Atomic Oxygen Treatment as a Method of Recovering Smoke Damaged Paintings

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Summary

A noncontact technique is described that uses atomic oxygen, generated under low pressure in the presence of nitrogen, to remove soot and charred varnish from the surface of a painting. The process, which involves surface oxidation, permits control of the amount of surface material removed. The effectiveness of the process was evaluated by reflectance measurements from selected areas made during the removal of soot from acrylic gesso, ink on paper, and varnished oil paint substrates. For the latter substrate, treatment also involved the removal of damaged varnish and paint binder from the surface.

1.0 Introduction

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 the results achieved with removal of various types of varnish, 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. This was believed by conservators to be a problem area that was in need of some additional restoration tools.

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) (Banks and Rutledge, 1988). In the reaction, the carbon is converted to carbon monoxide and some carbon dioxide. Water vapor is also a byproduct of the reaction if the surface contains carbon-hydrogen bonds. Depending on the material's chemical structure, the reaction can proceed through hydrogen atom abstraction, oxygen addition to form excited radicals followed by hydrogen atom elimination, oxygen insertion into the C-H bonds, and replacement by formation of alkoxy radicals (Banks and Rutledge, 1988) (Dever, 1991). The majority of the reaction products are volatile species. The rate of the reaction will vary with the surface chemistry, atomic arrangement, temperature, energy of the oxygen atoms, and the presence of electrons and other species. Materials that are already in a high oxidation state, such as metal oxides, are not affected by atomic oxygen.

Exposure to atomic oxygen can be harmful to a satellite if enough carbon containing materials that are critical to its operation are removed. Due to the importance of the problem and the need to test potential solutions for protecting surfaces from reaction, facilities have been developed for producing atomic oxygen on Earth (Banks and Rutledge, 1988)(Banks, et al., 1989). Radio frequency (RF) and microwave radiation or electron bombardment has been used to dissociate molecular oxygen into atomic oxygen. These atoms can either be directed at a surface as a gentle flow of gas, or the surface can be immersed in the gaseous atomic oxygen. The exposure is typically performed in a vacuum chamber where pressures can range from $1.3 \times 10^{-4}$ Pa (1.93x10$^{-3}$ psi) to 13.3 Pa (1.93x10$^{-3}$ psi) depending on the dissociation process used. This is defined as a rough vacuum and requires only a mechanical vacuum pump to achieve. The atomic oxygen reaction is confined to the surface because the oxygen atoms have a high reactivity and usually react with what is directly in their path either on first or second contact. Recombination into relatively inactive molecular oxygen becomes...
more likely with multiple collisions so reactions deep into the surface are very rare unless there are a lot of large, straight, open pores that extend deep into the material.

Atomic oxygen is of interest for cleaning paintings because the process is in the gas phase, there is no mechanical contact, and the reaction is confined to the surface, which reduces the risk of damaging the underlying paint or canvas. The atomic oxygen cleaning technique has been demonstrated to be effective at removing soot from small sample sections of canvas, acrylic gesso, and an unvarnished oil painting (Rutledge and Banks, 1996). This paper investigates its usefulness in removing soot from acrylic gesso and ink on paper, and removing soot and thermally damaged binder and varnish from an 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 (Banks and Rutledge patent, 1996).

2.0 Procedure

2.1 Test Objects

A commercially available artist's stretched canvas (cotton canvas primed with acrylic gesso) (~90×120 cm) was used to perform the initial test of the large area atomic oxygen treatment system. The stretcher was held above a wax candle flame, and the candle was moved back and forth underneath the stretcher to create soot streaks on both the paintable surface and on the back of the canvas.

Two fire damaged works of art were also used in testing the atomic oxygen cleaning technique. The first was a Roy Lichtenstein ink drawing on paper (untitled abstract from 1950, ~21.6×27.9 cm in size). The work had been heavily smoke-damaged and partially thermally decomposed in a fire. The McKay Lodge Fine Arts Conservation Lab in Oberlin, Ohio had previously tried float washing in alkaline water (8.0 pH ammonium hydroxide) for a few hours followed by immersion in a sodium borohydride solution (<1% v/v), but these processes had a minimal effect on the appearance of the drawing.

