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ANALYSIS AND TREATMENT OF A PAINTING BY KEES VAN DONGEN: FTIR AND ELISA AS COMPLEMENTARY TECHNIQUES IN THE ANALYSIS OF ART MATERIALS

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Recent examination and treatment of the Worcester Art Museum's Reclining Nude, c. 1925, oil on canvas, by the Dutch-born Fauve artist Kees Van Dongen (1877-1968) indicate that the artist used unorthodox materials and techniques, including selective varnishing to adjust color saturation and surface sheen. Examination also revealed resin-like beads exuded from unvarnished passages of paint considered artist-applied retouches. ATR-FTIR micro-spectroscopy of the exudate suggests the presence of gum arabic and sucrose, two common components in watercolor formulations. In order to verify the presence of gum arabic in the exudate, a newly developed ELISA protocol was used, which confirmed the presence of gum arabic. This may indicate that the artist modified his oil paint with gouache or watercolor, ultimately resulting in phase separation and subsequent beading up of water-soluble components from within the paint's predominantly oil component. The identification of water-soluble materials within an otherwise non-water-soluble paint surface proved critical in formulating an appropriate cleaning approach. Although the exact cause of the exudate is debatable, it serves as a cautionary note for conservators faced with the challenge of treating paintings by Van Dongen.

1 Introduction

Kees Van Dongen, born in 1877 outside of Rotterdam, the Netherlands, is known primarily for his erotic depictions of the female figure and, later in his career, portraits of the fashionable Paris elite. During his training of 1892 to 97 at the Royal Academy of Fine Arts in Rotterdam, he was drawn to the city's red light district where sailors and prostitutes were his main subjects. In 1897, he moved to Paris where he became established as a member of the *Fauve* movement in 1905/6. His work of the 1920s, considered to be the best of his career, shifted towards Expressionism, while his late work took on a more commercial appeal. He died in Monaco in 1968.

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Figure 1: Kees Van Dongen, Reclining Nude, c.1925, oil on canvas, 81 x 101 cm, 2003.76, from the Estate of Mrs. Manuel Berman as a gift of Mr. and Mrs. Manuel Berman, Worcester Art Museum. Before treatment.

In 2003, Van Dongen's *Reclining Nude* (Figure 1) that depicts Marcelle Rageout, the sister-in-law of the French film director Jean Cocteau was donated to the Worcester Art Museum. In order to answer questions regarding the artist's materials and techniques that arose during the course of the painting's treatment, technical analysis was done. Comparative information was drawn from visual examinations of a number of works by the artist, as well as a technical examination of a portrait from the same period in the Stedelijk collection, Amsterdam.

Reclining Nude conforms to the working methods seen in many other paintings by Van Dongen. Generally he blocked in the figure first, worked the drapery or background around it and incorporated exposed ground into the design. In contrast to flat expanses of color, he used thick applications of paint and localized varnish to emphasize certain features. Van Dongen's use of localized varnish applications presented conservators with the challenges of identifying and preserving these final aesthetic choices regarding surface sheen.

Although previously restored and coated with a thin restorer's wax overall, remnants of discolored varnish were visible on selected areas of *Reclining Nude*. An unusual bead-like exudate was also observed in discreet passages associated with anomalous paint applications. These exudate-containing passages posed questions regarding their composition and origin.

The challenge of analyzing the exudate that was associated with localized paint applications led to a novel pairing of Fourier transform infrared (FTIR) microspectroscopy with the immunological method known as enzyme linked immunosorbent assay (ELISA). This complementary pairing builds on the ability of FTIR to characterize many analytes according to the larger groups of compounds to which they belong, such as proteins or carbohydrates. Findings from FTIR analysis are then used to direct the course of analysis involving ELISA, an antibody based assay that can identify and quantify unique molecules in complex mixtures of analyte.

In the related fields of archeology, forensic science, and biodeterioration,[1-20] applications of immunological methods have received increased attention over the last several years. However, in the field of art conservation, these methods have received comparatively little attention.[21-27] Immunological methods utilize the high binding specificity that antibodies have to their respective antigens (target molecules). In the context of an animal's adaptive immune response, antibodies form a key line of defense against pathogenic organisms such as viruses, fungi, bacteria, or vaccines by recognizing macromolecules commonly composed of proteins, carbohydrates, or nucleic acids. Selective production of antibodies against a specific antigen is possible by introducing the antigen into a host species in a form that elicits an immune response. The antibodies produced by the host species can then be harvested from the host serum as antigen specific polyclonal antibodies, alternatively host spleen cells can be immortalized to secrete antigen-specific monoclonal antibodies.[28] Due to the extreme sensitivity of ELISAs, they can be used with small sample sizes, while detecting target molecules in the picogram or even femtogram/ml range.

2 Materials and Methods

2.1 Cross Section Analysis of Surface Coatings and Exudate from Reclining Nude

Samples were mounted in polyester resin Bio-Plastic (Ward's Natural Science, Rochester, NY) and polished in cross section using a series of increasingly finer grades of micromesh (Micro-Surface Finishing Products Inc., Wilton, IA). The mounted sample was examined with an Olympus BX50 polarized light microscope (Olympus, Center Valley, PA) equipped with multiple light sources including a 100W mercury short arc lamp for examining samples under ultraviolet epi-illumination. Photomicrographs were obtained using a 5.0 megapixel Olympus Q-Color5™ imaging system with FireWire™ IEEE1394 digital interface (Olympus).

