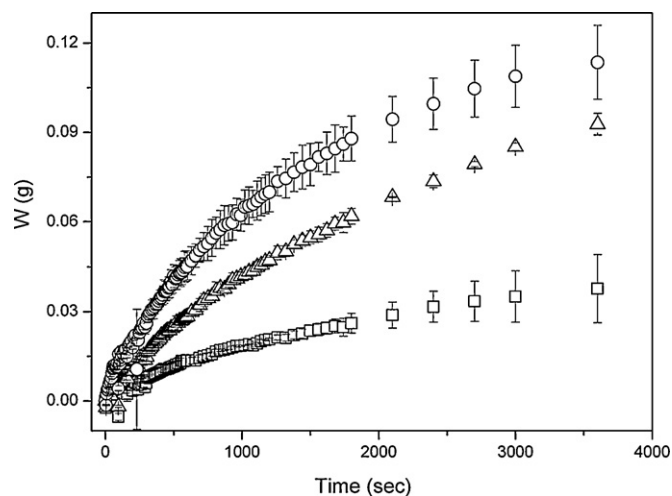


Fig. 8. Amount (W/g) of acetone evaporated from 2 g samples of PVA/borax system containing 5 (squares), 10 (triangles), and 15 wt% acetone (circles) as a function of time. Error bars are the standard deviations.

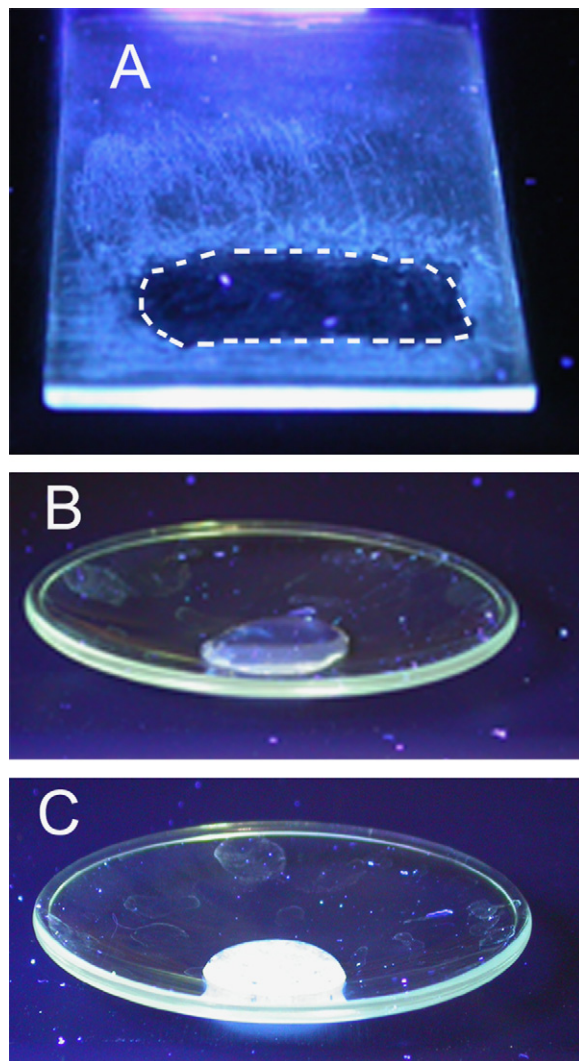


Fig. 9. UV-induced fluorescence image under a Wood lamp (emission maximum 364 nm) of A. A microscope glass covered by a thin layer of shellac resin after application and removal of a transparent dispersion of PVA/borax with 15 wt% acetone in a small region delimited by the dotted line. B. A dispersion of PVA/borax with 15 wt% acetone on a clean watch-glass. C. The same sample as in B after its removal from a glass surface covered by a thin layer of shellac resin.