The second work that was tested was a copy of the Raphael painting “Madonna of the Chair.” It was painted by Bianchini of the Studio Viale Petrarca in Firenze, Italy and it was originally displayed in St. Alban’s Episcopal Church in Cleveland until an arson fire destroyed the Church in June of 1989. This painting was given to the Cleveland Museum of Art for restoration. The Madonna painting, a varnished oil painting approximately 74.3×74.3 cm in size, was heavily smoke-damaged and partially charred. A section of the painting was initially treated at the museum with acetone, then with methylene chloride and some additional solvents. Some of the soot and varnish were removed by these techniques, but the surface was still very dark and features were difficult to distinguish. The Madonna painting was considered to be unsalvageable and was donated for testing of the atomic oxygen treatment process.

2.2 Apparatus for Atomic Oxygen Cleaning

Cleaning of the test objects was performed in a large vacuum chamber that could hold a stretched painting roughly 1.5 by 2.1 m in size. The vacuum chamber was not specifically designed to hold paintings but was modified to be able to accommodate paintings of this size suspended in a vertical position inside.

The vacuum in the chamber is provided by conventional mechanical vacuum pumps, which can be used with traps but for these tests were not. Pressures during treatment range from 0.13 Pa (1.93×10⁻³ psi) to 0.667 Pa (9.67×10⁻¹ psi). Two large aluminum parallel plates inside the chamber are used as electrodes to create the atomic oxygen through RF excitation. One plate is connected to an RF power supply manufactured by RF Power Products Inc. operating at roughly 400 W; the second plate is at ground potential. From the ground plate protrude several bolts from which test objects to be cleaned can be suspended directly or by hanging with fine wire. The objects are hung so that the ground plate is in contact with the back of the object, thereby shielding the back side from the atomic oxygen during cleaning. A controlled entry of air into the chamber at rates between 50 and 280 stdcm³/min provides the source of the atomic oxygen. Radio frequency oscillating voltage between the two plates causes dissociation of the molecular oxygen and nitrogen in the air into atomic species, creating a plasma discharge between the plates which has a pink glow. The atomic nitrogen has been found not to have an effect on carbon removal, and no detrimental effects, such as changes in coloration, have been observed on any of the test objects to date due to its presence. An automated timer and NASA designed and constructed controller on the system allows the cleaning to proceed over a desired timeframe unattended and will turn the system off if a loss in vacuum, water cooling to the pumps and power supply, or drop in plasma intensity is detected.
2.3 Monitoring/Assessment

Monitoring and assessment of the treatment process was performed by removing the canvases from the vacuum chamber and measuring the diffuse reflectance from selected portions of the test objects in air at periodic intervals in the cleaning process. 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 hit the surface of a painting at roughly a 45 degree angle. A photodiode detector was placed near the light source. The equipment was placed in a dark room to minimize effects from stray light. 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 diameter so it was necessary to select areas from the test articles 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 could be determined by looking for a leveling off of the reflected light signal indicating that no further change is taking place.

3.0 Results and Discussion

3.1 Cleaning of Smoke Streaks from Gesso

The first test of the large area treatment capability was performed on a prepared canvas that had been streaked on the front and back with soot from a wax candle flame as described in section 2.1. Figure 1(a) shows the front side of the prepared canvas with smoke streaks prior to atomic oxygen exposure. After ~14 hr of cleaning in atomic oxygen, the smoke streaks were completely removed from the gesso surface as shown in figure 1(b). The rear of the canvas remained untouched as shown by the comparable photos of the back side of the canvas shown in figures 2(a) and (b). This demonstrated the ability of the system to uniformly remove soot over a large area and verified that the proximity of the back side to the plate would prevent atomic oxygen from arriving at the unprimed canvas on this side. Too long of an exposure of canvas directly to atomic oxygen can cause removal of the sizing and weaken it if not shielded from atomic oxygen arrival during cleaning. This has been observed with some long exposures of unprimed canvas. Light cleaning of the stretcher and canvas on the back side could be achieved with a short exposure to atomic oxygen at the start of the cleaning of the primed and painted side. This would be achieved by moving the stretcher farther away from the ground plate so that there would be a gap between the stretcher and plate of greater than an inch.

