NASA/TM—1999-209435

Recovery of a Charred Painting Using Atomic Oxygen Treatment

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August 1999

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12th Triennial Meeting of the International Committee for Conservation
sponsored by the International Council of Museums
Lyon, France, August 29—September 4, 1999

National Aeronautics and
Space Administration

Glenn Research Center

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Acknowledgments

The authors would like to thank Mr. Kenneth Bé of the Cleveland Museum of Art for providing the painting for these tests and for his helpful comments, discussion and advice. We would also like to thank Father Bob Weaver and the members of St. Alban's Episcopal Church for their helpfulness and enthusiasm surrounding the restoration of their paintings.

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Summary

A noncontact method is described which uses atomic oxygen to remove soot and char from the surface of a painting. The atomic oxygen was generated by the dissociation of oxygen in low pressure air using radio frequency energy. The treatment, which is an oxidation process, allows control of the amount of material to be removed. The effectiveness of char removal from half of a fire-damaged oil painting was studied using reflected light measurements from selected areas of the painting and by visual and photographic observation. The atomic oxygen was able to effectively remove char and soot from the treated half of the painting. The remaining loosely bound pigment was lightly sprayed with a mist to replace the binder and then varnish was reapplied. Caution should be used when treating an untested paint medium using atomic oxygen. A representative edge or corner should be tested first in order to determine if the process would be safe for the pigments present. As more testing occurs, a greater knowledge base will be developed as to what types of paints and varnishes can or cannot be treated using this technique. With the proper precautions, atomic oxygen treatment does appear to be a technique with great potential for allowing very charred, previously unrestorable art to be salvaged.

Introduction

Fire in any structure housing an art collection can result in great cultural loss if the art is unrecoverable by conventional methods due to extensive charring of the surface. Paintings in particular are challenging to restore because the carbonaceous char of the varnish and binder is usually intermixed with the paint pigments. It is difficult to remove the char without removing or moving the pigment. A noncontact treatment technique using atomic oxygen, however, is able to distinguish many paint pigments from char and allow the char to be selectively removed leaving the pigment on the surface.

Research into using atomic oxygen as a treatment technique started through inquiries made by the Conservation Department of the Cleveland Museum of Art as to available NASA technologies that could be used to remove urethane varnish. Presentation of these results and discussion with conservators from other organizations led to investigating the technique for removing soot and char from the surface of paintings and other fine art. Fire damage was believed by conservators to be a problem area that was in need of some additional restorative tools.

Although NASA's focus is on research involving improvements in civil aviation and the peaceful exploration of space, an important function of the agency is to take technologies developed for these programs and make them available for applications on Earth that benefit everyone. That is why techniques to investigate the effects of atomic oxygen on various spacecraft materials are being studied for potential benefit to the art conservation community.

Atomic oxygen is present in the atmosphere surrounding the Earth at altitudes where satellites typically orbit. It has been shown to react chemically with surface coatings or deposits that contain carbon (Banks, et al. 1988). In the reaction, the carbon is converted to carbon monoxide and some carbon dioxide. Water vapor can also be a byproduct if hydrocarbons are present. This process can be harmful to a satellite if enough carbon

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containing materials that are critical to its operation are removed. Due to the importance of understanding the reaction, and the need to test potential solutions for protecting surfaces from reaction, facilities have been developed for producing atomic oxygen on Earth (Banks, et al., 1989). Radio frequency, microwave, or electron bombardment has been used to dissociate molecular oxygen into atomic oxygen. These atoms can be either directed at the surface as a gentle flow of gas or the surface can be immersed in the gaseous atomic oxygen. Large area exposure is typically performed in a vacuum chamber where pressures range from 0.001 to 100 mtorr depending on the technique used. Smaller areas can be treated at atmospheric pressure using a DC arc device described in a publication by Banks, et al. (1998). Because the process is dry and the reaction is confined to the surface, there is less risk of damaging the underlying paint or canvas.

The atomic oxygen cleaning technique has been demonstrated to be effective at removing soot from canvas, acrylic gesso, unvarnished oil paint and varnished oil paint. (Rutledge, et al., 1996; Rutledge, et al., 1998). This paper investigates its usefulness in removing char from a varnished oil painting. The process, which has been patented by NASA, is not intended to be a replacement for conventional techniques, but to be an additional tool for use where conventional techniques may not be effective (US Patent #5560781, 1996).