2.2 FTIR Analysis of Surface Coatings and Exudate

Samples were removed by scalpel while viewing the painting under magnification. Each sample was examined using an Olympus BX50 polarized light microscope and then analyzed using an IlluminatIR™ infrared microspectrometer (SensIR, now Smiths Detection, Danbury, CT), specially designed to interface with conventional microscopes such as the Olympus BX50. The optics and electronics of the IlluminatIR's FTIR spectrometer are contained in a compact enclosure that is mounted between the microscope frame and the observation tube mount. The IlluminatIR™ is equipped with an MCT (mercury telluride, cadmium telluride) detector and interchangeable objectives including a contact attenuated total reflectance (ATR) objective with zinc selenide focusing crystal and diamond ATR window, and a 10X infinity corrected objective for normal viewing in transmitted or reflected light.

For FTIR, the samples were placed on a low E-glass slide (Smiths) and pressed out using the contact ATR objective. FTIR analysis included 64 scans in the 4000–650 cm^{-1} region at a resolution of 4 cm^{-1}. Spectra were captured in absorbance mode, spectral processed according to a 1^{st} derivative absolute value and searched against a number of spectral libraries, including the IRUG Spectral Database Edition 2000. Spectral software included QualID 2.51(Smiths Detection), as well as GRAMS 7.01 and Spectral ID 3.02 (Thermo Galactic, Waltham, MA). Through reduced aperture spot measurements, FTIR analyses of specific regions within the exudate sample were possible.

2.3 Analysis of Surface Exudate Using ELISA

Surface exudate was analyzed using an ELISA assay. In the ELISA method used for this research the antigen assayed was directly adsorbed to a solid phase (plate well wall). Three monoclonal antibodies developed by the Complex Carbohydrates Research Center (CCRC) (University of Georgia, Atlanta, GA) that recognize specific arabinogalactan proteins and plant gums, were used as primary detecting antibodies: 1) JIM13, a rat monoclonal IgM; 2) JIM19, a rat monoclonal IgM; and, 3) MAC265, a rat-monoclonal IgG2a. As a means of amplifying the detection signal, biotin-conjugated species and isotype-specific secondary antibodies were used. The biotin complex was later incubated with strepavidin-alkaline-phoshatase (SA-AP) an enzyme capable of producing colorimetric results when reacted with the substrate 4-nitrophenyl phosphate (pNPP). Qualitative and quantitative data for the sample was obtained using a spectrophotometer to measure the optical density values of each well at specific wavelengths. A serially diluted standard of a known antigen was used to assess each detecting antibody's sensitivity and specificity. The optical density of the standard and unknown was compared in order to quantify the target molecules in the sample solution.

Approximately 0.2 mg of exudate sample was collected in a micro-centrifuge tube with the aid of a stereomicroscope and scalpel. The sample was allowed to dissolve for three days in 1 ml of elution buffer (50 mM Tris-HCl, 50 mM EDTA, 10 MM dithiothreitol, 8M urea, 0.1% SDS, pH 7.6). The sample solutions were periodically vortexed to encourage complete dissolution. After the three day elution period, 100 µl of the sample elution was added to 1400 µl of plating buffer (0.1 M sodium carbonate, pH 9.2) and vortexed in a micro-centrifuge tube for approximately 3 s. A series of 10-fold dilutions of the unknown sample were made in plating buffer and 100 µl aliquots plated in triplicate onto Nunc Maxisorb 96-well plates (Thermo Fisher Scientific, Rochester, NY). A standard consisting of gum arabic (Sigma, St Louis, MO) was prepared in a similar manner by adding 5 mg of gum arabic into 1 ml of elution buffer, allowed to dissolve for three days, diluted down to concentrations of 20, 4, 0.8, and 0.16 ng/100 µl, and plated in triplicate for use with each antibody. Some wells were left free of antigen in order to determine the background signal for each antibody.

The plate was incubated overnight at 4 °C, emptied and washed 3X by adding 200 µl of washing buffer (0.02% Tween in 1X PBS) to each well. After washing, 200 µl of 2% agamma horse serum (Omega Scientific, Tarzan, CA) in 1X PBS was added to each well as a blocking buffer, incubated for 1 hour at 37 °C, plates emptied and 100 µl of a 1:50 dilution of the primary antibody JIM13, JIM19, or MAC265 in 1X PBS with 0.2% Tween 20 added. After incubation, the plates were washed 5X with wash buffer and 100 µl of a 1:2000 dilution of biotinylated rabbit anti-rat IgM secondary antibody #61-9840 (Zymed Laboratories, Inc. South San Francisco, CA) was added to rows previously incubated with JIM13 or JIM19, and 100 µl of a 1:2000 dilution of biotinylated goat anti-rat IgG #R40015 (CALTAG™ Laboratories, now part of Invitrogen, Carlsbad, CA) was added to rows incubated with MAC265. After one-hour incubation at 37 °C, the plate was washed 5X and 100 µl of a 1:1000 dilution of strepavidin-alkaline-phoshatase (SA-AP) was added to each well for one hour at 37 °C.

Plates were washed 5X and developed by adding 100 µl/well of a 1 mg 4-nitrophenyl phosphate disodium salt (Sigma)/ml 1M diethanolamine (Sigma), 0.5 mM $MgCl_2$, pH 9.8. After 30 min, each well was fixed by adding 100 µl of 3M NaOH. The plate was then read by a SpectraMAX 250 spectrophotometer (Molecular Devices, Union City, CA) at a wavelength of 405 nm. Background levels for each antibody were measured from the wells left free of antigen in the initial plating step and the average subtracted from the optical density values obtained for all other wells.

