

THE MUNICH DÜRER ATTACK: THE REMOVAL OF SULPHURIC ACID AND ACID COMPOUNDS BY USE OF A CONDITIONED ION-EXCHANGE RESIN

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ABSTRACT

In April 1988 five panels by A. Dürer at the Alte Pinakothek, Munich were damaged by an act of vandalism. Large areas of the paint layers, the ground and even the wooden support were severely affected by concentrated sulphuric acid. This contribution discusses first measures taken after the attack. Possible chemical reactions between the painting materials and the acid are identified. The analytical results allow re-evaluation of the conventional adsorption and neutralization procedures so far applied. An alternative treatment with a specially conditioned ion-exchange resin is proposed. Its application turned out to be very effective in softening the crusts, adsorbing acid reaction products as well as neutralizing the remaining parts. The preparation and the handling of the ion-exchange resin are discussed in detail.

1 INTRODUCTION

In spring 1988 an act of vandalism with concentrated sulphuric acid severely damaged five panel paintings by A. Dürer (1471-1528) (see Heimberg, Fig. 1, colour plates). This contribution will focus on a few aspects of the conservation measures taken after this attack. A more general discussion of the basic reaction mechanisms of sulphuric acid on paintings, of our feelings and considerations shortly after the attack and of the final decisions is given elsewhere [1, 2]. A broader publication of the extensive scientific work done to understand the action of the ion-exchange resin used here will be presented after the conservation and restoration campaign has been completed.

The problem may be considered from several points of view: what was the paint layer structure before the attack? what are the pigments, the painting media? what are the peculiarities of concentrated sulphuric acid? how does this acid react with inorganic as well as organic materials on the paintings? The answers will allow the setting up of appropriate guidelines and lead to simple conclusions concerning the deacidifying measures to be taken — or, more importantly, not taken — before starting any restoration work.

2 EXPERIMENTAL SECTION

2.1 Analytical procedures

Most of the experimental procedures used here are standard, such as optical microscopy, microchemistry, optical emission spectroscopy (OES), X-ray powder diffraction (XRD, Straumanis and vertical goniometer), X-ray fluorescence (XRF), gas chromatography (GC) and mass spectrometry (MS) [3-5]. The pH measurements were done with Merck non-bleeding pH-indicator strips (pH 0-14 (Art. 9535), pH 0-2.5 (Art. 9540), pH 2.5-4.5 (Art. 9541) and pH 4.0-7.0 (Art. 9542)) as well as with a conventional pH-meter (Metrohm). Ion chromatography (IC) was used to detect anionic species. Scanning electron microscopy in combination with EDX was carried out at the Institut für Holzforschung (Prof. Dr D. Fengel, LMU München).

2.2 Conditioning of the ion-exchange resin

2.2.1 Preliminary remarks

The ion-exchange resin Lewasorb A50 used here comes ready charged with hydroxyl ions. During storage it undergoes slight decomposition (Hofmann elimination), setting free small amounts of the strong bases alkylammonium hydroxide and amine(s). In the beginning it is therefore a strongly alkaline substance, small particles of which may cause skin and eye irritation, and which develops a pungent fishy amine odour. Before use, the alkaline impurities have to be removed by washing with

water. All handling should be done under a hood or using a respirator, wearing safety goggles, gloves and suitable clothing.

2.2.2 Preparation

Pour 100g of the resin into 400ml of distilled or deionized water, stir mechanically for 30 minutes, allow to settle for 10 minutes and decant. To remove the washing liquid, spread out the wet cake on a thick pad of tissue covered with a leaf of filter-paper. Repeat the whole procedure three times. The pH value of the washing water will decrease from between 10 and 11 to 9 and finally to a value between 6 and 7. Subsequently the wet cake is ground as finely as possible in an agate mortar. To charge the resin with carbonate ions it is slowly poured into a stirred solution of 50g sodium carbonate (Na_2CO_3) in 200ml of distilled or deionized water. Stir, decant and adsorb the residual liquid with a pad of tissue as described above. This procedure has to be repeated three times. Finally, the carbonate-charged resin is washed again as described until a pH between 6 and 7 is measured. This takes at least seven washing procedures.

3 RESULTS AND DISCUSSION

3.1 Dürer's paintings before the attack

Although no detailed description of Dürer's painting materials and techniques is intended, a summary of our findings should help in understanding the situation of the damaged surfaces after the attack.

In all cases investigated so far, the wooden support is primed with a white chalk ground (Fig. 1, see colour plates). The ground has been identified by XRD as calcium carbonate. Infrared reflectography reveals a delicate preparatory drawing effected in carbon black. The usually very thin paint layers contain common pigments as listed in the Table. The paint media identified are a proteinaceous medium, so far found in blue areas only, and linseed oil (see section 3.4.3).