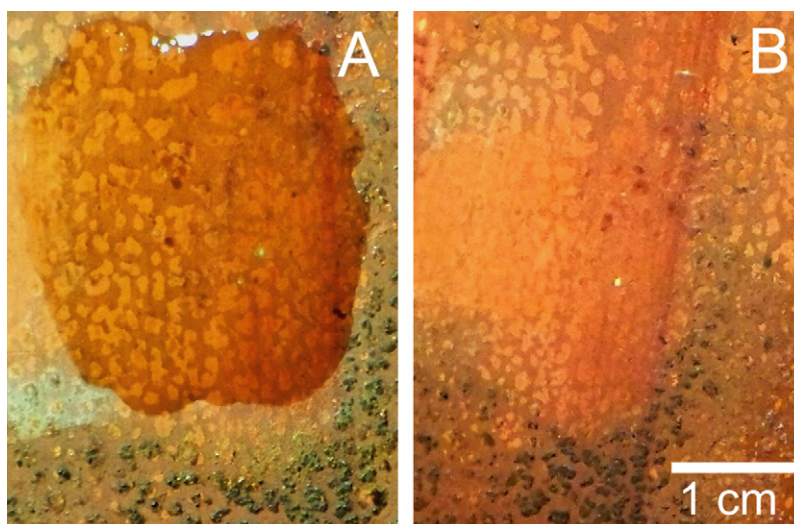


Fig. 10. Images of the surface area of the “Coronation of the Virgin with Saints” subjected to a cleaning test (see box in Fig. 2): A. Transparent dispersion of PVA-borax with 15 wt% acetone, applied on the painting surface where the clots had been already removed and only the dark undercoating layer that strongly adhered to the red pigment layer remained. B. The surface after the removal of the dispersion. The distance bar applies to both images.

containing 10 or 15 wt% of acetone, is not expected to decrease significantly during a 5-minute application.

Before applying the cleaning agent based on the PVA/borax system containing 15 wt% of acetone, we carried out several measurements on laboratory specimens coated with various types of not aged and aged shellac resins. The results were quite intriguing: in some cases, softening/swelling or solubilisation did not occur, while in others, it did and allowed complete removal. This, in part, helps to explain the aforementioned unexpected results with acetone as a good solvent for the aged shellac coating on the Neri di Bicci panel. As an example of good performance, Fig. 9 shows the effect of cleaning by the PVA/borax system containing 15 wt% of acetone as followed by fluorescence imaging. The typical fluorescence of shellac is shown in (A), a microscope slide completely covered by a thin layer of this varnish; application of the cleaning agent leads to removal of the varnish layer (as deduced from the region marked with dotted line [A]). Interestingly, the typical fluorescence of shellac “migrated” into the cleaning agent, as shown in (C) where the cleaning system is strongly fluorescent compared to the same system before application in (B).

Fig. 10 shows details of the region of the “Coronation of the Virgin with Saints” (Fig. 2) where the cleaning test was conducted. After a first application of a PVA/borax system containing 15 wt% of acetone for ca. 5 minutes (see *Materials and methods* section for details), the clots were softened (see Fig. 3A left side and 3B) and a weak mechanical action, carried out with a spatula, was sufficient to remove them completely. However, the lower inhomogeneous texture of dark residual resin (see Fig. 3A right side) was not removed

by an aliquot of the same dispersion in some regions of the painting. In these cases, complete cleaning was possible only after application of a second aliquot of the dispersion. Fig. 10A shows a region with the dark texture beneath the clots removed by the first application; the dark coating is visible because the polymeric dispersion is transparent, an attribute that allows the cleaning action to be followed visually by a conservator. The additional cleaning action by the second application is apparent in Fig. 10B – there is a very large reduction in the amount of dark brown coating only in the treated area.

Additional optical microscopy investigations, always in situ, were carried out with a USB microscope interfaced with a computer. Fig. 11B shows false colour micrograph of the same region after the first application. Note that the appearances of the surface with the clots, with the lower undercoating layer, and without any coatings (as collected from other regions of the painting) allow the features noted in Fig. 11B and C to be attributed to the lower undercoating layer and to the completely cleaned painting layer, respectively. No traces of the dark clots constituting the degraded organic surface materials (see Fig. 3B) were present in Fig. 11B; a real colour image of the texture of the surface after the removal of the clots is reported in Fig. 11A. Complete softening of the lower undercoating layer was achieved after an additional application of the dispersion (Fig. 11C). Importantly and unlike the results from cleaning procedures using traditional methods with conventional liquids (i.e., ungelled or unthickened solvents), softening of the coating here was accomplished without any apparent damage to the red pigment layer.

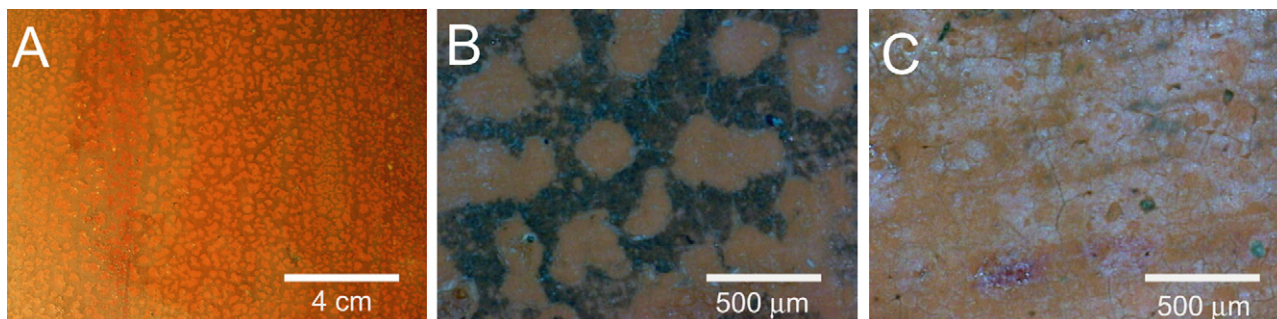


Fig. 11. True colour image of the texture of the residual resin after removal of the clots A and USB false colour micrographs before B and after C a second application of the cleaning dispersion.

