Stain removal on ivory using cyclododecane as a hydrophobic sealing agent

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〈ABSTRACT〉

Stain removal on ivory has been, for a long time, considered an undesirable treatment in conservation field because ivory is hygroscopic and anisotropic, having different physical properties in different directions. Cyclododecane, which sublimes at room temperature, has been investigated for its use in conservation field since 1995, as a reversible temporary consolidant, sealing agent or coating, water repellent, and barrier layer. This research aims to remove stains on ivory, temporarily protecting the none-stained area or painted area from methanol, acetone or the aqueous cleaning system using cyclododecane as a hydrophobic sealing agent. This research also aims to obtain information regarding whether cyclododecane can be safely and effectively used on archaeological wet ivory. Melted cyclododecane and saturated solutions of cyclododecane in mineral spirits, and hexanes were applied to ivory samples. Application methods, working properties of cyclododecane on ivory, and effect of cyclododecane coating on moisture content of wet ivory were evaluated.

The sealing layer formed by molten cyclododecane or by saturated cyclododecane solution in hexane or saturated cyclododecane solution in mineral spirits did not form a secure contact with the surface of the highly polished ivory. The sealing formed with two different layers, in which saturated cyclododecane solution in hexane was applied initially and then molten cyclododecane was applied over the first layer, was found to securely protect the painted area. When the wet samples were kept in 100% RH environments for a month, active mold growths were observed except in the samples sealed with molten cyclododecane. In conclusion, cyclododecane was an efficient hydrophobic sealing agent to protect painting area while cleaning stains on ivory. It also prevented mold growing on wet ivory and wet bone.

Evenness of cyclododecane film on ivory will be determined in UV light. Analytical techniques will include visual observation, polarized light microscopy, Scanning Electron Microscope, and Gas Chromatography.

〔주제어〕 ivory, bone, cyclododecane, treatment, conservation, mold

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Chapter Ⅰ: Introduction

1. General introduction

Ivory from animal tusks has a long history of use in utilitarian and art objects throughout the world since antiquity. The sources of these ivories are mammoths, male and female African elephants (Elephas africanus), male Indian elephants (Elephas maximus), hippopotamuses (Hippopotamus amphibus sp.), boars (warthog of South Africa), walruses, sperm-whales, and narwhals. Odontolite[1)] or fossil turquoise[2)] is blue mammoth ivory, which has fossilized and is used for costume jewelry. True ivory, however, comes only from the tusks of ancient and modern elephants.

Ivory and bone are both anisotropic i.e., having different physical properties in different directions. Accordingly, ivory tends to warp with fluctuations of humidity and temperature. Ivory becomes porous and brittle with age, losing organic material, fat, and moisture. Because of its porosity and light color, ivory has good surface penetration and therefore stains easily. This property allows ivory to be stained deliberately or painted for decorative purposes but causes a problem since ivory tends to take up the color of its environment. If it is in contact with ferric oxide for a length of time, ivory will be stained golden brown. Since ivory becomes brittle and cracks on the surface with age, early craftsmen rubbed vegetable oils into the surface to prevent cracking. As the oils oxidized, the surface changed to a red brown color.

Removal of stains on ivory, like those on bone, has not been highly recommended, because both aqueous and non-aqueous treatment may damage the structure and texture. When aqueous cleaning treatment is inevitable because of dirt on the surface, the treatment should be done as quickly as possible. Ivory objects must not remain in contact with any aqueous solution for more than necessary. For this reason, removing stains from ivory has been difficult in the conservation field for a long time.

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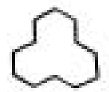
1) Odontolite means literally tooth-stone from Greek.
2) They are stained in brilliant turquoise blue colors as the result of being buried near mineral deposits.

Cyclododecane, which sublimes at room temperature, was first introduced in the field of conservation in 1995.[3] Since then, numerous experiments and practices have been carried out on paintings, sculptures, paper, textiles, glass, wooden objects, metal objects, and ceramics using cyclododecane as a reversible temporary consolidant, sealing or coating layer, and a water repellent.