Procedure

Description of the Painting

The Cleveland Museum of Art donated the charred varnished oil painting used for testing of the treatment process. It was originally displayed in St. Alban's Episcopal Church in Cleveland until an arson fire destroyed the church in June of 1989. The museum received a pair of paintings from the church for restoration. The subject of this testing was a painting depicting a female saint with upraised head and eyes. The painting was heavily soot covered with extensive charring and blistering of the full thickness of the paint. Charring was evident as a very black and brittle layer. The other painting of the pair, which depicted the Madonna, infant and a third figure which is probably a young John the Baptist, experienced much less blistering and charring. Restoration attempts were made on the latter painting at the Cleveland Museum of Art using acetone. Methylene chloride was also tried. These processes removed some of the soot and varnish, however, the surface was still very dark and features were difficult to distinguish. Both paintings were considered to be unsalvageable and were donated to NASA for testing of the atomic oxygen treatment process. Because there was less surface charring, the painting depicting the Madonna and infant was treated first (Rutledge et al. 1998). Success with this painting led to the attempt to try to remove the much more extensive charring from the surface of the second painting, which we named the Saint Painting.

Atomic Oxygen Cleaning

Cleaning of the painting was performed inside a large vacuum chamber that can accommodate a painting of ~1.5 by 2.1 m in size. The vacuum in the chamber is provided by conventional vacuum pumps with pressures during treatment, which range from 1 to 5 mtorr. Two large aluminum parallel plates inside the chamber produce the atomic oxygen. One plate is connected to a radio frequency power supply operating at 400 W, while the other plate is at ground potential. The ground plate has several bolts attached to it from which works of art to be cleaned can be suspended in a vertical position either by attachment of fine wire, or by acting as a support for a painting stretcher. Canvases too large to fit in the chamber in one dimension, which can be rolled, could be treated in sections by use of a roll and take-up reel inside the vacuum chamber. Paintings to be cleaned are suspended so that the ground plate is as close as possible to shield the backside from atomic oxygen exposure during treatment. A photograph showing a painting mounted inside the chamber is contained in figure 1. A controlled entry of air into the chamber at rates between ~130 and 280 standard cm^3/min provides the source of the oxygen. Radio frequency oscillation of electrons between the two aluminum plates produces dissociation of the oxygen in the air into atomic oxygen. The radio frequency was generated by a power supply manufactured by RF Power Products Inc. The dissociation of the air into atomic species creates a pink colored glow between the plates. The nitrogen in the air has been found not to have an effect on the removal of carbon and behaves as an inert gas for the treatment exposure. An automated timer and controller on the system allows the cleaning to proceed over a desired timeframe unattended and will turn off the system if a loss in vacuum, water cooling to the pumps and power supply, or drop in plasma intensity is detected.

Analysis

A quartz halogen microscope light set at full intensity, with a color temperature of 3200 K (Blackbody peak wavelength of 900 nm), was mounted on an aluminum beam so that the light could fall on the surface of the painting at roughly a 45° angle. Quartz halogen was selected as the light source because its spectrum is closer to that of daylight giving a more balanced source of light across the entire color spectrum than conventional incandescent or fluorescent light. This configuration was used to monitor diffuse reflectance from selected portions of the painting at various intervals during the cleaning process. The detector was placed near the light source. The painting was removed from vacuum for these measurements and then returned for further exposure. The reflectance from a magnesium oxide coated glass slide was used to correct the data from the detector to eliminate drifts in the intensity of the light source between measurements. The area that could be illuminated was ~1.91 cm in diameter, so it was necessary to select areas from the painting that were both uniform over this size range and had potential for changing the most (largest contrast) during the cleaning process. In this way, the end point of the cleaning process could be determined by looking for a leveling off of the reflected light signal indicating that no further change is taking place.

Results And Discussion

The Saint Painting was ~0.733 by 0.58 m in size. A photograph of this oil painting as it was received for treatment is contained in figure 2. A close-up photograph showing the blistering around the face is contained in figure 3. Because it is sometimes difficult to get an accurate color match in before and after photographs, it was decided to restore only half of the painting so that a direct comparison would be available. Two sheets of 0.0127 cm thick polyimide Kapton® manufactured by DuPont were used as a mask over the right half of the painting. Any type of nonmetallic covering could be used such as cardboard, paper, or some other plastic sheeting. Kapton® was used because of its availability and its ability to lay in close contact with the surface (stiff but pliable) without putting excessive pressure on the blisters. These sheets were positioned so that a portion of the face and the right side of the central figure would not undergo atomic oxygen treatment. The sheets were wrapped to the backside of the painting and then stapled to the stretcher to hold them in place. Close contact with the surface was needed to produce a crisp boundary between the treated and untreated areas of the painting. A photo of the polymer mask covering half of the painting is shown in figure 4.