3 Results and Discussion

3.1 Van Dongen's Approach to Varnishing

Like many of his contemporaries desirous of a matte surface sheen, Van Dongen generally left his paintings unvarnished. In some cases however, as a means for achieving a particular effect, he chose particular areas of thickly painted highlights on flesh, jewelry or drapery for selective varnishing. One notable example, *The Countess de Noailles* from 1931 in the Stedelijk Museum, has localized applications of varnish on portions of the thickly painted drapery, jewelry and arms of the figure. This painting has not been cleaned, and therefore, the artist's original surface is considered intact (Figures 2 and 3).

Figure 2: Kees Van Dongen, The Countess de Noailles, 1931, oil on canvas, 197 x 132 cm, Stedelijk Museum

Consistent with observations made on *The Countess de Noailles*, evidence indicated that Van Dongen also selectively varnished areas on the textured paint surface of *Reclining Nude* (Figure 4). This varnish appears to have been limited to the highly textured white highlights of the bed sheets that discretely conceal portions of the

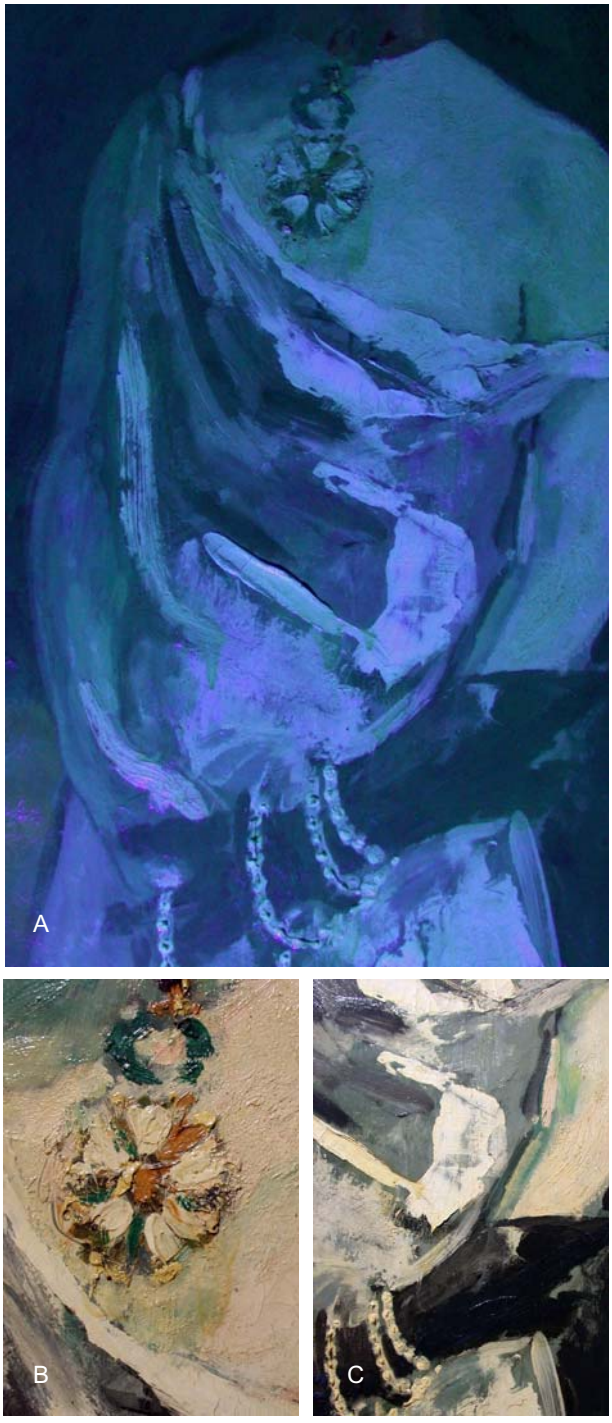

Figure 3: Details of The Countess de Noailles, as seen under UV illumination showing yellowish-green fluorescence of the natural resin varnish on necklace, bracelet, proper left forearm and drapery fold along proper right arm (3a); in reflected light, necklace ornament showing drips of discolored varnish (3b); localized varnish on proper left forearm pearl bracelet and drapery fold, in reflected light (3c).

Figure 4: Evidence of partial varnishing on Reclining Nude, detail of impasto showing remnants of yellowed varnish in the recesses of the textured brushwork.

woman's body. Using a stereomicroscope, examination of the surface of *Reclining Nude* revealed that only remnants of this varnish remained, most of it having been removed during a previous cleaning. In order to understand the artist's intent better, a diagram mapping out the distribution of original varnish was made. This information was used as a guide by the conservator during the restoration when making decisions about the surface sheen of the picture.

3.2 Analysis of Surface Coatings

A small sample of paint with surface coatings was removed by scalpel from an area of white highlight on the bed sheet in *Reclining Nude*. Cross section analysis revealed two thin coatings on the surface: the uppermost coating is non-fluorescent under UV epi-illumination and shows evidence of ingrained grime; the lower coating is strongly auto-fluorescent and is likely a thin remnant of a natural resin varnish that was partially removed in a past cleaning (Figure 5). The paint layer appeared to consist of largely lead white oil paint.