These results indicate that the aqueous PVA/borax systems containing acetone allow both excellent control of the cleaning action and a gradual loss of difficult to remove materials from a painting surface. These PVA-based dispersions are an important improvement over traditional cleaning methods because they permit removal of a surface coating while minimising the risk of altering or damaging the colour layers underneath, and the cleaning action can be monitored visually or in situ with a microscope.

4. Conclusions

Aqueous PVA/borax polymeric dispersions containing acetone have been developed, characterized, and used as cleaning agents for an easel painting with an aged and oxidized coating. The mechanical properties of the dispersions were found to be dependent on the composition of the continuous phase. The optimal ones could be removed from a painting surface by gentle peeling using a spatula or a forceps. The efficacy of the cleaning process, removal of a surface organic coating from "*Coronation of the Virgin with Saints*", an egg tempera wood panel by Neri di Bicci, was ascertained both macroscopically and by means of optical microscopy.

The major innovation in the application of these systems for cultural heritage conservation is that the cleaning agent can be easily removed in one step from a surface simply by peeling. This methodology did not lead to measurable amounts of surface residues from the aqueous PVA/borax dispersions. Yet, these systems retain many of the best qualities of gels and other thickened liquids used in conservation and cleaning of objects of art: they are very viscous (so that lateral flow on the surface does not occur and only the area desired to be cleaned is exposed to the cleaning agent), they are transparent and uncoloured (so that the cleaning action can be monitored visually by a conservator), and they slow the rate of penetration of the solvent into the painting matrix. For these reasons, the PVA/borax systems, especially when organic liquids are added to the aqueous continuous phases, appear to be very promising cleaning agents for conservators. Additional studies with other cosolvents and analytical tests are ongoing to determine the range of applications of these high viscosity polymeric dispersions in cultural heritage.