3.2 What is concentrated sulphuric acid?

Concentrated sulphuric acid has several peculiarities which are of interest here. It is a clear, colourless and odourless, oily liquid of high density (D 1.84). Sulphuric acid is very hygroscopic and is therefore used as a drying medium. Its volatility is very low (boiling point 338°C). Sulphuric acid is known to be a strong acid; when diluted with water the acidity is even greater. Moreover, the process of dilution causes a very high reaction heat (95.32kJ mol^{-1}). Under certain conditions, concentrated sulphuric acid is a very strong oxidizing agent.

3.3 Visual description of the damaged areas

The impression a few minutes after the attack was that the surface — where hit by the acid — was covered with an oily, dark and malodorous liquid. The areas damaged showed sharp boundaries, and the liquid itself had high surface tension which fortunately prevented any further displacement into undamaged areas. After an initial intense foaming, only single gas bubbles were observed. Immediate pH measurements showed a pH of about 1; *in situ* tests with dilute barium chloride solution confirmed the nature of the acid as sulphuric acid. Judging by the oily, clear appearance of the rest of the acid, left in one of the two small containers handed over by the attacker, concentrated sulphuric acid seemed indicated, and this was later confirmed.

The opacity of the reactive liquid prevented any reliable optical

evaluation of the state of preservation of the affected areas.

As described elsewhere [1], we decided to keep the paintings in a horizontal position and under low relative humidity. After a few days the damaged areas seemed to have dried out (see Heimberg, Fig. 2). This allowed us to open the crusts at a few points to gauge the effect of the acid in relation to the depth of infiltration. The following sequence of layers could be observed: (a) the wooden panel, (b) a white layer, (c) an ebony-coloured 'wet' layer, (d) a caramel-like layer, in colour as well as consistency — all of them no thicker than the former ground layer — and finally (e) a porous, dry, thick crust covered with tiny whitish transparent crystals. All exposed wood hit by the acid was soft, black, sticky and still wet, even after several days.



Fig. 2 The ion-exchange resin before application (magnification $32\times$).

3.4 Scientific description of the damaged areas

From the very first minutes after the attack we were convinced that any conservation decision should be based on as much information as possible. In our case, unlike former attacks (Rubens [6], Rembrandt [7, 8]) where thick varnish layers protected the paint layers, the damage affected all layers of the paintings — the wooden panel, the ground and the pigments as well as the media.

3.4.1 The wooden panel

Investigation of particles of the wooden support (see Heimberg, Fig. 3) by SEM and EDX showed a very high concentration of sulphur in the areas where end-grained wood had been penetrated by the acid. A clearly visible discoloration of the wood is related to the extent of penetration along the wood channels, where the lignin structure has been completely destroyed and transformed into a black mass. Fortunately, the carbohydrates and other re-

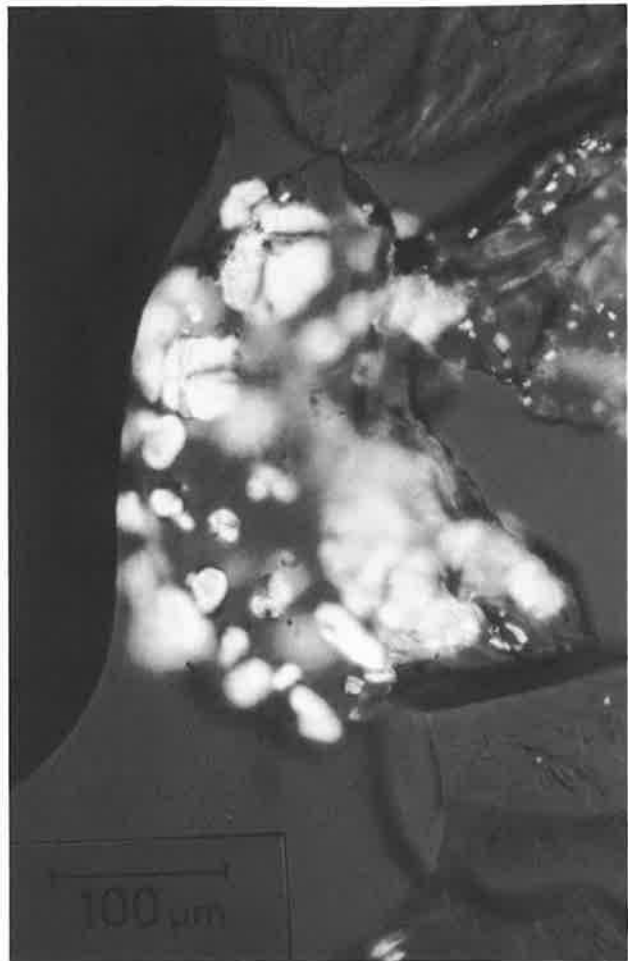


Fig. 3 Some particles of the ion-exchange resin after application. The tiny, as yet unidentified, crystals can be clearly seen on the surface (magnification $63\times$)

action products formed from the cellulose rendered the reaction medium less fluid; it became sticky and finally closed the wood channels. This might explain why the acid did not penetrate more than a few millimetres into the panels parallel to the wood channels and even less where the acid had to penetrate at a right-angle to the wood channels through the paint layers and the ground.