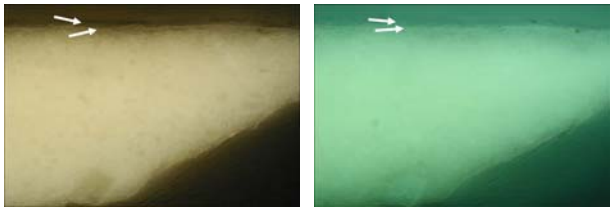

Figure 5: Photomicrographs of cross section sample from an area of white impasto on Reclining Nude, visible light (left) and ultraviolet epi-illumination (right) (20x objective used at capture)

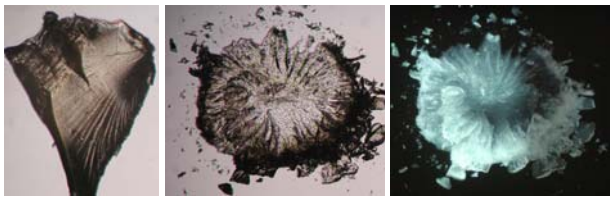

Figure 6: Varnish sample from The Countess de Noailles in transmitted light (left), after being pressed out with the contact diamond point ATR objective (center), and under ultra violet epi-illumination (right). (10x objective used at capture)

FTIR analysis was performed on a sample of surface coating from *The Countess de Noailles*. When pressed out with the diamond point ATR objective the sample shattered in a manner characteristic of a brittle varnish. When viewed under ultraviolet epi-illumination, the sample exhibited the type of strong fluorescence associated with an aged natural resin varnish (Figure 6). The IR spectrum for the same sample showed peaks consistent with a natural resin varnish, having a best spectral match to mastic resin (Figure 7).

FTIR analysis of a surface coating sample from *Reclining Nude* also produced a good spectral match for mastic, but with additional peaks associated with beeswax (e.g., peaks at 2918, 2850, 1737, 1172, and the small doublet at 730 and 719 cm^{-1}, Figure 7). This determination is consistent with observations made in cross-section analysis in which two different layers were identified: one fluorescent (mastic) and the other non-fluorescent (beeswax) (Figure 5). Solubility tests carried out directly on the paint surface were consistent with a multi-layered surface coating consisting of an upper layer of wax and a lower layer of natural resin varnish.

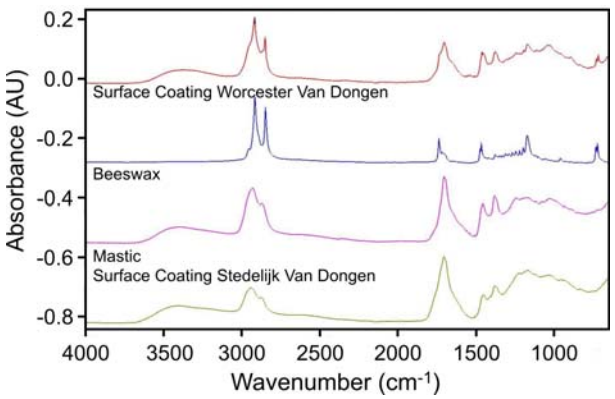

Figure 7: FTIR spectra for surface coating samples from both the Worcester (top) and the Stedelijk (bottom) paintings, along with reference spectra of beeswax and mastic resin.

By identifying a similar yet distinctive manner of distribution of the same natural resin varnish in the previously-cleaned *Reclining Nude* and the untreated *The Countess de Noailles*, it was reasonable to conclude that the use of localized applications of mastic varnish was a technique of Van Dongen's. The localized application of varnish to the paint surface suggested that the artist intended to enhance the luminosity of specific areas of textured highlights and passages of flesh by imparting a differential gloss to those areas. The unorthodox use of varnish in *Reclining Nude*, as well as the painting's subsequent treatment history, including partial cleaning and the application of a wax coating, presented significant challenges in developing a conservation treatment strategy sensitive to the artist's aesthetic intent.

3.3 Surface Exudate

Transparent beads of exudate were noted in a roughly one-inch square area of paint on the figure's mid-section and in a number of gray areas around the edges of the painting associated with the extension of the painted area after the dimensions of the canvas were enlarged (see boxes A and B in Figure 8). Under magnification, the exudate appears to have erupted from beneath the paint layer, causing fissures within the paint as it migrated towards the surface. In ultraviolet light, the paint associated with the exudate fluoresces in a manner characteristic of zinc white, distinctly different from the rest of the paint surface. The presence of zinc was confirmed by XRF analysis. Consideration of whether the paint was artist or restorer-applied was essential in determining a course of treatment.

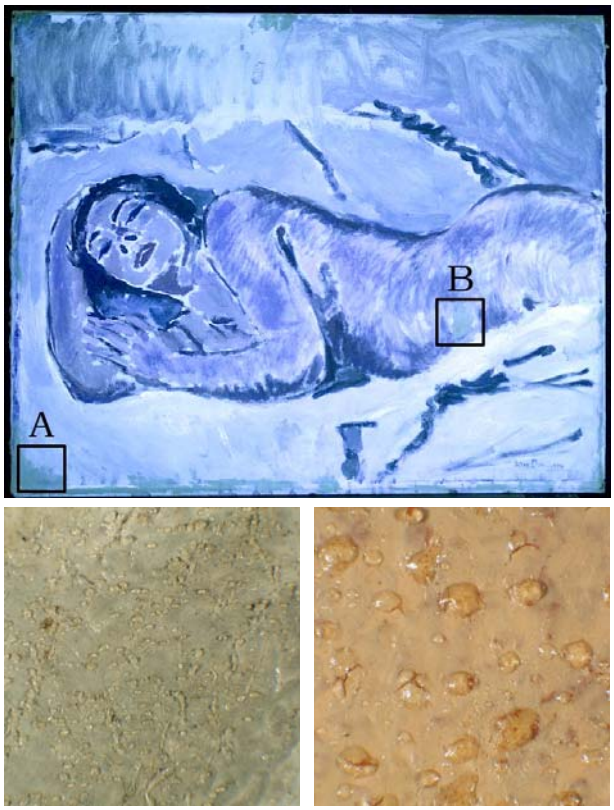

Figure 8: Reclining Nude under ultraviolet illumination with outlines of general location of photomicrograph of surface exudates found on gray paint and flesh tone (top). Photomicrographs of exudate in area A (left) and area B (right).