Cyclododecane ($C_{12}H_{24}$)

Cyclododecane is very useful, non-toxic and does not leave any residue after sublimation. The most important characteristic of using cyclododecane is that its application is easily reversible without additional use of chemicals. Previous research on the use of cyclododecane has been approached from several perspectives: how to apply it, whether in melted form or in solution; if used in solution, what kind of medium to used; what the period of sublimation from objects is; and the possibility of residue on objects after sublimation.

This research aims to study the use of cyclododecane as a hydrophobic sealing agent to remove stains on ivory, temporarily protecting the non-stained area or painted area from methanol, acetone or the aqueous cleaning system. This research also aims to obtain information regarding whether cyclododecane can be safely and effectively used on archaeological wet ivory.

2. Historical background of ivory use

Throughout the ancient world, ivory was a precious art material used in jewelry, furniture and sculptures. Craftsmen in the Paleolithic Age used mammoth ivory to make beads, pendants and bracelets. Elephants in ancient time were found in many geographic areas. Not only imported ivory from Africa or India but also domestic ivory was available in many areas. Early Chinese ivory objects, like early bronze vessels, appeared to be used for ritual purpose.

3) E. Jägers et al., Volatile Binding Media Useful Tools for Conservation, *Reversibility Does It Exist? British Museum Occasional Paper,* No. 135 (London, British Museum:1999): 37.

In Egypt, ivory craftsmanship was highly developed. Ivory was used for luxury items and an important decorative material. Ivory was said to contribute greatly to the impression of immense wealth of the pharaohs.[4] Polychrome ivory originated from Egypt, dated back to as early as 1325B.C. Since then, many ivory objects have been not only beautifully carved but also colorfully painted and gilded. In Imperial Roman times,[5] ivory relief carving became one of the significant art forms. Sometimes ivory objects were stained to give depth to the carving. In the Gothic period, three-dimensional figurine carving was predominant. In the Baroque period, a variety of carving and decorative techniques were applied on ivory. Watercolor painting on ivory was popular in the 18th and 19th centuries for portrait miniatures.[6] In the middle of the 19th century, ivory came to be used more for industrial purposes than for artistic purposes, for example, for piano and organ keys, billiard balls, chess sets, surgical tools, and cutlery and umbrella handles. For the finest quality of musical instruments, ivory was used to make thin slabs for keys. The thicknesses of the slabs were 1/8 inch for organ keys, and 1/12 to 1/16 inch for the best piano keys,[7] and 1/22 for low priced instruments. The slabs were usually bleached under sunlight or by chemicals. Sometimes, they were not bleached but were polished with whitening and rubbed with French polishing.

Most ivory objects may have been subjected to smoothing and polishing for their final appearances. From shark or squid skin to vegetable oil, various materials have been used since ancient time.[8] Ivory objects may also have been subjected to finishing operations with lime, wood ash, calcined pumice, and oil of turpentine, often under sunlight. Further finishing treatments, including bleaching and degreasing processes, were often conducted in order to prepare ivory for painting and gilding.

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4) M. Vickers et al., *Ivory: A History and Collector's Guide* (London: 1987): 36.
5) M. Vickers: 52-64.
6) J. Murrell, Structural Defects in British Portrait Miniatures, *Conservation Today* (1988): 72-74.
C. Krisai-Chizzola, A large Ivory Miniature: Conservation Problems of the Support, *ICOM Committee for Conservation, 10th Triennial Meeting* (Washington, DC: 1993): 690.
7) A. Maskell, Ivory, in Commerce and in Arts, *Journal of the Society of Arts* (Nov. 1906): 1176.
8) E. Cristoferi, et al., Polishing Treatments on Ivory Materials in the National Museum Ravenna, *Studies on Conservation* 37(1992): 259.

3. The structure of ivory

The tusks are the elephant' s enlarged incisors of the upper jaw (fig. 1). The very center of the tusk is hollow to accommodate a large central nerve, running about half the length of the tusk. Like a tree trunk, ivory is built up in concentric growth circles and its cross section tells its age. The tusks are built up in thin layers of dentin, giving ivory its distinctive cone-in-cone[9] or laminated structure. The outer surfaces of the tusk are not coated with enamel but are covered with a bark-like coating, “cementum”, which is similar in density to ivory and is difficult to peel off (fig. 2). Elephant ivory in transverse section has striations arranged in arcs,[10] which is one of the best diagnostic characteristics for identification. In longitudinal sections, elephant ivory has straight lines with white and more opaque long, thin, parallel milky areas in between the lines. In ivory, compared with bone, the lacunae are finer and lighter in color and the dentine is dense. Ivory has a more closely packed structural appearance than bone.