Prior to treatment, two areas were selected to receive reflected light monitoring at intervals in the treatment process. The center of the forehead was chosen because it should represent a broad area of a light color. The background next to the halo was chosen because it was believed that this area should remain dark. It was desired to find two areas that would have the greatest contrast at the conclusion of the treatment and then use the measure of the contrast as an indicator of the completeness of the treatment. Lacking initial photographs of the painting, making a determination of the lightness or darkness of particular areas on the painting was extremely difficult. The soot deposits and char were also not uniform on the surface. This resulted in the cleaning of some areas more quickly than other areas. Unfortunately, this was the case for the two areas that were initially selected. Figure 5 contains the reflectance as a function of cleaning time for the forehead and background areas. Figure 6 contains a plot of the contrast data, which is the difference in reflectance between the forehead and background areas. The background did remain dark during the cleaning process as expected, but the forehead area quickly lightened and then remained fairly constant in reflectance. Other areas of the painting lightened at different rates. This made it difficult to determine the endpoint through the use of reflected light from the selected locations. The authors are in the process of testing an alternative technique that scans the reflected light signal over the entire surface and determines the standard deviation of the signal in order to give a better indication of the contrast change for the entire painting. For this painting, we had to resort to judging the endpoint visually.

Figure 7 contains a photograph of the painting with the polymer mask lifted off of the surface after treating the left half of the painting 10.9 hr with atomic oxygen. At this point, many surface details became much more visible such as the detail pattern on the sleeve of the robe, the brooch, and the white lace. Further cleaning removed more of the discolored varnish that appears in the photograph as streaks on the surface of the painting. Although there were areas where the varnish appeared to have been removed down to the paint after 10.9 hr, further cleaning did not appear to change the appearance or coloration. At the conclusion of the cleaning, the paint pigment was loosely bound on the surface. Because the atomic oxygen reaction is confined to the surface, it will remove binder that is in-between and on top of pigment particles but will leave a small amount underneath that loosely attaches the particle to the surface. This has been observed with early scanning electron microscope studies of oil paint exposed to atomic oxygen (Rutledge, et al., 1994). Because the attachment point is small, it would be possible to remove pigment by mechanical contact with the surface such as brushing. Therefore, with the guidance of conservators from the Cleveland Museum of Art, a fine spray mist of a Grumbacher nonyellowing resin based varnish for oils was applied to fix the pigment on the surface (See Materials section). After this step was complete, an Acryloid® F-10 based picture varnish (Grumbacher) was applied by brush to the treated half of the painting. This varnish was selected because the conservators could remove it if at some future date they desired to complete the restoration by consolidation and in painting. Figure 8 shows the painting after treatment and revarnishing of the left half. Details on this side are clearly shown and the blistering is much less noticeable although it is still present on the surface.

There is a potential for dehydration shrinkage to occur during the treatment process due to the fact that it is performed under a partial vacuum. For this painting, there was no deformation observed during treatment. It appeared that if shrinkage did occur, that the canvas, paint and stretcher shrank at approximately the same rate because no additional cracking beyond that originally present on the painting was observed after treatment. This may not be the case for every material combination.

The authors were unable to obtain a photograph of the painting before the fire damage occurred so it was difficult to determine if there were any shifts in paint coloration due to the treatment process. There did not appear to be any yellowing of the surface. The white lace, whites of the eyes and pearls in the brooch were white after treatment. There have been a number of oil paints tested for changes in coloration using reflectance spectroscopy prior to and after exposure to atomic oxygen (Rutledge, et al., 1994). Changes in coloration were not observed for these materials, however they were more modern paint formulations. Caution must be used when treating an untested paint medium using atomic oxygen if the cleaning will progress into the paint pigment. A representative edge or corner of the painting which contains most of the paint colors present should be treated using atomic oxygen with the remainder masked off so that a determination can be made if this process will be safe for the pigments present. Organic paint pigments will experience oxidation and removal so care must be taken during cleaning to minimize the loss of organic pigment. As more testing occurs, a greater knowledge base will be developed as to what types of paints and varnishes can or cannot be treated using this technique. With the proper precautions, atomic oxygen treatment does appear to be a technique with great potential for allowing very charred, previously unrestorable art to be salvaged.