When viewed in visible light, the areas of paint with exudate have the same quality of brushwork seen in surrounding non-exudate bearing paint. Only two pinhead-sized paint losses near the bottom edge of the canvas were covered by the questionable paint, but their size was negligible compared to the total surface area of the application. Therefore, it seemed likely that the zinc white-containing paint was artist's revision, as opposed to a restorer's attempt to disguise damage.

Supporting evidence was needed to establish whether Van Dongen re-worked his paintings. Late in his career when Van Dongen had reached artistic acclaim, he was known to sell works from his own studio. In these circumstances, the artist had ample opportunity to rework his earlier, unsold works. A London-based conservator reported similar suspected areas of revision present on privately owned Van Dongen paintings that she had examined.[29] Based on the similarities in brushwork, as well as supportive evidence that Van Dongen likely reworked his paintings, a consensus was reached among conservators and curators to treat the questionable areas as artist revisions.

Questions remained as to the composition of the exudate, as well as the reason for its formation. Though analysis would help in answering these questions, it should also be mentioned that extended exposure to a non-climate controlled environment might have played a significant role in the latter. The painting previously hung on a North-facing exterior wall of a stucco clad New England home and accumulated a considerable amount of mildew on the backs of the frame and the canvas, indicative of sustained exposure to humid conditions.

3.4 Analysis of Surface Exudate

Using a stereomicroscope and moistened swabs, the solubility of a small portion of exudate on the paint surface was tested. The exudate proved sensitive to water and the associated fissures in the paint surface were prone to further disruption upon exposure. The water sensitivity of the exudate was

confirmed when a small sample placed on a glass slide and viewed under magnification was observed to dissolve when exposed to a drop of water.

3.4.1 Cross-Section Analysis

Cross section analysis of the exudate as it occurs in the paint surface reveals that a dark red paint composed of red and black pigments was painted over with a much lighter predominantly zinc white-containing flesh tone, presumably to adjust the modeling in this area, or perhaps even to mask a previous misplacement of the figure's navel (Figure 9). The sample clearly shows the exudate as a translucent material that formed within the upper paint layer and migrated up, out and onto the paint surface. In ultraviolet epi-illumination the

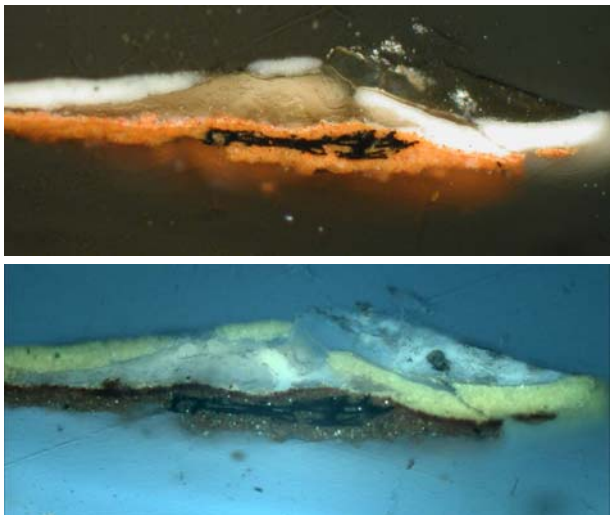

Figure 9: Photomicrographs of cross section of exudate containing paint layers in area of flesh as seen under visible light illumination (top) and ultraviolet epi-illumination (bottom, 20x objective used at capture)

exudate material shows areas of non-fluorescence and bluish-white fluorescence, whereas the zinc white pigments of the upper paint layer fluoresce a characteristic bright greenish-yellow.

3.4.2 FTIR Analysis

As with the varnish sample, a sample of the exudate was taken from the flesh area and viewed

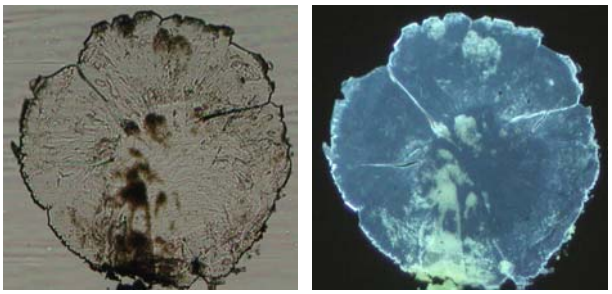

Figure 10: Sample of exudate - as seen in transmitted light (left) and (right) after pressing out (10x objective used at capture).

under the microscope in its pressed out state with both transmitted light and ultraviolet epi-illumination (Figure 10). The action of pressing out the sample revealed something about its material properties; as one might expect, it did not fracture on compression, but proved to be malleable.

The heterogeneous nature of the sample was clearly apparent when viewed in transmitted light, revealing a small amount of an opaque component within a largely transparent material. Under ultraviolet epi-illumination the two materials exhibited different qualities of fluorescence. The component that appeared opaque in transmitted light shows a distinctive greenish-yellow fluorescence under ultraviolet epi-illumination, characteristic of zinc white. The components that appeared transparent in transmitted light exhibit bluish-white fluorescence under ultraviolet epi-illumination.