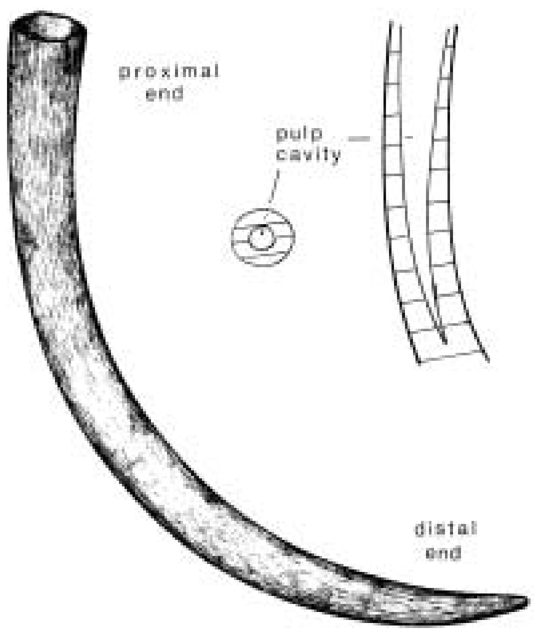

Fig. 1 Elephant tusk, showing principal features.
(Form Ivory and Related Materials)

9) O. Krzyszkowska, *Ivory and Related Materials* (London: 1990): 34.
10) This is the diamond pattern or ‘engine-turned decussating appearance’ created by the intersection

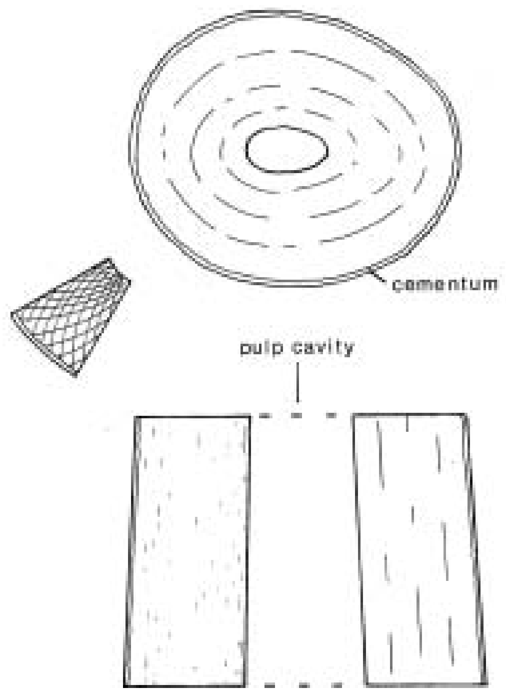

Fig. 2 Elephant ivory, sections. Above, transverse section showing lines of Owen: below, longitudinal section showing pattern of lamellae (left) and lines of Owen (right). Inset, part of a transverse section showing lines of Retzius. These may be seen on sections cut at an angle to the main axis of the tusk but ara most noticeable toward the perihery where the 'diamonds' are larger.
(Pictures from ivory and Realated Materials.)

Ivory and bone are composed of both organic and inorganic materials. The inorganic material (60%), consisting of phosphorous, calcium, and magnesium, is known as hydroxyapatite, a calcium hydroxy phosphate $Ca_{10} (PO_4)_6 (OH)_2$. Considering that biological phosphates contain up to 5% carbonate, a more correct composition of the inorganic material is $Ca_{10} (PO_4)_6 (CO_3) H_2O$.[11)] The organic material (about 40%) is mainly collagen and small

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of dentinal tubules radiating in clockwise and anti-clockwise arcs from the center of the tusk. See O. Krzyszkowska, *Ivory and Related Materials* (1990: London): 34. Also, E. O. Espinoza et al., "The History and Significance of the Schreger Pattern in Proboscidean Ivory Characterization," *JAIC* 32(1993): 241-48.