Conclusions

Atomic oxygen treatment has been shown to be able to effectively remove char and soot from a fire damaged, varnished oil painting. In order to remove the charred varnish and paint binder, the paint pigment is exposed. The process leaves the pigment loosely bound on the surface. The pigment can be rebound to the surface using a fine spray mist of a material of the conservator's choice. This can be followed by further treatment by the conservator. Atomic oxygen treatment can be used to perform extensive cleaning as in this case, or for a light surface cleaning. It is important to first verify that the materials present in the painting are safe for atomic oxygen cleaning by cleaning a small representative edge or corner prior to treatment of the entire painting. This technique appears to have great potential for removing heavy soot and char from the surface of art damaged during a fire and may be able to allow restoration of previously unrestorable works of art. The process is not intended to be a replacement for conventional techniques, but as an additional conservation tool in applications where conventional techniques have not been effective.

References

Banks, B.A., and Rutledge, S.K.: Proceedings of the Fourth European Symposium on Spacecraft Materials in the Space Environment, CERT, Toulouse, France, Sept. 6–9, 1988, pp. 371–392.

Banks, B.A. et al.: Proceedings of the 18th Annual Symposium on Applied Vacuum Science and Technology, 1989, NASA TM–101971.

Banks B.A., Rutledge, S.K., and Norris, M.J.: An Atmospheric Atomic Oxygen Source for Cleaning Smoke Damaged Art Objects, Proceedings of the 26th Annual AIC Meeting, Arlington, Virginia, June 1–7, 1998, NASA/TM 1998–208506.

Rutledge, S.K., Banks, B.A., and Cales, M.: Atomic Oxygen Treatment for Non-Contact Removal of Organic Protective Coatings From Painting Surfaces, Materials Issues in Art and Archaeology IV, Materials Research Society, Cancun, QR Mexico, May 16–20, 1994, NASA TM–106650.

Rutledge, S.K., and Banks, B.A.: Atomic Oxygen Treatment Technique for Removal of Smoke Damage from Paintings, Proceedings of the Materials Research Society Meeting, Boston, Massachusetts, December 1996, NASA TM–107403.
Rutledge, S.K., et al.: Atomic Oxygen Treatment as a Method of Recovering Smoke Damaged Paintings, Proceedings of the 26th Annual AIC Meeting, Arlington, Virginia, June 1–7, 1998, NASA TM 1998–208507.
US Patent #5,560,781; Banks, B.A., and Rutledge, S.K.: Process for Non-Contact Removal of Organic Coatings from the Surface of Paintings, 1996.

Materials

Kapton® polyimide
E.I. DuPont de Nemours & Co. Inc.
1007 S. Market Street
Wilmington, Delaware, 19801 USA
1-302-774-1000

Resin Based Varnish for Oils: N-hexane, Turpentine, Propane, Stoddard Solvent, Isobutane, N-butane
M. Grumbacher Inc.
Bloomsbury, New Jersey 08804 USA
1-908-479-4124

Picture Varnish: D-Limonene 5989-27-5, 2-Ethoxyl Acetate (EEA) 111-15-9, Rohm & Haas Acryloid® F-10
M. Grumbacher Inc.
Bloomsbury, New Jersey 08804 USA
1-908-479-4124

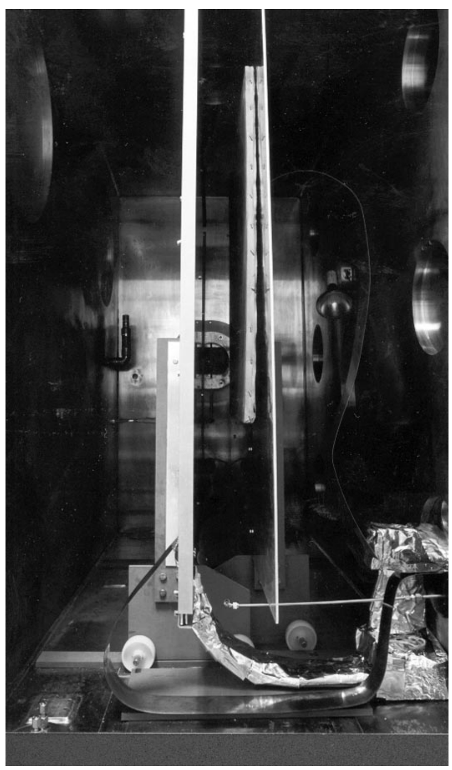

Figure 1.—Photograph of the inside of the vacuum chamber showing the two vertical aluminum plate electrodes and a painting hanging on the ground plate (to the right).