The exudate sample was then analyzed using FTIR. An IR spectrum corresponding to the translucent component of the sample is shown in red at the top of the chart in Figure 11; the three reference spectra beneath it are suggested component parts of the exudate sample. The source of the sucrose is likely some type of syrup or honey, both common additives in watercolor paint formulations. Gum arabic is the traditional binding medium used in watercolor paint. And the presence of a fatty acid salt such as zinc stearate, or zinc palmitate, is proposed as a minor component accounting for the small peaks in the sample spectra at 2919 nm, 2851 nm, (from asymetric and symmetric CH_2 stretching respectively) and 1539 nm (from the asymmetric stretch of the COO- group). The presence of a carboxylate such as zinc stearate is likely from its direct addition in the original paint formulation (zinc stearate is a common gloss modifier in paints) or from a soap used to emulsify the gum arabic into the oil paint. An alternative explanation for the carboxylate being a metal soap[30,31] formed between zinc ions and free fatty acid degradation products of the surrounding oil paint (spectra for oil paint not shown) seems unli-

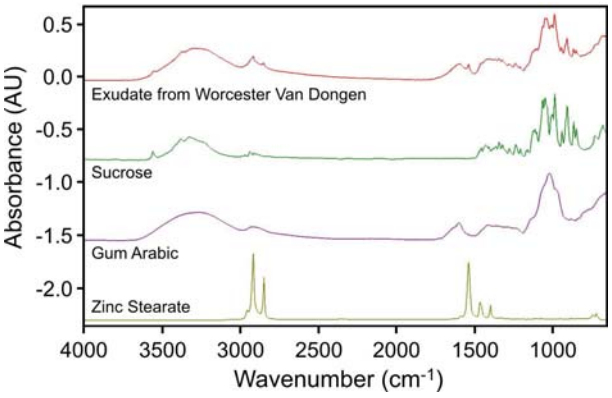

Figure 11: FTIR Spectral analysis of the exudate.

kely, particularly in light of the fact that gum arabic and sucrose appear to be the predominant materials present and that the painting is less than one hundred years old.

3.4.3 ELISA Analysis

The results from ELISA analysis of the exudate are shown in Figure 12. These results support the conclusion that a plant gum, likely gum arabic, is a major component of the exudate. A standard curve generated from JIM13 and gum arabic (Figure 13) was used to approximate the quantity of gum arabic in the diluted exudate sample solution. The JIM13 and JIM19 antibodies bind to a number of polysaccharides, gums and glycoproteins, some of which are common to both antibodies including gum arabic, the typical binding media for watercolor paints in western art. The MAC265 antibody binds to gum tragacanth, a glycoprotein commonly used as a binding media for pastels, but not to gum arabic. The specific epitope recognized by JIM13 in arabinogalactan and arabinogalactan proteins is β-D-GlcA-(1,3)-α-D-GalA-(1,2)-α-L-Rha.[32] The specific epitope for JIM19 is presently unknown, though it is known to bind to a periodate-sensitive epitope present on a 40 kDa polypeptide from pea, to a range of polypeptides 120-210 kDa, and to the exudate gums: arabic, ghatti, and tragacanth.[32,33] The specific epitope for MAC265 has yet to be determined.

Although there are other polysaccharides jointly recognized by JIM13 and JIM19, and not recognized by MAC265, different means were used to help narrow the field of possible candidates. FTIR analysis eliminated some possibilities, as did the unlikelihood of many of the candidates being found in art materials (e.g. lettuce RG-I, green tomato fruit RG-I, high acetyl sugarbeet-pectin, tomato pectic polysaccharides, tomato xyloglucan and tomato glucomannan). In addition, the proportional strength of binding signal between the two antibodies and the sample exudate helped in the process of elimination. Though various pectins are recognized by both JIM13 and JIM19, the strength of recognition is stronger for JIM19, which is opposite to the results for the exudate. Ghatti gum, a binder in watercolor paints, particularly in India and Sri Lanka, is recognized by both JIM13 and JIM19, however ELISAs including a dilution range of ghatti gum produced nearly equal signal strengths between JIM13 and JIM19.[34] Cherry gum, another tree gum at times used in artist materials, is recognized by JIM13, but not by JIM19.[34]

Though testing of JIM13's ability to recognize a wide range of plant gums and polysaccharides has been done,[25] ongoing tests with JIM19 may lend further clarity to the exact identity of the exudate by suggesting or ruling out other possibilities. Likewise, additional antibodies with alternative specificities could provide a greater degree of confidence in the results of this particular ELISA. For example, MAC204 (CCRC), which recognizes gum arabic but not ghatti gum could be used. Obviously, the choice of antibodies in such ELISA tests is critical, particularly with polysaccharides and glycoproteins where cross reactions are common and samples available for analysis greatly limit the number of tests that can be done. It is hoped therefore that, as more antibodies are made available through research such as that at CCRC, the options available to conservation scientists will improve.

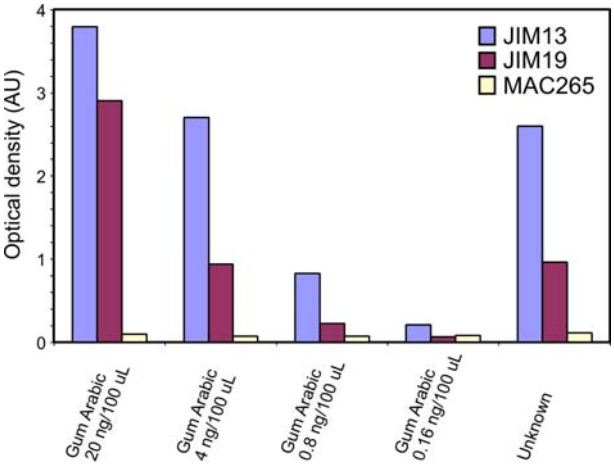

Figure 12: ELISA results of three monoclonal antibodies (JIM13, JIM19, and MAC265) with a dilution range of pure gum arabic and the unknown exudate sample. Samples shown are the average of triplicate samples.