3.2 Cleaning of Roy Lichtenstein Ink Drawing on Paper

The Lichtenstein drawing proved to be a very difficult test subject for several reasons. Black ink typically contains a carbon pigment, so it was unknown whether the cleaning process could preferentially remove the soot without also removing the ink. Also, the paper appeared to have experienced thermal decomposition as evidenced by a dark yellowing and browning of the paper and an increased brittleness. Therefore, it would probably be difficult to remove this damage from the paper without weakening it.

Before attempting to clean the drawing, it was necessary to determine whether soot could be removed more quickly than ink. In order to test this, 1.9 cm wide stripes of various types of ink and watercolor were applied onto the surface of watercolor paper. A wide soot streak was also applied across the clean paper by passing it over the flame of a wax candle. The reflectance of light provided by a quartz halogen lamp, as described in section 2.3, was then monitored from each type of drawing medium and from the candle soot at various intervals during the atomic oxygen cleaning process. The resulting graph shown in figure 3 indicates that the candle soot is removed much more rapidly than the media tested and the soot coated paper is quickly brought back to near its original reflectance, as shown by the dashed and dotted reference line. All of the media tested experienced some loss of material after about an hour of cleaning, except for the Shellac filled ink, which appeared to be very durable. This ink probably contains inorganic pigment that would greatly slow down the loss of the carbon in the ink due to reaction with atomic oxygen.

Each soot deposit from a fire will be of different composition due to the nature of the fire and the types of objects burning around the artwork. Therefore it is difficult to accurately determine the reaction rate for a specific drawing or painting. Some careful testing of the surrounding objects such as a section of the frame, edge of the painting, and other nearby objects can give information about how long it will take to remove the soot.
deposit under the cleaning conditions that will be used. Eventually it is necessary to mask off all but a representative edge of the painting and expose this to atomic oxygen. This not only will give an estimate for the cleaning time, but will also help to assure that the pigments are safe for cleaning with atomic oxygen.

Because the ink samples tested appeared to be a little more resistant to oxidation than first believed, it was decided to first try to clean an exposed corner of the Lichtenstein drawing. This was in order to determine if the paper could be lightened and if the type of media used for this drawing could be cleaned without being removed. The Lichtenstein drawing was masked with a sheet of polyimide Kapton roughly 0.005 cm thick by laying the Kapton over the drawing so that an edge of the drawing was exposed and then taping the Kapton down to the matting around the drawing. Mylar or other polymer sheeting can also be used as long as it has been tested first to ensure that its reaction products will not transfer onto the painting surface as it oxidizes. An initial cleaning of ~12 min showed some lightening of the surface without affecting the ink areas as determined by visual inspection. The mask was then removed and the entire surface was cleaned for intervals of 12, 30 and 60 min. At this point, cleaning was stopped because it did not appear that the paper background could be lightened further without loss of some of the thinner ink features. At the request of the conservator, we did mask off the bulk of the ink areas and tried to further lighten the paper in the upper left corner of the drawing. We again used a Kapton mask, but rolled up the edges of the mask to create a graduated cleaning that would prevent sharp cleaning lines from appearing on the surface. Figure 4 shows the reflected light data from two areas on the paper that are being cleaned, one with a light smoke residue and the other which had a much heavier deposit. After a total cleaning exposure of about 300 min, there was no noticeable improvement in the drawing. The area still had a light yellow cast, which was most likely due to thermal damage of the paper. Figure 5 contains photographs of the Lichtenstein drawing before and after cleaning with atomic oxygen.

Some of the important lessons learned from the cleaning of this drawing were that areas could be successfully masked for cleaning without creating cleaning lines, and that ink and soot are removed at different rates.

3.3 Cleaning of Madonna of the Chair Painting

The “Madonna of the Chair” painting posed a different type of challenge (fig. 7). This work had experienced very heavy smoke damage and some thermal decomposition. Areas of the varnish were charred in appearance. Prior to treatment, several areas were chosen on the painting for reflected light measurement at selected intervals during cleaning in order to determine the endpoint of the treatment process. The upper and lower background areas were selected because these should remain relatively dark and approximately the same during cleaning. The Madonna’s garment was selected because it should clean to a higher level of reflectance than the background. The greatest contrast between the original and the treated piece was expected to be the reflected light from the infant’s leg. Cleaning would be considered complete when a change in the diffusely reflected light from these surfaces would no longer be measurable.

