Ingo Rogner

New Methods to Characterise and to Consolidate the Polychrome Qi-lacquer of the Terracotta Army

Abstract

A method for the conservation of aged qi-lacquer layers on silicate material such as terracotta is described. Detachment of the layers would result in the loss of the paint layer. The terracotta army of the Chinese emperor Qin Shihuangdi in Lintong / China is a prominent example of this problem because the paint layer is bound to the surface by an intermediate qi-lacquer layer. This layer has aged 2200 years, buried in wet clay and will detach from the surface if relative humidity drops below 84 % after the excavation. Methacrylic monomers were of special interest as solidifying materials because of their long lifetime and their excellent transparency. Lacquer samples were treated with watersoluble 2-hydroxyethyl-methacrylate (HEMA) which was polymerised by electron-beam radiation with an electron energy of 1.0 MeV. In the experiments the dose was administered in three steps of 20 kGy. Micro-organisms and mould are destroyed by the electron-beam radiation. Infra-red- and mass spectroscopical evaluation shows no damaging effect of electron-beam radiation (300 kGy) on the qi-lacquer. Original qi-lacquer and lacquer consolidated with the method described above were characterised by laser desorption mass spectroscopy (LD-MS). The formation of HEMA polymers with 4-6 monomer units within the lacquer was proved by laser desorption MS. Infrared spectroscopy reveals that the degree of polymerisation is proportional to the applied dose.

Three original polychrome fragments were successfully treated by electron beam curing. The qi-lacquer is bound to the terracotta, the fragments can be dried, a natural look (not shiny) of the polychrome surface is obtained. Laser video holography was employed to investigate if drastic changes in humidity will affect the consolidated polychrome layer. No damage could be detected after four humidity cycles (35-83 % r. h.). The long term stability will have to be evaluated.

The application of electron-beam polymerisation seems to be a promising method for the conservation of the terracotta army of Qin Shihuangdi and other works of art.

Introduction

The change of polymeric bindings with time is an important factor for the ageing of art objects. The detachment of qi-lacquer layers (urushi) from the basic material would result in the loss of paint layers and solidifying such layers is a central point in the conservation of such works of art. The terracotta army of the Chinese emperor Qin Shihuangdi in Lintong / China is one of the most important archaeological objects and is a prominent example of this example because the paint layer is bound to the terracotta surface by an intermediate qi-lacquer layer[1]. This layer has changed during the long time span of 2200 years, buried in wet clay so that it detaches from the surface if relative humidity drops below 84 %. This condition occurs during excavation of the coloured fragments. Until now, the conservation of the paint layers is an unsolved problem.

Results and Discussion

We tried to rebind the qi-lacquer layer to the terracotta by the application of organic polymers. This seems to be an extraordinarily difficult problem if the support is not an organic material, but a highly hydrophilic surface of a silicate such as terracotta. The application of radical initiators and monomers such as methacrylic esters solidified the qi-lacquer, but could not bring about a firm connection of the lacquer to the terracotta support. Inorganic pigments constitute the polychromy of the conserved works of art. A second problem was the lustrous surface of the solidified material which impairs the visual impression by changing the tonality of the colours.

We wanted to avoid these problems by the application of a two-step process. Firstly the terracotta and the overlying layers were impregnated with cotton wool compresses containing the liquid monomer. The monomer concentration in water was increased to 100 % in several steps. During this process unwanted polymerisation was inhibited by the stabilisers which are generally added to the monomers to allow storage (up to 650 ppm hydroquinone-monomethylether). Thus the monomer had enough time to penetrate all organic and in organic material.

Secondly the polymerisation was induced. This could be done neither by conventional thermal radical initiators nor by photopolymerisation which was prevented by the dark colour of the lacquer layer. Therefore we tried initiation by penetrating radiation with which we could start polymerisation from within the terracotta support.

Polymerisation by the application of X-rays gave very poor results. The photons were not absorbed properly within the thin qi-lacquer layer and the silicate material to induce polymer formation.