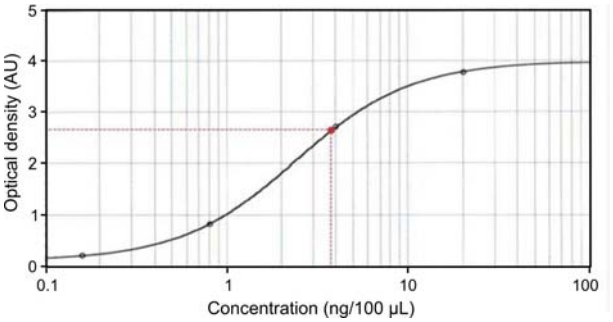

Figure 13: Standard curve generated from JIM13 antibody binding to varying dilutions of gum arabic. The x-axis is the concentration of gum arabic in units of ng/100 µL. The y-axis is the mean value of the three OD values obtained minus the background signal. Optical density was measured at 405 nm after a 30 min incubation period. When the corrected mean OD value from JIM13 on the unknown sample is plotted on the standard curve (shown in red), a concentration of just below 4 ng/100 µl of sample solution is obtained.

Figure 14: Reclining Nude as seen in raking light (before treatment).

Figure 15: Detail of tacking edge showing canvas loss at the stretcher corner.

Figure 16: Details during treatment showing the use of Gore-Tex® felt, moistened blotter paper, and applied weight to reduce deformations in the canvas (top) and the tacking edge after strip-lining with thin polyester monofilament and Beva film adhesive (bottom).

3.5 Treatment

3.5.1 Structural Treatment

As part of the larger conservation treatment of *Reclining Nude,* deformations in the canvas support were reduced and failing tacking edges reinforced. The canvas had pronounced bar marks from a cruciform stretcher and broad undulations that were most severe in the corners (Figure 14). Corroded tack heads had degraded the surrounding canvas on the tacking edges and caused the canvas to detach in places. Portions of canvas were missing altogether from the tacking margins (Figure 15) and small tears were at risk of propagating beyond the perimeter and into the picture plan.

Before cleaning the painting, it was first necessary to stabilize its structural weaknesses. The soiled and out of plane canvas was removed from its wood stretcher and cleaned on the reverse using a low-suction vacuum and dusting brush. After testing negatively for moisture sensitivity, canvas deformations were flattened by applying lightly dampened blotter paper on top of a Gore-Tex® felt membrane. After allowing humidity to reach the canvas, the introduction of weight was applied gradually. Gore-Tex®, which is designed to allow only water vapor to pass through its membrane, was used to ensure a higher degree of control over the amount of moisture introduced to the canvas.

Strip-lining the painting was done in a manner that maintained the upright folds of the tacking margins during the process. The lining fabric was a finely woven, polyester, monofilament fabric (PECAP), with a thread count of 330 threads per inch, which was thin enough to avoid imprinting its inside edge on the canvas from the verso. The strip-lining provided the dimensional stability and appropriate strength and length required for re-attaching the canvas to its stretcher (Figure 16).

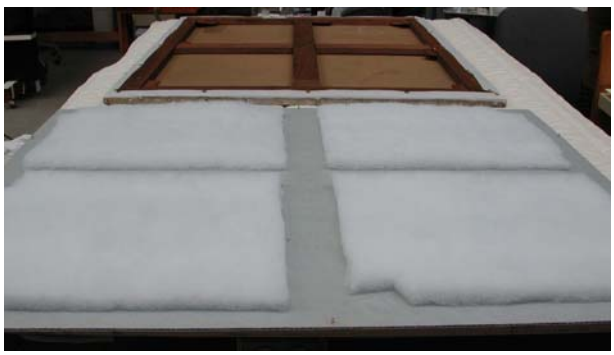

Figure 17: Acid-free backing board with attached polyester batting material (foreground) and the verso of Reclining Nude, face down on a sheet of silicon-coated Mylar® (Talas, New York, NY) and padded surface (background).

An acid-free blue board backing (Lineco, Inc., Holyoke, MA) was cut to size and fitted with polyester batting (Conservation Materials, Ltd., Sparks, NV). The purpose of the batting was to reduce canvas vibrations during handling by filling in the air spaces of the stretcher pockets. The batting was attached to the backing board using a novel technique developed by Klausmeyer that eliminated the need for less desirable methods of attachment involving sewing or adhesives.

The technique employed strips of hook-sided Velcro® tape (U.S. Slide Fastener) attached to the inner face of the backing board corresponding to the openings of the stretcher. Polyester batting was cut to fit, inserted into the stretcher pockets, and the tape-side of the backing board was lowered into place. By gently running one's hand over the outside surface of the backing board, adhesion between the batting and Velcro® was achieved. Before re-attaching the board to the back of the stretcher with brass screws and collars, it was removed and inspected to ensure that proper adhesion and alignment of the batting material had taken place (Figure 17). By providing added stability to the canvas at this stage of the treatment, the painting was also protected from any vibrations that might occur during the cleaning phase of the treatment.