Figure 2.—The St. Alban's Church Saint Painting as received from the Cleveland Museum of Art.

Figure 3.—Close up of the Saint Painting showing blistering.

Figure 4.—The Saint Painting with a polymer mask covering the right half for comparison purposes to prevent this side from being treated.

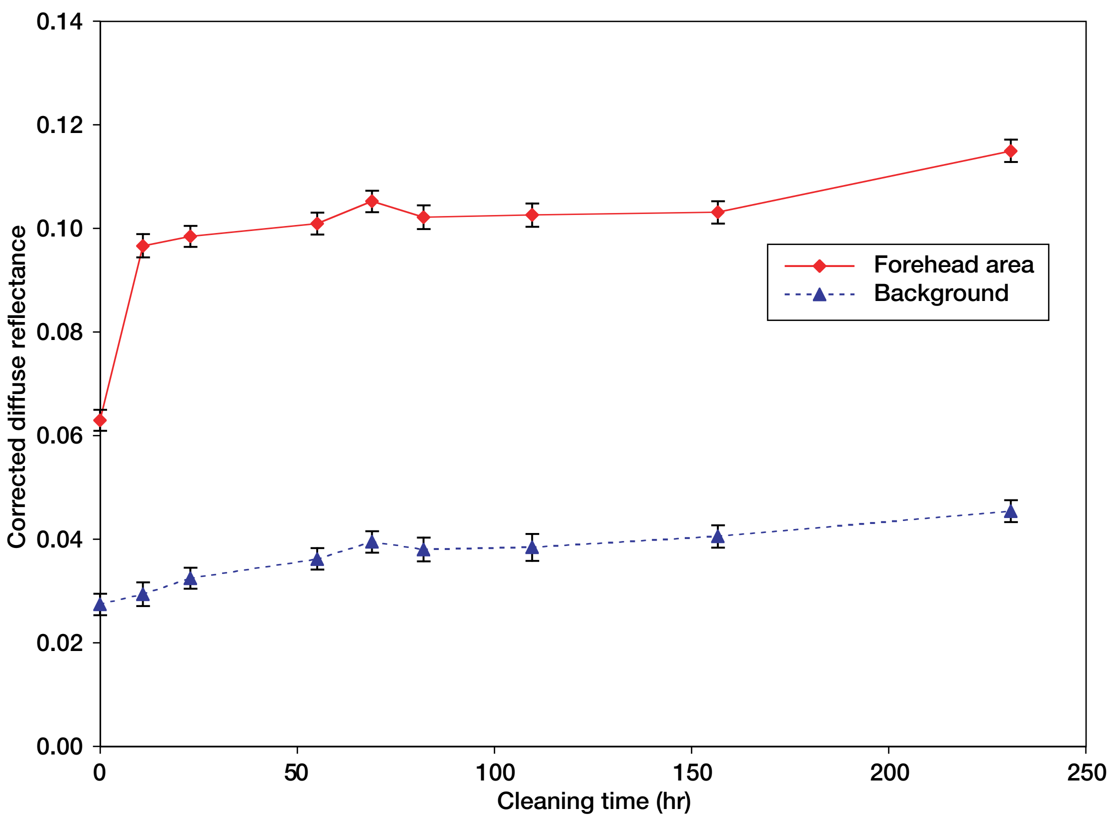

Figure 5.—Plot of the diffuse reflectance of light as a function of cleaning time for the forehead and background areas of the painting.