However, good results were obtained by the application of an electron beam for initiation. This forced the start of the polymerisation within the terracotta propagating toward the outside through the monomer impregnated qi-lacquer to the outside air. After the electron radiation is switched off, there is no radioactivity left within the irradiated material; of course there is a very intense X-ray radiation during the application of the electron beam which must be thoroughly shielded. Methyacrylic monomers were of special interest as solidifying materials because of the long lifetime and excellent transparency of their respective polymers. Methylmethacrylate seemed to be less suitable because of its low polarity so that watersoluble 2-hydroxyethyl-methacrylate (HEMA) gave even better results. It was applied as a commercial formulation Plex 6803-1 (Röhm). Detachment of consolidated qi-lacquer by volume shrinking of HEMA cannot occur because of the thin HEMA layer.

Polymerised HEMA can take up water up to 40 % of its own mass. This implies that the polymerised product lets water penetrate. If applied to wet terracotta water can cross the polymerised HEMA film and evaporate. In contrast to a film which seals the surface, the formation of blisters can be avoided.

The application of an electron beam (EB) initiates a radical polymerisation which is inhibited by molecular oxygen contained in air[2]. Therefore oxygen must usually be thoroughly excluded to obtain a smooth and solid surface. On the other hand, the influence of oxygen is desirable for obtaining a lustreless surface of the solidified works of art. Therefore one should initiate the polymerisation with electron beam radiation with air surrounding the monomer soaked qi-lacquer layer. After the EB cure small residues of monomer can easily be removed from the surface by wiping off or by evaporation of the monomer at room temperature.

A central difficulty in conserving paint layers by the application of electron beam polymerisation is the potential damage of the lacquer by radiation. Ions and radicals remaining after the radiation process can be starting points for further decay. The qi-lacquer, however, contains ortho-hydroxy phenyl moieties[3] which are known to be radical scavengers.

Electron beam curing experiments were carried out at the Institut für Polymerforschung (IPF) in Dresden with the Russian electron accelerator ELV-2, INP Nowosibirsk. A sketch of the electron accelerator is shown in fig. 1. Electron energies can be varied between 0.6 to 1.5 MeV, the maximum radiation current amounts to 25 mA. For further experiments in Xi`an the electron accelerator ELV-8 can be used. This apparatus is from the same Russian producer and provides a wider range of electron energies.

The electron beam (EB) is focused and scans the substrate. Extensive shielding is required due to "bremsstrahlung". The absorbed dose the sample receives as a result of passing under the beam is obtained by integration of the Gaussian function for the beam shape. The sample speed is thus inversely proportional to the absorbed dose. In the experiment the dose was administered in steps of 10 and 100 kGy. The total dose absorbed is the sum of all the individual doses.

For all experiments an electron energy of 1 MeV was used. This value determines how deep the radiation can penetrate into a substrate. At an energy of 1 MeV electrons can penetrate up to 5 mm into a medium of density 1 (water), with a maximum intensity at 1.6 mm. At longer EB exposures if all monomers are consumed by the polymerisation reaction main chain scission is possible.

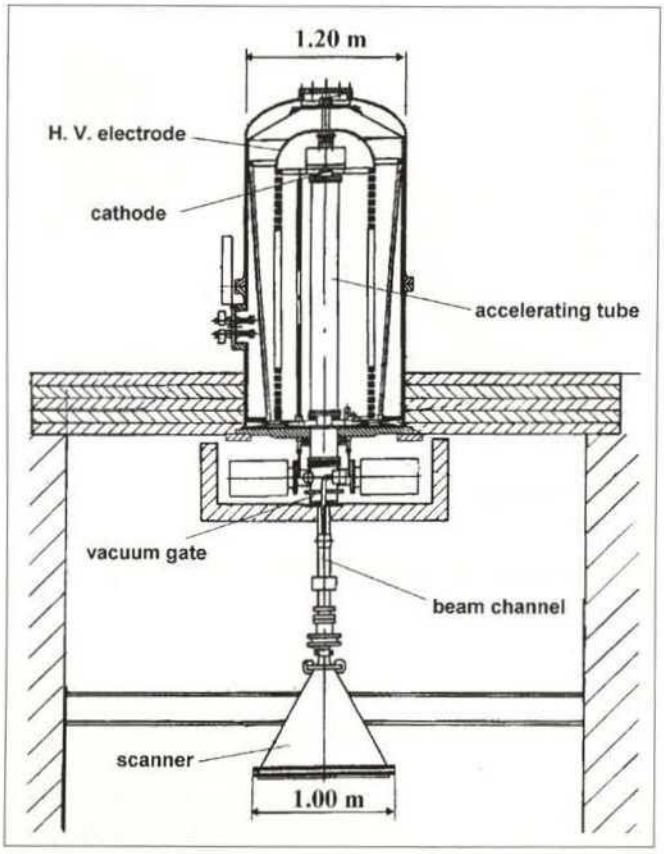

Fig. 1. Sketch of the electron accelerator ELV-2, INP Novosibirsk.