3.5.2 Cleaning and Surface Treatment

Before treatment, the painting's surface included passages of exposed ground, thin and thickly applied paint, remnants of partial varnishing, an overall wax layer and surface grime. After a cleaning that likely took place before the 1960s, only traces of the original localized varnish remained; and, it is probable that the overall wax layer present on the surface was also applied at that time.

Tests showed that aqueous-based cleaning solutions enabled selective removal of the upper grime layer without disturbing the wax coating. Due to the water sensitivity of the exudate, a more appropriate cleaning system would need to be devised in order to preserve it. Curators and conservators evaluated the painting's appearance at each stage before proceeding to the next one.

A range of aqueous solutions was prepared and tested at different pH values, both with and without additions of different non-ionic surfactants, including Pluronic L 64 (BASF, Mount Olive, NJ) and Triton XL-80N (Sigma Aldrich, St. Louis, MO). Some of these solutions were successful at removing much of the grime, but a noticeable portion of grime remained intact. The chelating agent diammonium citrate was tested at different pH values starting at pH 5.5 and moving upward in small increments. Satisfactory cleaning results were obtained at pH 6.0, thereby working within the optimal range for an oil painting (Figure 18).

Figure 18: Detail showing removal of upper grime layer from an area on the right side of Reclining Nude.

Since the surface grime above the exudate was the same as elsewhere on the painting, an emulsion was made consisting of a small amount of the above aqueous solution emulsified into a continuous phase of aliphatic hydrocarbon solvent (Shell Sol 340 HT, Shell) using Pluronic L64, a non-ionic surfactant consisting of block co-polymers of ethoxylate and propoxylate (BASF). This approach allowed for minimal use of the aqueous cleaning solution, while simultaneously limiting its exposure to the water sensitive paint surface. Cotton swabs were used to remove the vast majority of the cleaning emulsion from the newly cleaned surface, and then the areas were allowed to air dry. The surface was rinsed again with Shell Sol 340 HT to ensure clearance of the surfactant. Microscopic examination of the water sensitive surface exudate after cleaning showed no disruption of the exudate.

Though considerable visual improvement was gained through overall grime removal, the wax coating imparted an inappropriately glossy and uniform surface sheen. Due to its discoloration

Figure 19: Detail showing area before and after cleaning with solvent gel.

and imbedded grime the wax also compromised the appearance of the painting. A method for removing the wax coating had to meet the following criteria: 1) it had to effectively and safely remove the wax; 2) the integrity and luster of the paint had to be preserved in a consistent and overall manner; and 3) the wax had to be removed while preserving the varnish remnants that remained in areas where the artist had selectively applied it.

A solvent gel mixture consisting of 225 ml of Shell Sol 340 HT, 75 ml of isopropanol, 35 ml of Ethomeen C12 (Museum Services Corp, Burnsville, MN), 4 g of Carbopol 934 (Talas), and approximately 7 ml of deionized water was the most effective cleaning method that met the first two criteria (Figure 19). To preserve the remainder of the artist's varnish, a 300 ml Shell Sol 340 HT gel was used. Though slower to take effect, this variation removed the wax layer while preserving the underlying varnish remnants.

After removal of the grime and wax layers, curators and conservators reached a consensus on the relative merits of preserving or removing the degraded varnish. Although original, the discolored remnants were removed since they were distracting and no longer served the artist's original purpose. The conservator proceeded by documenting its location and then removing it using the 1 part isopropanol, 3 parts Shell Sol 340 HT gel mentioned above.

Those areas identified as once possessing localized varnish applications were subsequently re-varnished with a thin application of Regalrez 1094 synthetic varnish (Eastman Chemicals, Jefferson, PA). Since much of the varnish had been removed in a previous treatment and the extent of the original varnish therefore was unknown, the objective was to impart a change in the surface sheen from the surrounding matte paint.

4 Conclusions

Technical analyses of *Reclining Nude* played a crucial role not only in understanding the artist's materials and techniques and establishing the nature of earlier restorations, but also in determining appropriate strategies for treatment. By removing the accumulated grime and overall wax coating, curators and conservators were better able to approximate the painting's original surface properties, which incorporated selectively varnished passages within a larger field of unvarnished paint. Technical examination of *The Countess de Noailles* carried out in conjunction with that of the Worcester painting also helped to inform the treatment. Most notable was the decision to remove and replace localized areas of varnish and reinstate what is believed to be an intended variation of surface sheen.

Based on the physical appearance of the paint surface and the fact that gum arabic and sugar (or honey) are common ingredients in watercolor and gouache paint formulations, it seems likely that the exudate on the surface is either the result of the artist's attempt to combine otherwise immiscible paints in order to achieve specific aesthetic properties, or the result of poorly formulated commercial paint. A possible scenario in support of the former explanation is that Van Dongen may have modified his oil paint with a substantial amount of gum-based paint in order to create a more matte quality to his revisions, perhaps in an attempt to correspond more closely with the unvarnished surface appearance of the original, slightly aged oil paint surface. The unstable nature of the formulation was exacerbated when the painting was kept in an uncontrolled environment, accelerating the separation of the gum component and causing it to migrate toward the more polar surface/air interface.

This research also shows the combined strengths of both FTIR microspectrometry and ELISA to be more effective in identifying unknown materials than FTIR alone. In the case of the exudate material from the Van Dongen painting, the complementary pairing of FTIR and ELISA helped researchers move from a general identification of the presence of a polysaccharide to a more specific determination of the type of polysaccharide. The same potential exists for proteins; whereas FTIR can typically only indicate that a protein is present in a sample, ELISA can be used to determine the specific type (or types) of protein present.

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