11) I. M. Godfrey, et al., "The Analysis of Ivory from a Marine Environment, *Studies in Conservation* 47(2002): 30.
L. J. Matienzo, et al., The Chemical Effects of Hydrochloric Acid and Organic Solvents on the Surface of Ivory," *Studies in Conservation* 31(1986): 133.

amounts of lipids, which exist within the inorganic matrix. Collagen is composed of a tropocollagen unit, in which three polypeptide chains (glycine, proline, and hydroxyproline) are wrapped in a helical conformation.

Fresh African elephant ivory is finer grained and has a distinctively brilliant, pale blonde transparency[12]. With age, it becomes increasingly whiter. Indian elephant ivory is usually softer, denser and more opaque white. Fresh Indian ivory is a creamy color with a mellow sheen.

The distinctions between hard and soft ivory are difficult to define. Soft ivory contains more moisture and resists fluctuations of climate and does not crack easily. Hard ivory has been more used because it is less expensive than soft ivory. The hard ivory is used for fancy brushes and toilet ware, for cutlery handles, for second quality piano keys and for billiard balls. Hard ivory is glassy and transparent.

4. Conservation of ivory

4.1. Cleaning and Stain Removal

Ivory objects considered for cleaning should always be in reasonably good condition. The type of stain must be carefully examined to determine whether the stain was a deliberate application.

Hydrogen peroxide (H_2O_2) with or without a few drops of ammonia[13] has frequently been used to bleach stains on ivory. The treatment is, however, considered to damage the structure of ivory.

Ethanol, acetone, mineral spirits, or de-ionized water with soap or surfactant have been commonly used. Acetone with a few drops of ammonia[14] has also been suggested.

4.2. Stabilization of Archaeological Ivory

The burial environment determines the condition of recovered ivory and bone objects.

Archeological ivory excavated from the earth has usually lost much of its organic material.

12) A. Maskell: 1174.
13) Per E. Guldbeck, The Care of Antiques and Historical Collections (Tennessee: AASLH Press): 196.
14) L. J. Majewski, "On Conservation," *Museum News* (March 1973): 10.

The organic material of ivory is subjected to hydrolytic decomposition when exposed to moist conditions for an extended length of time. In the course of the decomposition, collagen forms soluble peptides and amino acids and subsequently leaches out from the ivory structure. The breakdown of collagen, which causes more porosity, increases the exposure of the hydroxyapatite matrix to the surrounding minerals and causes a change in the inherent crystallinity. The inorganic material of ivory is easily attacked by acid, which causes decay. Treatment with dilute HCl alters the surface composition and morphology of ivory and causes the formation of amino acid salts. A stable waterlogged environment with appropriate pH is known to preserve ivory and bone well.[15)]

In the case of ivory or bone in poor condition, which cannot be safely removed from the ground without risk of damage, the object is often consolidated in situ with synthetic resins, no matter whether the object is dry or wet. It is important that the minimum amount of consolidants should be used, to facilitate later treatment in the conservation lab. In the case of ivory or bone in good condition, which is found in a wet archaeological site, the wet object is sealed in a plastic bag or box and often stored in a refrigerator until actual treatment in the lab. Dried objects from the ground are usually wrapped with tissue paper and packed in plastic bags.

R. H. Lafontaine et al. (1982) have tested polyvinylidene chloride latexes (PVDC) on ivory as a moisture barrier against relative humidity fluctuations. M. Bunn (1987) also tested Saran[16)] as a moisture barrier for bone.

5. Historical background of cyclododecane use in conservation

Cyclododecane is a cyclic hydrocarbon with translucent white crystals. Once cyclododecane is melted and brushed on an object, its waxy texture appears on the surface. The melting point ranges between 58℃ and 61℃ and sublimes slowly with continuous exposure to air at room temperature. It is known to be soluble in non-polar solvents, but insoluble in polar solvents such as water, acetone, and ethanol, which are widely used in the

15) I. M. Godfrey, “The Analysis of Ivory from a Marine Environment,” *Studies in Conservation* 47(2002): 31.
16) Saran is a trade name for PVDC.

conservation field.