图 1. ELV-2, INP Novosibrsk 电子加速器示意图。

Preliminary Experiments

In preliminary experiments original qi-lacquer ground layer flakes were flattened on a terracotta support with H_2O dest. and were impregnated during three days with various consolidants before electron beam irradiation.

The HEMA formulations polymerised at an energy dose of 50 to 60 kGy. Polymerised Plex 6803-1 shows the best results concerning the mechanical strength of the binding of the qi-lacquer. Unreacted monomers on the surface evaporated after a few days. After three years the original Qin-dynasty qi-lacquer is still firmly bound to the terracotta, the surface is not shiny or lustrous and the terracotta has completely dried.

Analytical Methods

Among the methods that we have used, I want to focus shortly on the following three:
Infra-red spectroscopy, cross sections / microscopical evaluation and laser desorption mass spectroscopy.

Infra-red Spectroscopy

Infra-red Spectroscopy does not show damaging effects of the electron radiation up to 300 kGy. Spectra taken from irradiated and not irradiated samples were alike. No damage by electron beam irradiation can be detected by infra-red spectroscopy.

Infra-red Investigation of the Degree of Polymerisation of Pure Monomer

In order to find the best conditions to consolidate the monomer soaked samples a multitude of preliminary experiments were carried out. Test tubes were filled with equal amounts of the respective consolidant. Some of the test tubes were filled with the inert gas argon to exclude oxygen which is known to be a radical scavenger and polymerisation inhibitor. The test tubes were exposed one or more times to a certain dose of electron beam radiation to evaluate differences in the effect of the irradiation.

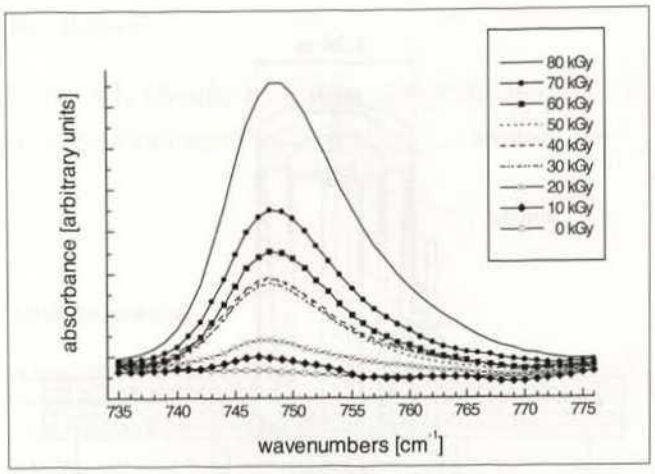

Fig. 2. Electron beam curing of Plex 6803-1 at different doses (one step treatment).

图 2. Plex 6803-1 经不同量电子辐射的处理(一步处理)。

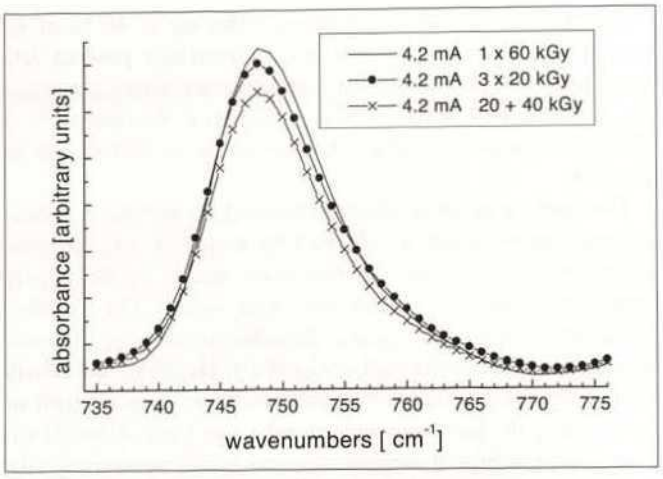

Fig. 3. Electron beam curing with 60 kGy dose

图 3. 用 60 kGy 的剂量电子辐射处理。

The effect of argon to exclude air (which contains oxygen and thus inhibits polymerisation) is only minimal. If Plex 6803-1 is irradiated in argon atmosphere the dose necessary for consolidation is only lowered by 10 kGy down to 50 kGy. The exclusion of oxygen can lead to the formation of a transparent and shining film on the surface of the consolidated original qi-lacquer. The use of argon "blanketing" is thus not recommended.