3.4.2 The ground, pigments and fillers

As was to be expected, the main reaction took place in the calcium carbonate ground. The acid was able to penetrate the paint layers in several ways: from the surface through the layers towards the ground and through larger cracks in the panel via craquelure in the ground and, finally, into the paint layers (Fig. 1, see colour plates). As can be seen from the Table, many of the pigments and fillers are carbonates. These carbonates, if not protected by proteinaceous media, have been attacked by the acid, resulting in the formation of different types of sulphates and in neutralization of some of the acid. The reaction products have been extensively investigated by XRD.

Most samples taken from different coloured areas of all five paintings showed a simple and homogeneous pattern of sulphates: lead sulphate $PbSO_4$, copper sulphate $CuSO_4\cdot 5H_2O$, gypsum $CaSO_4\cdot 2H_2O$, calcium sulphate hemi-hydrate $2CaSO_4\cdot H_2O$ and anhydrite $CaSO_4$. A semiquantitative interpretation of the diffractograms reflected a gradient distribution of these sulphates from the surface of the painting down to the wooden panel: high amounts of $PbSO_4$ and $CuSO_4\cdot 5H_2O$ in the upper paint layers, calcium sulphates towards the ground. To some extent the forma-

Table 1

	Chalk	Lead white	Azurite	Smalt	Verdigris	Lead-tin yellow	Vermilion	Red lake	Brown ochre	Carbon black
A. Dürer, 'Heiliger Georg', left wing of the Paumgartner Altar (Bayerische Staatsgemäldesammlungen Inv. No. 701)										
White ground	■ ^(a)									
Blue under grey, armour		●	●				(●)			(●)
Green, armour					●	●				
Green, dragon's tongue					●					
Yellow-green, dragon		●	●							●
Yellow, headgear		●	●			■ ^(c)	●	●		●
Red, dress		●	(●)				●			(●)
White, flagstaff	■ ^(b)									
Flesh tone, face		●	●				●	●		●
Black, dress		(●)	●				(●)		(●)	●
A. Dürer, 'Geburt Christi', centre panel of the Paumgartner Altar (Bayerische Staatsgemäldesammlungen Inv. No. 706)										
White ground	■ ^(a)									
Blue, sky and dress		●	■							
Green, tree		●			●	■ ^(c)				
Yellow, sun		●				■ ^(c)				
Red, dresses		●	(●)				●	●		(●)
White, cloth		■ ^(c)								
Flesh tone, leg		●	●				●			●
Brown, architecture		●				(●)	●	●	●	●
A. Dürer, 'Beweinung Christi' (Bayerische Staatsgemäldesammlungen Inv. No. 704)										
White ground	■ ^(a)									
Blue, dress		●	●	● ^(d)						(●)
Green, dress					(●) ^(d)	●				
Blue-green, dress		●	●	● ^(d)		●				
Yellow, cloth		●				■ ^(c)				
Red, kerchief		●				●	●	●		●
White, winding-sheet		■ ^(c)								
Flesh tone, hand		●	●			●	●			●
Brown, plants		●	●			●			●	(●)
A. Dürer, 'Maria als Schmerzensmutter' (Bayerische Staatsgemäldesammlungen Inv. No. 709)										
White ground	■ ^(a)									
Blue, dress		●	●							
Green, dress		●	●			●				
Blue-green, underpaint		●	●							(●)
Yellow, hair		●				■ ^(c)	(●)			
White, kerchief		■ ^(b)								
Flesh tone, arm		●	●			●	●			
Brown, hair		●	●			●	●		●	●
Black										●

Key:

● identified by OES, microscopy and microchemistry; ■ identified also by XRD; (●) minor amount; (a) identified by XRD; (b) identified by XRD as lead carbonate only; (c) identified by XRD as mixture of normal lead carbonate and basic lead carbonate; (d) colourless smalt; (e) identified by XRD as lead-tin yellow I.

tion of CO₂ resulted in a migration of calcium from the ground towards the upper layers. The presence of lead is restricted to the upper paint layers. All the reactions seem to have happened during the first minutes after the attack, because hardly any CO₂ formation could be observed when we reached the paintings.

The layers (a) to (d) are in some way softened. This effect can be explained by the formation of CO₂ gas bubbles making the layers porous, as well as by an increase in volume through addition of molecularly-bound water to the sulphates formed.

The decomposition of most of the components of the paint layer will yield considerable amounts of H₂O (besides the CO₂ mentioned). This reaction water enhanced the acidity as well as the mobility of the sulphuric acid. The acid then reacted while slowly penetrating into the paint layers or the ground according to the direction given by the force of gravity. Theoretically, this process continues until no acid is left and all sulphate is bound, for example in the very stable PbSO₄. If there is no more reaction water, the reaction will slow down and the formation of calcium sulphates with higher proportions of molecularly bound water will be rendered more difficult. This might explain the observation of calcium sulphates with a lower water content.