Since cyclododecane was first introduced for wall painting and stone conservation in Europe, several research projects have been done in North America. Aqueous treatment of paper was performed after water-sensitive media was protected with cyclododecane (Bruckle et al. 1999). Cyclododecane has been used as a temporary fixative. Porous objects were sealed with cyclododecane as an isolating layer to prevent staining with silicone rubber during mold making (Brückle et al. 1999). Renée Stein et al. (2000) tested the use of cyclododecane as a temporary consolidant on limestone and sandstone to stabilize the stone and prevent damage during transport.

Chapter Ⅱ: Experimental

1. Ivory sample preparation

Samples of elephant ivory were prepared from piano keys, from to the late 19^{th} century. The ivory slabs were separated from wooden supports and cut into smaller sizes. The undersides of the samples were cleaned with deionized water and acetone to remove the residue of glue. Nine 2.2×1㎝ samples were prepared from porous ivory slabs to evaluate cyclododecane coating on wet ivory.

Three highly polished upper side ivory slabs, which also had natural stains, were painted with oil paints, acrylic paints, and watercolor paints. These three ivory slabs were also artificially stained with aniline wood stains: ebony black oak aniline or peacock blue aniline. Deionized water was used as a medium. Prussian blue oil paint was made by Winson & Newton Ltd (England), and rose madder oil paint was made by Grumbacher Inc (New York). Oil painting was done without any addition and allowed to dry for three weeks. Acrylic painting was done using chromium oxide green, a Liquitex acrylic paint made by Binney & Smith Ltd. Watercolor painting was done with Vandyke brown watercolor paints, made by Royal Talens (Holland).

Six porous bone samples and six porous ivory samples were prepared to evaluate the use of cyclododecane as a moisture barrier coating.

2. Preparation of molten cyclododecane; saturated cyclododecane solution in mineral spirits; and saturated cyclododecane solution in hexane

Cyclododecane was purchased from Kremer Pigment Inc. Molten cyclododecane was prepared in a double boiler on a hot plate. Cyclododecane started melting as the water temperature reached 55℃, and completely melted at 57℃. Maintaining the water temperature from 61℃ to 65℃ kept the cyclododecane in its molten form. A saturated solution of cyclododecane in mineral spirits was prepared by adding approximately 17g of cyclododecane in 20g of mineral spirits (approximately 85% w/w). A saturated solution of cyclododecane in hexane was prepared by adding 27g of cyclododecane in 20g of hexane (approximately 135% w/w). Small amounts of solid cyclododecane remained in both solutions. The room temperature was 20℃ (68° F) and the relative humidity was 45%.

3. Preparation of aqueous cleaning system

A 1% (w/w) Triton X-100 solution in deionized water was prepared by adding 1g of Triton X-100 to 99g of deionized water. Ten ml of Laponite RD, synthetic inorganic colloid, was added in 30ml of 1% Triton X-100 solution in deionzed water (approximately 1:3 v/v), forming a gel type cleaning system. Triton X-100 is a non-ionic surfactant, made by Hartman Co. Laponite RD was made by Conservation Resource Int.

4. Preparation of thick cross section of molten cyclododecane coating on ivory for SEM

A half-filled square mold of Ward's Bioplastic®, a two-part resin system that requires a catalyst, was prepared and hardened in the fumehood overnight. A small piece of ivory sample was coated with molten cyclododecane. A drop of the same liquid resin was applied on the surface of the half-filled mold and the ivory sample was placed on it. The mold was then filled with the liquid resin and left to set overnight. The hardened mould was cut approximately 0.5 ㎜ away from the sample using a diamond saw and then was ground down using progressively softer grits of sandpaper until just before the sample was exposed. The sample in the resin block was then polished using a rotating wheel covered in slurry of Al_2O_3 and distilled water in order to remove any scratches from the surface and also make the surface shiny and smooth. The sample in the resin block was mounted onto a small slide using epoxy resin. Once this had set, the sample was ground down using progressively softer sandpaper until just before the ivory coated with cyclododecane was exposed. The thick cross section of the ivory sample coated with molten cyclododecane was examined with a scanning electron microscope (SEM)

5. Experimental procedure

5.1. Application of cyclododecane on ivory

This initial experiment was carried out to assess the working and sublimation properties of cyclododecane on ivory. The samples were coated with either molten cyclododecane, or saturated cyclododecane solution in mineral spirits, or saturated cyclododecane solution in hexane. The coating layers on the samples were examined under UV.