Pure HEMA cannot be polymerised as easily as the HEMA formula Plex 6803-1, which contains a few percent of cross-linker. Plex 6803-1 is therefore found to be superior to pure HEMA.

The dose necessary to obtain the solidification of Plex 6803-1 was found to be 60 kGy. In different experiments the dose was administered in one step, in two steps (20 kGy + 40 kGy) and in three steps (3 x 20 kGy). All experiments proved the Plex 6803-1 to be solid after the irradiation. It can thus be confirmed that the overall dose given is of importance, independent of the number of steps it is accumulated in.

During all experiments the accelerating voltage is kept constant at 1 MV. In the last set of experiments the radiation current of the electron beam was varied. The lower the radiation current the less electrons penetrate the monomer soaked samples. The lower the amount of electrons initiating a polymer chain, the longer the polymer chains grows. This means that longer polymers form at a lower radiation current. At 2.4 mA a dose of 60 kGy resulted in solidification and evaporation of monomer. Too much energy is transferred in this one step treatment. At the lowest radiation current of 0.6 mA the maximum dose obtainable in a single step is 25 kGy. This treatment led to the formation of a very hard solid.

The solidified samples of Plex 6803-1 were further investigated by quantitative infrared spectroscopy with a Perkin-Elmer IR-1420 FT-IR spectrometer. This method allows to determine the degree of polymerisation. The samples investigated had very different consistencies: liquid, viscous, rubber like and rock hard. It was preferred to monitor a peak that was linearly proportional to the degree of polymerisation. The polymerisation of Plex 6803-1 afforded the formation of linear chains like: -[-CH_2-CR_2-CH_2-CR_2-]-.

The newly formed methylene group (CH_2) is found at 748.5 cm^{-1} and its peak is proportional to the degree of polymerisation. The longer the chain the more methylene groups are formed, the higher the absorbance at this wavenumber.

After thorough investigation the IR-spectra were normalised for the -CH_2-H valence vibration at 2957 cm^{-1} (methyl group is not affected in the reaction). The baseline was corrected and the wavenumber 780 cm^{-1} was set to zero. Fig. 2. presents IR spectra focusing on the peak at 748.5 cm^{-1} taken after a single step electron beam curing with doses from 0 to 80 kGy. The proportional relationship between dose rate and absorbance is evident.

At a dose of 80 kGy the Plex 6803-1 became solid, independent of the number of steps. The single step electron beam treatment leads to a higher degree of polymerisation. Fragment F009-98 was consolidated with a dose of 4 x 20 kGy.

The lowest dose necessary to obtain solid Plex 6803-1 was found to be 60 kGy. The dose was applied in a single step, in two steps (20 kGy + 40 kGy) and in three steps (3 x 20 kGy). The resulting spectra are shown in fig. 3. All three curing methods afford about the same degree of polymerisation. This dose was to be used for one of the original polychrome fragments (Fragment F011-98).

In another set of experiments the electron beam current was varied. The lower the beam current, the longer the polymer chains, the higher the absorbance at the CH_2 rocking vibration (748.5 cm^{-1}). Fig. 4. shows the spectra taken from samples irradiated with an electron beam with a beam current of 0.6, 2.4 and 4.2 mA.

The highest degree of polymerisation was obtained at 0.6 mA. The solidified Plex 6803-1 was rock hard. The original fragment F006-98 was treated in this way. Irradiation with a beam current of 2.4 mA (60 kGy) resulted in the evaporation of the consolidant. Although longer polymers are formed the detrimental effect of the heat-up of the polychrome lacquer and the fragment disqualifies this curing method for further experiments.