After all reactions were finished, pH-values of about 7 were to be expected. Unfortunately, pH-values between 1 and 3 indicate that something very different must have happened. There are actually several explanations for this observation. First, there is still free sulphuric acid remaining because the viscosity of the reaction medium increased and all the transport mechanisms described (evaporation of CO₂, penetration of H₂SO₄ or H₂O) slowed down, resulting in an encapsulation of the reaction. Unfortunately, several attempts to determine free encapsulated sulphuric acid by IC yielded a percentage of far less than 5% of the reaction mass. Because of the sample preparation procedure chosen, the amount detected might even originate from dissolved sulphate. Therefore the presence of free sulphuric acid cannot be definitely proved. On the other hand, a reaction of the acid with the paint medium to give acid reaction products is very probable.

3.4.3 The paint medium

In our opinion, previous work on acid attacks did not give sufficient attention to the role of the paint medium. Our attempts to understand the reaction of sulphuric acid with the medium greatly influenced the conservation treatment presented here.

It should first be mentioned that the analysis of organic reaction products resulting from reactions between acid and paint medium poses great analytical difficulties which are still unsolved.

From a theoretical point of view, fatty oils react with sulphuric acid to form sulphated and perhaps also sulphonated oils. As we know, linseed oil was used by Dürer, so it might be worth looking for an appropriate model reaction. One of the best-known examples in this respect is the synthesis of Turkey red oil [9, 10]. In contrast to this controlled reaction, during the attack all the sulphations took place under uncontrolled reaction conditions. Therefore a lot of additional side-reactions, such as heavy oxidations, hydrolyses and dehydrations, must be expected. When considering conservation treatment, it may be of interest that most of these reaction products would be expected to be highly soluble in water, ethanol, acetone and most other polar solvents.

However, as mentioned, the verification of these theories turned out to be an analytical problem. One of the main difficulties was the analysis of the sulphated oils. This was attempted by GC/MS as well as by IC. Most samples analyzed from damaged areas indicate the use of linseed oil. The presence of oils can be readily concluded from the nature of the reaction products identified. In a few areas the presence of a proteinaceous medium is deduced indirectly from the low amounts of oil fragments in the samples. Resulting from saponification and strong oxidation processes, the triglycerides to be expected in oil or even proteinaceous medium have been transformed into carboxylic and dicarboxylic acids of low and very low molecular weight. As observed during a standard separation procedure for sulphated products [11], the fraction of sulphated compounds is great if a sample from an area with oil medium is analyzed. If proteins were present, low amounts of oils but no sulphonated products could be detected in that fraction. Finally it should be mentioned that

the sulphated fraction showed strongly acid behaviour when in contact with water.

It is obvious on the surface of the paintings, and can be closely related to the amount of oils detected, that the most heavily damaged areas are those with a high amount of oils. In areas of low oil content (i.e. where a proteinaceous medium seems to be present) even carbonates such as azurite are still partly preserved.

As predicted from the presence of sulphated compounds and in accordance with the finding of low molecular weight carboxylic acids, the crusts turned out to be highly soluble in most of the solvents used in conservation. Because of their migratory characteristics, any solvents used would transport dissolved compounds into unaffected parts of the paint layers, the ground or even the wooden panel. Moreover, sulphated fatty acids act as emulsifiers, which would overcome the protective characteristics of unaffected oily media and finally damage pigments enclosed in the medium. It should be mentioned that sulphated fatty acids were used as early surface active agents [12], for example the Turkey red oil mentioned above. Most importantly, sulphonated fatty acids with two functional anionic groups, namely carboxyl as well as sulphate, show the strongly acid behaviour mentioned. Additionally, in contact with water or even dampness, a slow hydrolysis will yield free sulphuric acid [13]. Finally, the presence of sulphuric acid esters (monoalkyl sulphuric acid) and (aromatic) sulphonic acids is expected, all of which are strong acids. These considerations might explain pH values of about 2 measured in the damaged areas of the painting after mechanical removal of the crusts.

3.5 Conservation treatment guidelines

Our observations, analytical results and discussions suggested that the reaction products, with their strong acidity, emulsifying activity and low stability towards water, were harmful. It seemed advisable to remove them prior to any further conservation treatment. However, there are a few guidelines to be taken into consideration. The removal, adsorption or neutralization of the acid compounds should finally allow the application of conventional restoration techniques. Any procedure should leave undamaged areas around and within the damaged areas and layers strictly unaffected.

3.6 Conventional treatments

Various treatments and combinations of treatments are described in the literature or recommended in institutional emergency guidelines: dry mechanical removal [7]; dry chemical adsorption [6, 14] in combination with dry or wet neutralization [15]; cleaning with solvents or pouring water on the painting [8, 16]; encapsulation by inert media and, finally, wet chemical neutralization [15, 16]. Each of these measures was developed in relation to specific paintings. This paper is intended to reflect our own experiences rather than to criticize other cases.