5.2. Rate of moisture content change in wet ivory and wet bone

This experiment was to investigate the efficiency of a cyclododecane sealing layer to reduce moisture loss from wet ivory. The weight of six ivory samples and six bone samples were measured. Three of the ivory samples and three of the bone samples were immersed in deionized water for three days and then measured. The wet samples were then each coated with either molten cyclododecane, saturated cyclododecane solution in mineral spirits, or saturated cyclododecane solution in hexane. The weight of the samples were measured and sealed in a transparent plastic box. One uncoated ivory sample and one uncoated bone sample were immersed in deionized water for three days, measured and then sealed in the same plastic box. Two further ivory samples and two bone samples were either coated with saturated cyclododecane solution in mineral spirits or saturated cyclododecane solution in hexane, and then enclosed in the same plastic box. A humidity card was inserted into the plastic box in order to read the change of RH in the box. The changes of the weight of the samples were recorded weekly for 26 days. After 26 days, the samples were subjected to 100% RH environment for 30 days. The weight of the samples was recorded weekly for one month.

5.3. Protection of a cyclododecane sealing layer on painted and stained ivory

This experiment was to assess the efficiency of cyclododecane sealing on ivory to protect oil, acrylic, and watercolor paints on the ivory during cleaning with acetone, ethanol, or aqueous cleaning systems. Each painted area on the three ivory samples was sealed with either molten cyclododecane, or saturated cyclododecane solution in mineral spirits, or saturated cyclododecane solution in hexane. An ivory sample was also sealed with two different layers, in which saturated cyclododecane solution in hexane was applied initially and then molten cyclododecane was applied over the first layer, securely protecting the painted area. All coatings were transparent enough to see the painting.

5.3.1. Cotton swab poulticing with acetone

A cotton swab soaked with acetone was applied to the stained areas, extending slightly over the cyclododecane sealing. The sample was then sandwiched between mylar for 15 minutes. The ivory sample was removed from the mylar and the cotton swab.

5.3.2. Cotton swab poulticing with ethanol

A cotton swab soaked with ethanol was applied on the stained areas, extending slightly over the cyclododecane sealing. The sample was then sandwiched between mylar for 15 minutes. The ivory sample was removed from the mylar and the cotton swab.

5.3.3. Laponite poulticing with 1% (w/w) Triton X-100 solution in deionized water

Gelled Laponite with 1% (w/w) Triton X-100 solution in deionized water was applied to the stained areas, extending slightly over the cyclododecane sealing. The samples were wrapped with mylar and enclosed in a plastic bag. The degree of removal of stain was checked for three days. The samples were removed from the plastic bag and the Laponite poultice was allowed to dry slowly for two days. The Laponite poultice was then removed from the samples.

Chapter Ⅲ: Results and Discussion

1. Results and discussion of tests

1.1. Application of cyclododecane on ivory

Application of molten cyclododecane on ivory samples with a brush was not as difficult as in the case of stones or metals. It was not easy to make even layers of the coating because the molten cyclododecane solidified so rapidly in the air that it formed a raised layer on the previous layer. It was difficult to build up the sealing layers on the ivory by application of saturated cyclododecane solution in hexane or mineral spirits, especially since the saturated cyclododecane in mineral spirits could not be applied evenly two times. Application of the second layer melted the layer previously applied. Accordingly, it was impossible to build up thick even sealing layers on the ivory with the saturated cyclododecane solution in mineral spirits. On the other hand, the saturated cyclododecane solution in hexane allowed the building up of two or three sealing layers on the ivory samples. Crystals formed by application of molten cyclododecane on the ivory samples had a dense, wax-looking appearance. Application of saturated cyclododecane solution in hexane on the ivory samples produced powdery-like crystals. Saturated cyclododecane solution in mineral spirits formed needle-like crystals[17)] on the ivory samples, which showed a large open network between the crystals. The coating layers appeared to be purple under UV. The open network of the coating layers formed by saturated cyclododecane solution in hexane was shown to be uneven with tiny crystals in UV. The coating layers formed by molten cyclododecane appeared to be transparent and even.