Although FT-IR Spectra allow for a quantitative measurement of the relative polymer length, further experiments will have to be done to determine the distribution of the absolute length of

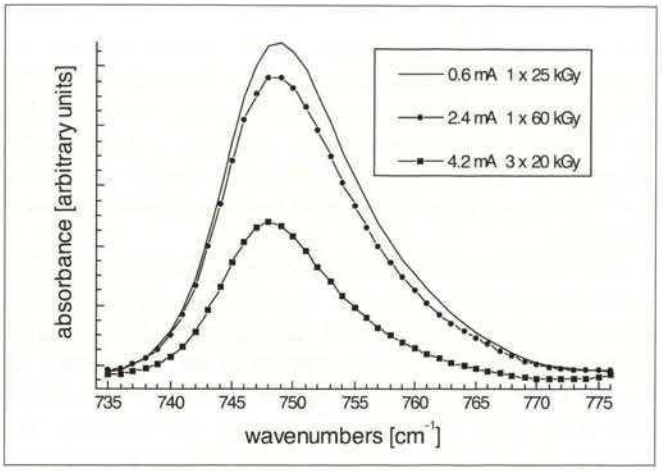

Fig. 4. Electron beam irradiated samples with a beam current of 0.6, 2.4 and 4.2 mA.

图 4. 使用 0.6, 2.4 和 4.2 mA 的辐射电流辐射试样。

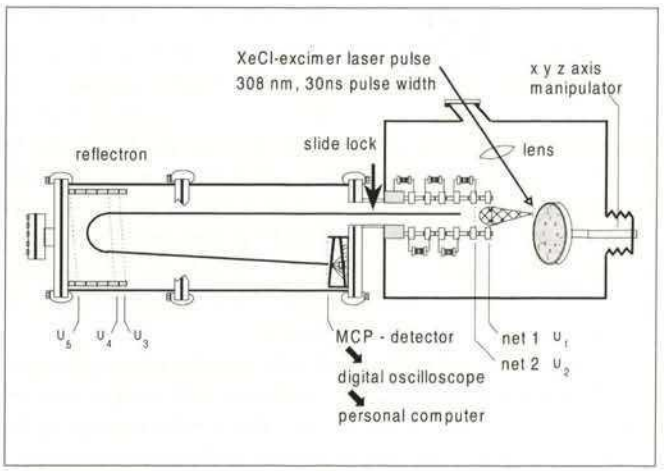

Fig. 5. Section of the laser desorption mass spectrometer.

图 5. 激光解吸质谱仪示意图。

the polymer chains after electron beam curing. Laser desorption mass spectroscopy (LD-MS) is an elegant method to obtain the exact mass distribution.

Cross Sections and Microscopical Evaluation

Light microscopical investigation and cross sections provide another possibility to evaluate the penetration of the consolidant into the lacquer and the terracotta. Original qi-lacquer samples consolidated with electron beam and the HEMA formulation Plex 6803-1 were used. At magnifications of 50 x to 200 x a colourless transparent polymer film of Plex 6803-1 can be detected between terracotta and qi-lacquer. This can be clearly seen in the cross section. However, on top of the qi-lacquer no polymer film is found. Owing to this the surface of the consolidated qi-lacquer appears dull, it does not shine.

In this cross section the polymerised HEMA layer is thicker than the original qi-lacquer layer. This is due to the fact that detached original flakes were consolidated onto a new terracotta support. Original samples, where the lacquer layer still adheres to the original terracotta, do not show an intermediate HEMA layer after consolidation.

Laser Desorption Mass-spectroscopy

Laser desorption mass spectroscopy (LDMS) was carried out on irradiated samples at the Max-Born-Institute in Berlin, Adlershof, Germany. The degree of polymerisation of the applied monomer and possible EB cure damaging effects were monitored. For laser desorption a XeCl excimer laser LPX-100 Lambda Physik (308 nm, 30 ns pulse width) was used. The positively charged ions generated were separated by a non-commercial reflectron time-of-flight mass-spectrometer (RETOF-MS, see fig. 5.) with a mass resolution[4] of $m / \Delta m = 2000$. In contrast to most commercial systems, the laser desorbed ions were allowed to drift for ca. 2 cm before being extracted by a pulsed electric field. The ions were detected by dual multi-