As our extensive experiments showed, dry mechanical removal of the crusts could easily be done and is strongly recommended. After successful completion of the mechanical removal the outer appearance of the surface might give the impression that a conventional continuation of the work is now possible. But the remaining layers (a and b), although appearing intact and softened in structure, are still acid: pH values of 3 or, in most cases, less prove that only the morphology of the paint layer is preserved: the situation from a chemical point of view is completely different.

Dry adsorption in combination with neutralization measures is widely recommended. There are only two cases where no neutralization has been conducted [6, 7, 14, 17]. Most of the procedures reported turned out to have several disadvantages. First, if one puts the dry adsorbing powders (gypsum [6], kaolin,

aluminium oxide or diatomaceous earth [15]) into the sticky damaged areas, the liquid may be absorbed but the resulting non-transparent mass cannot be easily removed in its wet state. Once dried, the mass becomes hard and crusty. As reported [6, 7], it then has to be removed mechanically with scalpels. Secondly, it is proposed to apply neutralization agents dry (with barium carbonate [15]) or wet (barium carbonate as a wet paste or, in special cases, solutions of sodium hydrogen carbonate [15]) after the dry adsorption on the dried crusts. But as our own and other [6, 14] experiments showed, any contact of slow-absorbing or neutralizing materials as paste or in solution with the dry surface will result in an uncontrollable 'one-way' displacement or soaking of the (wetting) agent into still undamaged areas. This might not cause any problem when the damage is restricted to the varnish, but it is a serious limiting factor if delicate paint layers are affected.

Wet cleaning methods using non-aqueous solvents will change dry crusts into dissolved compounds. Because of the high solubility of the hydrophilic and lipophilic polar reaction products and the softened morphology of the damaged areas or layers, these compounds will then penetrate into damaged or even undamaged areas. A subsequent reaction of acid compounds must be expected. In the case of the addition of water in excess (as done on a Delvaux [16] and on a Rembrandt [8]), the water might damage intact areas, increase the acidity of the sulphuric acid, and displace the diluted reaction products into undamaged areas. If the decision is taken to remove the crusts mechanically — as we subsequently did — any further transport of harmful compounds into undamaged areas might be restricted by their encapsulation with inert materials such as beeswax. This seems an obvious measure to isolate harmful compounds; however, the lipophilic nature of the sulphated acids will allow migration phenomena inside the wax. Therefore the 'encapsulation' might turn out to be the opposite.

We therefore came to the conclusion that after mechanical removal of the dried crusts, wet neutralization of the acid compounds, where possible, was essential. In most former treatments wet neutralization was applied or recommended by adding solutions of NaHCO_3 [15, 16]. When added in excess, complete neutralization is expected. The reaction products must later be removed with solvents (water [15]), removed as dry crusts (which turned out to be impossible [6]), or left alone. There are several disadvantages: additional chemicals are introduced to the painting and locally uncontrollable (neutralization) reactions will then take place. Furthermore, the solution applied is weakly basic in nature and, from our experience, saponification of the drying oils can therefore be expected.

We came to the conclusion that none of these treatments should be applied, because of their obvious disadvantages. We did not want to add more chemicals, we did not want to initiate uncontrollable neutralization reactions, and we did not want the harmful products slowly to soak into the unaffected areas. A new treatment had to be developed.

One exception must be mentioned. We decided to use conventional wet neutralization treatments (saturated solutions of NaHCO_3 and later KHCO_3 in distilled water) to conserve the damaged wooden panel, which seemed to be slowly degrading. By monitoring sodium or potassium by SEM we were able to avoid the applied agent penetrating further than the acid.

3.7 The alternative treatment: ion-exchange resin

Ion-exchange resins consist of a water-insoluble polymeric resin matrix, mostly modified polystyrene, which can carry various types and amounts of chemically bound and electrically charged functional groups. Electrical charge and chemical type of the functional group will determine the kind of ions being retained

— cations or anions — and the bonding strength, while the amount of these 'anchor' groups will determine the ion-exchange capacity. In the present case the ion-exchange resin carries positively charged groups of the kind that will strongly bind anions, the negatively charged ions of various acids. Its binding capacity is also rather high.

The anions fixed to the 'anchor' groups may be exchanged with other dissolved anions in the vicinity of the resin surface. In the case of sulphuric acid, the sulphate anion is exchanged with a carbonate, which then forms carbonic acid (H_2CO_3) in aqueous solution. This substance decomposes at once, forming CO_2 and water, leaving a neutral pH value.

3.7.1 *The conservation aspect*

Although ion-exchange resins have rarely been used in the field of conservation, there are examples on stone [18], on metals [19-22] and on paper [23].