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References

- [1] A. Phenix, The swelling of artists' paints in organic solvents. Part 1, a simple method for measuring the in-plane swelling of unsupported paint films, *J. Amer. Inst. Conserv.* 41 (2002) 43–60.
- [2] A. Phenix, The swelling of artists' paints in organic solvents. Part 2, comparative swelling powers of selected organic solvents and solvent mixtures, *J. Amer. Inst. Conserv.* 41 (2002) 61–90.
- [3] A. Phenix, K. Sutherland, The cleaning of paintings: effects of organic solvents on oil paint films, *Reviews in Conservation 2 IIC, London* (2001) 47–60.
- [4] R. Wolbers, *Cleaning painted surfaces: aqueous methods*, Archetype, London, UK, 2000.
- [5] S. Bertolucci, E. Bianchini, C. Biave, F. Caliarì, P. Cremonesi, S. Gravina, M. Zammataro, B. Zangani, Preparazione e utilizzo di soluzioni acquose addensate, reagenti per la pulitura di opere policrome, *Progetto Restauro* 8 (2001) 11–21.
- [6] D. Stulik, H. Khanjian, V. Dorge, A. de Tagle, J. Maish, B. Considine, D. Miller, N. Khandekar, Scientific investigation of surface cleaning processes: quantitative study of gel residue on porous and topographically complex surfaces, in: *ICOM Committee for Conservation, ICOM-CC: 13th Triennial Meeting, Rio de Janeiro, 22–27 September 2002*: James & James, London, 2002, pp. 245–251.
- [7] V. Dorge (Ed.), *Solvent gels for the cleaning of works of art: the residue question*, Getty Publications, Los Angeles, USA, 2004.
- [8] A. Burnstock, T. Kieslich, A study of the clearance of solvent gels used for varnish removal from paintings, in: *ICOM Committee for Conservation, 11th Triennial Meeting in Edinburgh*, James & James, London, 1996, pp. 253–262.
- [9] E. Carretti, L. Dei, P. Baglioni, R.G. Weiss, Synthesis and characterization of gels from polyallylamine and carbon dioxide as gellant, *J. Amer. Chem. Soc.* 125 (2003) 5121–5129.
- [10] E. Carretti, A. Macherelli, L. Dei, R.G. Weiss, Rheoreversible polymeric organogels: the art of science for art conservation, *Langmuir* 20 (2004) 8414–8418.
- [11] K. Juntanon, S. Niamlang, R. Rujiravanit, A. Sirivat, Electrically controlled release of sulfosalicylic acid from crosslinked poly(vinyl alcohol) hydrogel, *Int. J. Pharm.* 356 (2008) 1–11.
- [12] L. Wu, C. Brazel, Modifying the release of proxyphylline from PVA hydrogels using surface crosslinking, *Int. J. Pharm.* 349 (2008) 144–151.
- [13] C.Y. Chen, T.L. Yu, Dynamic light scattering of poly(vinyl alcohol)-borax aqueous solution near overlap concentration, *Polymer* 38 (1997) 2019–2025.
- [14] A. Koike, N. Nemoto, T. Inoue, K. Osaki, Dynamic light scattering and dynamic viscoelasticity of poly(vinyl alcohol) in aqueous borax solutions. 1. Concentration effect, *Macromolecules* 28 (1995) 2339–2344.
- [15] W. Wu, M. Shibayama, S. Roy, H. Kurokawa, L.D. Coyne, S. Nomura, R.S. Stein, Physical gels of aqueous poly(vinyl alcohol) solutions: a small-angle neutron scattering study, *Macromolecules* 23 (1990) 2245–2251.
- [16] G. Keita, A. Ricard, R. Audebert, E. Pezron, L. Leibler, The poly(vinyl alcohol)-borate system: influence of polyelectrolyte effects on phase diagrams, *Polymer* 36 (1995) 49–54.
- [17] H.L. Lin, Y.F. Liu, T.L. Yu, W.H. Liu, S.P. Rwei, Light scattering and viscoelasticity study of poly(vinyl alcohol)-borax aqueous solutions and gels, *Polymer* 46 (2005) 5541–5549.
- [18] H.A. Barnes, J.F. Hutton, K. Walters, *An introduction to rheology*, Elsevier, Amsterdam, ND, 1989.
- [19] E. Carretti, S. Grassi, M. Cossalter, I. Natali, G. Caminati, R.G. Weiss, P. Baglioni, L. Dei, Poly(vinyl alcohol)-borate hydro/cosolvent gels. Viscoelastic properties, solubilizing power and application in art conservation, *Langmuir* 25 (2009) 8656–8662.
- [20] P. Cremonesi, Un approccio più scientifico alla pulitura dei dipinti: il test di solubilità di Feller, *Progetto Restauro* 8 (1998) 38–42.
- [21] S. Bracci, A. Fietta, A. Salvini, unpublished results in "Spectroscopic characterisation of varnishes for musical instruments: artificial aging", First level degree thesis in technology for cultural heritage conservation, Library of Sciences, University of Florence, Italy, 2008.
- [22] M. Ortega-Avilés, P. Vandenabeele, D. Tenorio, G. Murillo, M. Jiménez-Reyes, N. Gutiérrez, *Anal. Chim. Acta* 550 (2005) 164–172.
- [23] M. Shibayama, T. Takeuchi, S. Nomura, Swelling/shrinking and dynamic light scattering studies on chemically cross-linked poly(vinyl alcohol) gels in the presence of borate ions, *Macromolecules* 27 (1994) 5350–5358.
- [24] P. Bauduin, A. Renoncourt, A. Kopf, D. Touraud, W. Kunz, Unified concept of solubilization in water by hydrotropes and cosolvents, *Langmuir* 21 (2005) 6769–6775.
- [25] B.A. Schubert, E.W. Kaler, N.J. Wagner, The microstructure and rheology of mixed cationic/anionic wormlike micelles, *Langmuir* 19 (2003) 4079–4089.
- [26] J.W. Goodwin, R.W. Hughes, *Rheology for chemists, an introduction*, Royal Society of Chemistry, London, UK, 2000.
- [27] L. Piculell, M. Egermayer, J. Sjostrom, Rheology of mixed solutions of an associating polymer with a surfactant. Why are different surfactants different? *Langmuir* 19 (2003) 3643–3649.
- [28] A. Idrissi, S. Longelin, F. Sokolic, Study of aqueous acetone solution at various concentrations: low-frequency Raman and molecular dynamics simulations, *J. Phys. Chem. B* 105 (2001) 6004–6009.

- [1] A. Phenix, The swelling of artists' paints in organic solvents. Part 1, a simple method for measuring the in-plane swelling of unsupported paint films, *J. Amer. Inst. Conserv.* 41 (2002) 43–60.