Figure 6 contains the reflected light data for the Madonna painting as a function of cleaning time. After ~350 hr, the majority of the darkened varnish was removed from the surface. There were still some thin streaks on the surface. The majority of these were removed after ~600 hr of treatment. Treatment was allowed to progress part of the way into the binder in order to remove the damaged portion as much as possible. This extent of cleaning was chosen for this painting because of the severe nature of the fire damage and the desire of the owners to bring the pigment back to the surface as much as possible. The process can be stopped earlier so as to minimize or prevent removal of the binder if desired. 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 the conservator from the Cleveland Museum of Art, a fine spray mist of Grumbacher aerosol Damar varnish was applied to fix the pigment to the surface. A brush was then used to apply a thicker coating of Winsor & Newton Damar varnish over the surface. Figure 7 contains photographs of the Madonna painting as received (fig. 7(a)) and after cleaning with atomic oxygen and application of varnish (fig. 7(b)). The details of the painting are now clearly visible.

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 dehydration shrinkage did occur, that the canvas, paint and stretcher shrunk 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. A risk assessment should be made prior to treatment in this manner in order to determine if the shrinkage of the base material and the medium are...
closely matched or not. Paintings on some types of wood may be more at risk. This technique has typically been used to restore severely damaged objects, so the benefit of being able to salvage it has been much greater than the risk of shrinkage.

Removal of all of the varnish on the surface, and the top layer of binder material is not necessary in all cases. Some fire damaged works, however, may require extreme cleaning to be able to restore them so that they can be enjoyed again. 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 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 layer. A representative corner or edge 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 pigments will experience oxidation and removal so care must be taken during cleaning to minimize their loss. 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 previously unrestorable art to be salvaged. Further testing of this cleaning technique is being conducted to determine its effectiveness for cleaning smoke damaged acrylic paintings and watercolors.

4.0 Conclusions

Atomic oxygen treatment has been shown to be able to effectively remove soot and charred varnish from a full size oil painting and to be able to partially clean a fire damaged ink drawing on paper. Masking techniques can be used to treat one area more extensively without leaving visible cleaning lines. Treatment can progress at the discretion of the conservator from light surface cleaning, to more extensive removal of fire damage. In some cases it may be necessary to remove some of the paint binder. This would leave the pigment loosely bound on the surface. The pigment can be rebound by using a fine spray mist of a material of the conservator’s choice. When cleaning, it is important to verify that the materials present in the art work are safe for atomic oxygen cleaning by cleaning a small representative edge or corner first prior to treatment of the entire painting. This technique appears to have great potential for removing soot and char from the surface of art damaged during a fire and may 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.

5.0 References

Figure 1.—Gesso surface showing candle soot streaks prior to (a) and after (b) cleaning with atomic oxygen. (Small circles on the canvas were polymer disks used to measure atomic oxygen arrival).
Figure 2.—Back side of the gesso showing candle soot streaks prior to (a) and after (b) cleaning with atomic oxygen (Back side was against the ground plate during cleaning allowing shielding to occur).
Figure 3.—Reflected light at 900 nm wavelength from the surface of soot and various inks as a function of atomic oxygen cleaning time.

Figure 4.—Reflected light at 900 nm wavelength from the surface of light and dark smoked regions in the upper left corner of the Lichtenstein as a function of atomic oxygen cleaning time.
Figure 5—Lichtenstein untitled ink on paper prior to (a) and after (b) cleaning with atomic oxygen.
Figure 6.—Reflected light at 900 nm wavelength from selected areas of the Madonna of the Chair painting as a function of atomic oxygen cleaning time.
Figure 7.—Madonna of the Chair painting prior to (a) and after (b) cleaning with atomic oxygen.
# Atomic Oxygen Treatment as a Method of Recovering Smoke Damaged Paintings

## Abstract

A noncontact technique is described that uses atomic oxygen, generated under low pressure in the presence of nitrogen, to remove soot and charred varnish from the surface of a painting. The process, which involves surface oxidation, permits control of the amount of surface material removed. The effectiveness of the process was evaluated by reflectance measurements from selected areas made during the removal of soot from acrylic gesso, ink on paper, and varnished oil paint substrates. For the latter substrate, treatment also involved the removal of damaged varnish and paint binder from the surface.

## Subject Terms

- Treatment: Atomic oxygen; Smoke damage; Painting; Acrylic gesso; Ink on paper; Oil painting

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