Ten years ago the Doerner-Institut was involved in the Kassel Rembrandt attack [7, 17]. After other treatments, a weak basic anion-exchange resin was applied to neutralize acid ionic compounds. The ion-exchange resin was pre-mixed in little water and was applied several times [7, 17]. However, during their neutralization experiments the authors came to the conclusion that any neutralization — especially wet chemical treatments including the ion-exchange resin — is unnecessary, for three main reasons. A complete neutralization seemed impossible, the water might damage undamaged paint layers and, finally, transport phenomena might take place. The decision not to neutralize is specific to the present case.

During all our discussions on adsorption and neutralization treatments the application of ion-exchange resins was taken into consideration. Lack of experience within our institution, however, prevented an immediate application test during the first days after the attack. At this point, one of the authors (HK) urged the use of ion-exchange resins and recommended Lewasorb A50, for the following reasons. The resin, which is mainly used in mixture with the appropriate cation exchanger to remove soluble corrosion products and other harmful contaminations from purified water, comes charged with hydroxyl ions ready for use. We first tried to use it in this form without any additional treatment. The light brown, powdery material, provided by Bayer AG, is very fine-grained compared to other similar products. This is important, as the velocity of the ion-exchange process is controlled by diffusion, which works fast only for very small distances.

Our first tests with the resin in its original condition, conducted on a few small spots, proved completely unsuccessful. Besides causing skin irritation, the pH of impaired areas changed from strongly acidic to strongly basic values around 10, high enough to cause irreversible damage to remaining or surrounding intact paint medium.

We therefore decided to load the ion-exchange resin with carbonate ions as described above. Additionally, the application procedure was improved in cooperation with the conservators involved. During this optimization process it turned out to be necessary to grind the ion-exchange resin, to wash it carefully to avoid any excess chemicals and — very important — to pre-mix it in as little water as possible. In future emergencies it should be noted that the loading of the ion-exchange resin with carbonate stabilizes it so that it can be kept in a dry state for a longer period.

What is our actual experience with this alternative de-acidifying treatment? From a scientific point of view, the conditioned ion-exchange resin softened sticky crusts, quickly deacidified damaged areas and was easy to apply. The high surface tension of the added water restricted the application to the intended areas. The velocity of exchange between the ion-exchange resin and the acid areas could be checked by observing the CO_2 development

as well as the change in colour from yellow-brown to blue-green in the areas where copper ions were present (see Heimberg, Fig. 4, colour plates). This happened during the first minute and confirmed the immediate interaction between the loaded ion-exchange resin with strong polar groups and the water-soluble polar compounds of the area treated. In general, our observations indicate a 'one-way' interaction: the adsorption between the immobile positively charged resin and the mobile anionic species seems to be very strong, preventing any uncontrolled displacement of harmful compounds into the paint layers or the ground. The carbonates set free during this process are transformed into CO_2 (which can be observed on the surface of the resin grains) or they are bound as carbonates. After a while this one-way transfer may be aided by absorbing the water with a tissue as well as by the natural evaporation of the water. Moreover, this exchange seemed to be complete in a very few minutes. In some cases it was decided to leave the ion-exchange resin on the surface until dry, whereas in delicate areas the wet paste was removed mechanically after a few minutes.

After a single application, pH values of 6 to 7 were measured on the treated surface. This indicates that one application is sufficient. Undamaged areas near the area of application seemed completely unaffected. The treated areas themselves are softer but parts of them are still morphologically reminiscent of the surface before the acid attack.

However, some limitations should be mentioned. First, in some cases the water involved interacted with remaining paint medium or morphologically extant structures, resulting in blanching phenomena (see the paper by Heimberg in this volume). Experiments in progress are attempting to substitute other polar solvents. Secondly, the conservators involved held the treatment with the ion-exchange resin responsible for the poorer appearance of the area after treatment. They found it hard to accept that the surface was hit by concentrated sulphuric acid and changed into something which looked similar but chemically was completely different. The morphological similarity should not be underestimated: it could be of considerable help during the subsequent restoration procedures. We finally decided to leave some areas untreated, because their appearance is so similar to the original.

The description of the actual treatment of the panels is given in the paper by Heimberg in this volume.

3.7.2 *The scientific aspect*

Besides developing new conservation procedures, the conservation scientist should understand why any treatment does what it does. Therefore we made exhaustive attempts to identify the nature of the compounds adsorbed by the ion-exchange resin. However, the difficulties encountered while analyzing the ion-exchange resin were even worse than during the paint media analyses. Nevertheless, some interesting observations should be reported:

- 1 Figures 2 and 3 show the conditioned ion-exchange resin in higher magnification before and after application. The sharp splintery shape of the particles explains our empirical experience that removal of the dried ion-exchange resin by vacuum cleaner is safer than removal by brush. Additionally, its initial transparency and lack of colour changes to a somewhat brownish coloration after application. More interesting is the fact that some particles are covered with tiny crystals (Fig. 3). These cannot yet be identified by XRD.
- 2 XRF showed very high values for sulphur for the ion-exchange resin after application. Obviously it is absorbing sulphur-containing compounds.
- 3 Ion chromatography (IC) has been used to separate and

identify all the anionic compounds either *in situ* or those which are finally absorbed by the ion-exchange resin. There are several interesting observations which might help to explain why the attempt with IC was only partly successful:

- i We spent a considerable time in the development of a satisfactory preparation and separation procedure to isolate sulphated compounds from the *in situ* crusts as collected from the damaged areas. Unfortunately, the nature of the sulphated compounds (see section 3.4.3) made any preparation of the samples nearly impossible.
- ii We then tried to separate the different sulphated compounds by means of IC without any pre-treatment of the sample. But all these compounds are obviously irreversibly adsorbed on the separation column. Moreover, they tend to clog the column. The explanation is simple: all these columns are filled with ion-exchange resins very similar to the one used for conservation purposes. These will bind any sulphate or other strongly acid groups irreversibly to the polymeric matrix, while the long hydrocarbon chains of the sulphated fatty acids will protrude from the surface, thereby inactivating it and finally closing up the entire column.
- iii In general, sulphates are more strongly bound than any other organic ionic compounds. Therefore any attempt to re-charge the used ion-exchange resin resulted in high amounts of hydrogen carbonate, but no sulphate was ever detected. This at least allowed us to conclude that the adsorption capability of the ion-exchange resin after application was not exhausted.
- iv We had to conclude that ion chromatography is not suitable for analyzing the compounds present. Present attempts to improve this will be reported in a later contribution.

4 CONCLUSION

All the authors believe that (a) the adsorption and neutralization of acid compounds and (b) the application of a conditioned ion-exchange resin are an indispensable step during conservation measures. Our concept turned out to be successful from the point of view of both the conservators and the conservation scientists involved. The formulation of the ion-exchange resin is published here for the first time, to be available in case of emergencies. It is anticipated, however, that the product can be improved still more in the future, although we sincerely hope that future application of our methods will never be necessary. We do not view this solution as the only possibility; it is a first step towards the broader application of ion-exchange resins for conservation purposes rather than a definitive statement. Finally, it should be mentioned that the function of the ion-exchange resin on the damaged surface is not yet completely understood.

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MATERIALS AND SUPPLIERS

Lewasorb A50 (order no. 5-9100): Bayer AG, D-5090 Leverkusen, West Germany.