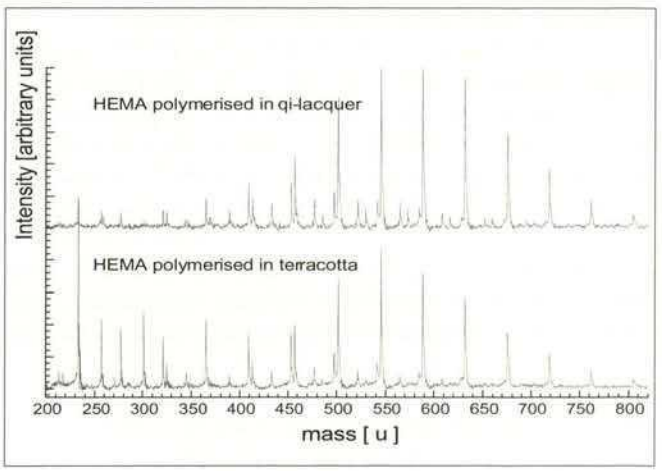

Fig. 6. Laser desorption mass spectra of 2-hydroxyethyl-methacrylate (HEMA) polymerised by electron beam irradiation. Upper spectrum: HEMA polymerised in hardened qi-lacquer. Lower spectrum: HEMA polymerised in the terracotta support.

图 6. 电子束辐射聚合的 2 羟乙基-异丁烯酸盐(HEMA)的激光解吸质谱。上谱: HEMA 在硬化的漆中聚合。下谱: HEMA 在陶体中聚合。

channel plates and the signal was collected by a digital oscilloscope. The spectra were then transferred to a PC for further evaluation. The delay between laser pulse and ion extraction allows one to preselect the mass of the ions detected.

Mass-spectroscopical evaluation shows no damaging effect of the EB radiation (300 kGy) on the qi-lacquer. To prove the polymerisation of the applied monomers within the terracotta and the original qi-lacquer LDMS spectra were taken. LDMS of HEMA polymerised by electron beam curing usually determines the average polymer chain length in the terracotta support and within the qi-lacquer. The spectra are depicted in fig 6.

In the terracotta support only polymer fragments mainly consisting of 2-4 monomer units were detected. Within the solidified original qi-lacquer layer solely fragments with 4-6 monomer units were found. Unfortunately the LDMS spectra do not show

long polymer chains, but only fragments of these. The reason for this is the three-dimensional cross-linking, which occurs during the polymerisation. A large network is formed and the laser pulse can only desorb small parts of this network. For every polymer a combination of peaks can be observed. This is due to sodium and lithium adduct peaks[5] and because of the cleavage or addition of a hydroxyethyl fragment (small bond dissociation value). In the mass spectrum of HEMA polymerised in terracotta fewer lithium adduct peaks can be found. Furthermore hydroxyl endgroups are detected which were formed through EB radiation by reaction with the terracotta.

Investigation of the influence of electron radiation on qi-lacquer by IR and mass spectroscopy confirmed that even a dose of 300 kGy (30 Mrad) does not result in a detectable damage of the qi-lacquer. However this dose is far beyond the dose which is necessary for polymerisation. Additionally the radio-biological effect of electron beam and "bremsstrahlung" destroys micro-organisms and can be used to disinfect contaminated lacquer[6].

After the promising preliminary experiments we started experiments with original samples. The experiments were performed at the Institute for Polymer Research in Dresden, Germany by the Bavarian State Conservation Center and three Chinese colleagues from the Museum of the Terracotta Warriors and Horses: Zhou Tie, Rong Bo and Zhang Zhijun.

Before the irradiation with the electron beam three original samples (Fragment 6-98, 9-98 and 11-98) were pre-treated as follows: During three days the samples were impregnated with the commercial formulation Plex 6803-1 which was applied with compresses. The concentration of Plex 6803-1 in water was raised from 33% on the first to 66% on the second and finally to 100% on the third day. Thus the consolidant had enough time to penetrate the qi-lacquer, its overlying paint layer and the terracotta. In order to evaluate different electron beam curing methods every original fragment was treated with a different method.

Fragment F006-98
Part of body armour with qi-lacquer and red iron oxide.
Treatment: 1 time 25 kGy at 1 MeV and 0.6 mA.
The fragment was not cleaned after the irradiation. Surplus consolidant was allowed to evaporate for several days. After irradiation the sample was stored under ambient conditions.

Fragment F011-98
Part of body armour with qi-lacquer and stripes of red cinnabar.
Treatment: 3 times 20 kGy at 1 MeV at 4.2 mA.
The fragment was not cleaned after the irradiation. Surplus consolidant was allowed to evaporate for several days. After irradiation the sample was stored under ambient conditions.