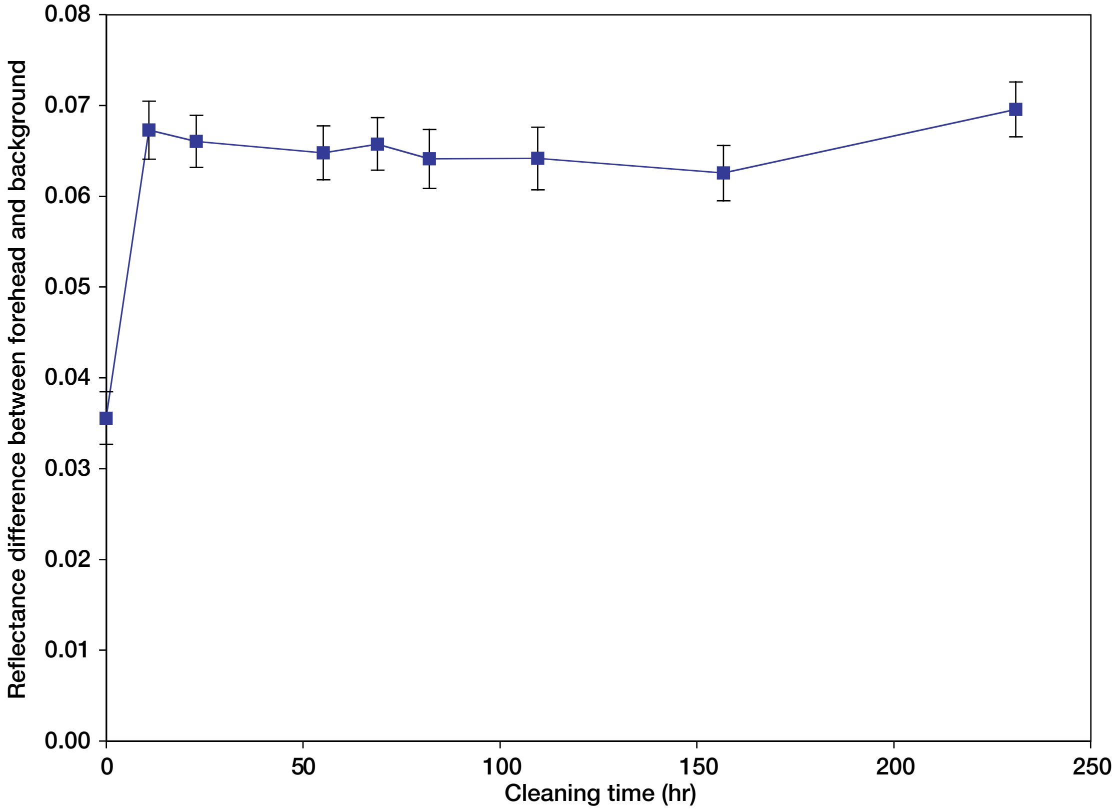

Figure 6.—Plot of the difference in diffuse reflectance of light between the background and forehead as a function of cleaning time (contrast).

Figure 7.—Photograph of the Saint Painting after treatment of the left half with atomic oxygen for 10.9 hours, (mask has been removed for comparison).

Figure 8.—Photograph of the Saint Painting after atomic oxygen treatment was completed on the left half and varnish reapplied; the right half was not treated.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 1999	Technical Memorandum

4. TITLE AND SUBTITLE

Recovery of a Charred Painting Using Atomic Oxygen Treatment

5. FUNDING NUMBERS

WU–505–23–2C–00

6. AUTHOR(S)

Sharon K. Rutledge, Bruce A. Banks and Virgil A. Chichernea

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–11900

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—1999-209435

11. SUPPLEMENTARY NOTES

Prepared for the 12th Triennial Meeting of the International Committee for Conservation sponsored by the International Council of Museums, Lyon, France, August 29—September 4, 1999. Sharon K. Rutledge and Bruce A. Banks, NASA Glenn Research Center, Cleveland, Ohio, and Virgil A. Chichernea, Cleveland State University, Cleveland, Ohio 44115. Responsible person, Sharon K. Rutledge, organization code 5480, (216) 433–2219.

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13. ABSTRACT *(Maximum 200 words)*

A noncontact method is described which uses atomic oxygen to remove soot and char from the surface of a painting. The atomic oxygen was generated by the dissociation of oxygen in low pressure air using radio frequency energy. The treatment, which is an oxidation process, allows control of the amount of material to be removed. The effectiveness of char removal from half of a fire-damaged oil painting was studied using reflected light measurements from selected areas of the painting and by visual and photographic observation. The atomic oxygen was able to effectively remove char and soot from the treated half of the painting. The remaining loosely bound pigment was lightly sprayed with a mist to replace the binder and then varnish was reapplied. Caution should be used when treating an untested paint medium using atomic oxygen. A representative edge or corner should be tested first in order to determine if the process would be safe for the pigments present. As more testing occurs, a greater knowledge base will be developed as to what types of paints and varnishes can or cannot be treated using this technique. With the proper precautions, atomic oxygen treatment does appear to be a technique with great potential for allowing very charred, previously unrestorable art to be salvaged.

14. SUBJECT TERMS

Atomic oxygen; Char; Paintings: Fire damage; Treatment; Cleaning

15. NUMBER OF PAGES

15

16. PRICE CODE

A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102