REFERENCES

- 1 Burmester, A., and Koller, J., 'Säureanschlag auf drei Dürer-Werke in der Alten Pinakothek: Schadensbeschreibung und Wege zur Konservierung aus naturwissenschaftlicher Sicht' in *Bayerische Staatsgemäldesammlungen Jahresbericht 1987-88*, 18-24; and *Restauro* 96(2) (1990) 89-95.
- 2 Heimberg, B., 'Säureanschlag auf drei Dürer-Werke in der Alten Pinakothek: Zustandsbefund, Konservierung und Restaurierung' in *Bayerische Staatsgemäldesammlungen Jahresbericht 1987-88*, 10-16 and *Restauro* 96(1) (1990) 16-21.
- 3 Burmester, A., and Koller, J., 'Known and new corrosion products on bronzes: their identification and assessment, particularly in relation to organic protective coatings' in *Recent Advances in the Conservation and Analysis of Artifacts*, Institute of Archaeology Summer Schools Press, University of London (1987) 97-103.
- 4 Burmester, A., 'Technische Beobachtungen zur 'Himmelfahrt Mariae' aus dem Bamberger Dom, Teil 2: Material und Maltechnik' in *Die Bamberger 'Himmelfahrt Mariae' von Jacopo Tintoretto*, Arbeitsheft 42 des Bayerischen Landesamtes für Denkmalpflege, Munich (1988) 119-136.
- 5 Koller, J., 'Technische Beobachtungen zur 'Himmelfahrt Mariae' aus dem Bamberger Dom, Teil 3: Die Untersuchung der organischen Malmaterialien' in *Die Bamberger 'Himmelfahrt Mariae' von Jacopo Tintoretto*, Arbeitsheft 42 des Bayerischen Landesamtes für Denkmalpflege, Munich (1988) 137-145.
- 6 Peter, U., 'Zur Restaurierung des Rubensgemäldes 'Erzherzog Albrecht von Österreich'', *Maltechnik/Restauro* 84 (1978) 178-181.
- 7 Sonnenburg, H. von, 'Rembrandts 'Segen Jakobs'', *Maltechnik/Restauro* 84 (1978) 217-241.
- 8 Hermitage Museum, Leningrad, personal communication (1989).
- 9 Hurst, G.H., *Textile Soaps and Oils*, London (1904).
- 10 Wichelhaus, H., *Sulfurieren, Alkalischemelzen der Sulfosäuren, Esterifizieren*, Leipzig (1911).
- 11 Awe, W., 'Über den Nachweis und die quantitative Bestimmung von Türkischrotöl in Arzneispezialitäten und von Pflanzenextrakten in türkischrotölhaltigen Arzneigemischen', *Fette und Seifen* 52 (1950) 474-476.
- 12 Hetzer, J., 'Chemische Grundlagen der Schaum-, Netz- und Dispergiermittel', *Fette und Seifen* 49 (1942) 364-371.
- 13 Hintermaier, A., 'Über die Nomenklatur von schwefelhaltigen waschaktiven Substanzen', *Fette und Seifen* 54 (1952) 780-782.
- 14 Krieger, G., 'Die Kunst braucht Klinken' in *Rheinischer Merkur No. 50*, 15.12.78.
- 15 Kühn, H., and Waldeis, P., unpublished report (1977); the authors propose a dry adsorption followed by a wet neutralization.
- 16 Masschelein-Kleiner, L., 'Die Lösungsmittel' in *Lösungsmittel in der Restaurierung*, ed. G. Banik and G. Krist, Vienna (1984) 145.
- 17 Preusser, F., 'Die Rolle der Chemie bei der Restaurierung von Kunstwerken dargestellt am Beispiel der Säureattentate von Kassel', *Werk + Wirken* 29(3) (1978) 6-9.
- 18 Domasłowski, W., and Zyzik, M., 'Experiments on the application of ion-exchange for desalting of stone objects', *Acta Universitatis Nicolai Copernici* 52 (1974) 217-226.
- 19 Matteini, M., and Moles, A., 'Kinetic control of the reactivity of some formulations utilized for the cleaning of bronze works of art' in *ICOM Committee for Conservation, 6th Triennial Meeting*, Ottawa (1981) 81/23/4.
- 20 Fiorentino, P., Marabelli, M., Matteini, M., and Moles, A., 'The condition of the Door of Paradise by L. Ghiberti. Tests and proposal for cleaning', *Studies in Conservation* 27 (1982) 145-153.
- 21 Foschi, E., 'Interventi di restauri e conservazione. Coppia di fibule 'a cicala' in argento dorato. Anello d'oro con pasta vitrea. Appendice I', *Bollettino d'Arte* 71(37/38) (1986) 67.
- 22 Kawinski, H., 'Zur Wirkungsweise und Anwendung von Ionenaustauschern' (Restoration and Conservation of Wooden Musical Instruments, Colloquium Report Fachgruppe Musikinstrumente, Germanisches Nationalmuseum Nürnberg 18-23.5.1987) in *Mitteilungen des AdR* (1988) 45-47.
- 23 Wächter, O., 'Die tückischen metallischen Tinten', *Maltechnik/Restauro* 93(3) (1987) 19-23.

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Fig. 1 'Paumgartner Altar: Saint Eustachius' (Bayerische Staatsgemäldesammlungen BStGS Inv. No. 702). The cross-section was taken near a larger crack: for further explanation see text. (32 × magnification.)

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Fig. 1 'Lamentation of Christ' (Bayerische Staatsgemäldesammlungen BStGS Inv. No. 704). Condition during the conservation treatment with the ion-exchange resin.

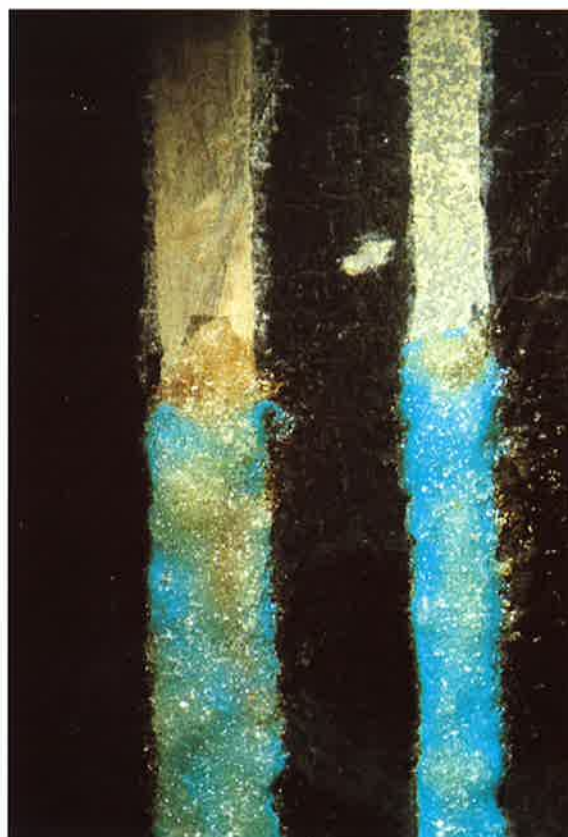


Fig. 4 Detail of 'Mary as Mater Dolorosa' (Bayerische Staatsgemäldesammlungen BStGS Inv. No. 709). Upper part formerly containing azurite during treatment with ion-exchange resin, lower part after removal of the dried resin.