Fragment F009-98
Collar with Han blue, cinnabar, pink colour and qi-lacquer
Treatment: 4 times 20 kGy at 1 MeV and 4.2 mA.
Surplus consolidant was removed between the irradiation experiments with a laboratory tissue. Along rims and creases liquid consolidant collected to form a pool which can harden and lead to shiny spots on the treated fragment. These pools were drained by pressing the edges of the tissue into the rims and creases. The fragment was immediately freed from surplus consolidant after the last irradiation by pressing the laboratory tissue onto the lacquer. The result was a fragment with virtually no shining spots on the surface. The sample was stored under ambient conditions.

After irradiation all fragments showed a good mechanical fixation of the original qi-lacquer and the overlying polychrome layer. A rub test was performed. The terracotta dries out completely after a few days, the stability of the polychrome qi-lacquer is retained. All three fragments are in good condition after three years at ambient temperature and humidity. The coloured lacquer layers are bound tightly to their original terracotta support. A natural look (not shiny) of the polychrome surface is obtained. Laser video holography was employed to investigate if drastic changes in humidity will affect the consolidated polychrome layer. No damage could be detected after four humidity cycles (35-83 % r. h.). We are all looking forward to seeing the effect of long-time storage under ambient conditions in Lintong, China.

Finally I would like to repeat all advantages offered by the new method:
- The consolidant is watersoluble in every ratio.
- The consolidant is similar to water in viscosity, colour and density, it has only a faint odour.
- Only two solutions of consolidant in water are required for the whole preparation. No more chemical operations needed.
- The consolidant is a commercial formulation of HEMA (Plex 6803-1) which is commercially available.
- It is used in very hostile environment for long term sealing of broken canal pipes.
- The consolidant is stable under normal conditions, no autopolymerisation occurs.
- Monomer treated samples can be stored because the polymerisation starts with the electron beam irradiation only.
- The polymer has an excellent transparency like most methacrylates, but treated samples do not have a shiny appearance.
- The polymer binds to qi-lacquer and terracotta alike.
- The polymer is not poisonous, it is the main component of contact lenses for the eye.
- Irradiation with an electron beam can be carried out in Xi'an, China with a suitable electron accelerator like the ELV-8. This apparatus was produced by the same company as the accelerator used in Dresden.
- Electron irradiation effectively destroys bacteria, microorganisms and most important: mould.

The application of the rapid electron beam polymerisation is therefore a promising method for the conservation of the terracotta-army of Qin Shihuangdi and other art objects.

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罗格纳

鉴定和加固兵马俑彩绘漆的新方法

摘要

本文介绍的是一种保护硅酸盐材料如陶俑上的老化漆层的方法。漆层的剥离会导致彩绘层的损失。这方面一个著名的例子即中国临潼秦始皇兵马俑，因其表面彩绘层与一层漆中间层相连。这些漆层在湿土下埋置了 2200 年，出土后一旦空气湿度降到 84 %以下，漆层便会与表面分离。作为固化材料，甲基丙烯酸单体值得特别重视，因为这种单体的寿命长，透明度好。漆样的处理，是通过 1.0 MeV 的电子能量来聚合水溶性羟乙基-异丁烯酸盐(HEMA)进行的。实验中分 3 步用 20 kGy 的剂量辐射。微生物和霉菌会被电子辐射杀死。红外线光谱和质谱分析显示，辐射(300 kGy)并不会对漆层造成损坏。原始漆块和漆样用上述方法加固后，再经过激光解吸质谱(LD-MS)分析。激光解吸质谱证实漆中有 4-6 个单体单位的 HEMA 聚合物。红外线光谱展示，聚合度系与使用的量成比例的。

我们用电子辐射成功地处理了 3 块原始彩绘残片。漆与陶体附着，残片可以干燥，彩绘表面视觉效果正常(不发光)。利用激光视频全息摄影，对剧烈的湿度变化是否会影响加固后的彩绘漆层作了观察。经 4 组湿度变化(35-83 %的相对湿度)，没有发现任何破坏。长期稳定性还有待进一步评估。

用电子辐射聚合看来是一种大有前途的保护秦始皇兵马俑以及类似艺术品的方法。

(英译中：陈钢林)