1.2. Rate of moisture content change in wet ivory and wet bone

The numerical results are found in Table 1 and 2, and the weight change is shown in Figure 3 and 4. The ivory slabs were too thin to be suitable as samples because they lost moisture too quickly. Significant loss of weight occurred on the wet samples in three days. In particular, the wet ivory sample without a cyclododecane sealing layer lost most moisture in three days and completely dried out in six days (Table 1). On the other hand, the dry samples sealed with saturated cyclododecane solution in hexane or saturated cyclododecane in mineral spirits lost weight at a regular rate.

The bone samples took more time to dry because of their heavier weight (Table 2). The wet bone samples also lost significant weight in three days (Fig. 4). The wet bone sample without cyclododecane sealing layer lost significant moisture in three days, but kept its moisture for a

17) I. Brückle et al., "Cyclododecane: Technical Note on Some Uses in Paper and Objects Conservation," *JAIC* 38(1999): 170.

long time because of its larger size. The dry bone samples sealed with saturated cyclododecane solution in hexane or saturated cyclododecane in mineral spirits lost weight at a regular rate (Table 2).

As the RH card in the box indicated from 65% to 55% RH for 26 days, moisture seemed to be slowly driven off from the wet ivory and bone samples as the cyclododecane sealing was sublimed. The sealing with even layers, such as the molten cyclododecane sealing layers, gave better stabilization to the wet ivory and bone samples. However, as the samples were subjected to 100% RH environment, those samples sealed with molten cyclododecane absorbed moisture. This means that the coating layers formed by molten cyclododecane did not completely seal out moisture from the wet ivory or bone samples.

When the samples were kept in 100% RH environments, active mold growths were observed on all samples except on the samples sealed with molten cyclododecane (Color plate 1). This research does not explain why the sealing specifically formed by molten cyclododecane prevented mold growth. It may be that an even layer of cyclododecane existed on the samples so that mold could not get into the samples. Some pores present in the sealing layer, which allowed moisture to escape continuously, may have been so small that spores of the mold might have not entered the sample.

Table 1. Measure of the weight of wet ivory samples over time

state / samples	dry state	wet state	with cyclododecane coating	3 days (65% RH)	6 days (60% RH)	10 days (60% RH)
ivory 1	0.3817	0.4241	0.6078	0.5830	0.5732	0.5672
ivory 2	0.3983	0.4376	0.4182	0.4110	0.4049	0.4005
ivory 3	0.3571	0.3960	0.4440	0.4109	0.4047	0.4004
ivory 4	0.3328	0.3679	-	0.3356	0.3316	0.3290
ivory 5	0.2919	-	0.3024	0.2988	0.2979	-
ivory 6	0.4400	-	0.4833	0.4809	0.4796	-

state / samples	14 days (60% RH)	20 days (55% RH)	26 days (55% RH)	7 days (100% RH)	15 days (100% RH)	30 days (100% RH)
ivory 1	0.5650	0.5623	0.5609	0.5896	0.6007	no mold
ivory 2	0.3985	0.3964	0.3951	0.4233	0.4328	mold growth
ivory 3	0.3978	0.3950	0.3933	0.4215	0.4299	mold growth
ivory 4	0.3277	0.3268	0.3262	0.3532	0.3608	mold growth
ivory 5	0.2970	0.2962	-	0.3158	0.3253	mold growth
ivory 6	0.4780	0.4768	-	0.5152	0.5282	mold growth

Ivory 1 was made wet and sealed with molten cyclododecane.

Ivory 2 was made wet and sealed with saturated cyclododecane solution in mineral spirits.

Ivory 3 was made wet and sealed with saturated cyclododecane solution in hexane.

Ivory 4 was made wet without cyclododecane sealing layers.

Ivory 5 was dry and sealed with saturated cyclododecane solution in mineral spirits.

Ivory 6 was dry and sealed with saturated cyclododecane solution in hexane.

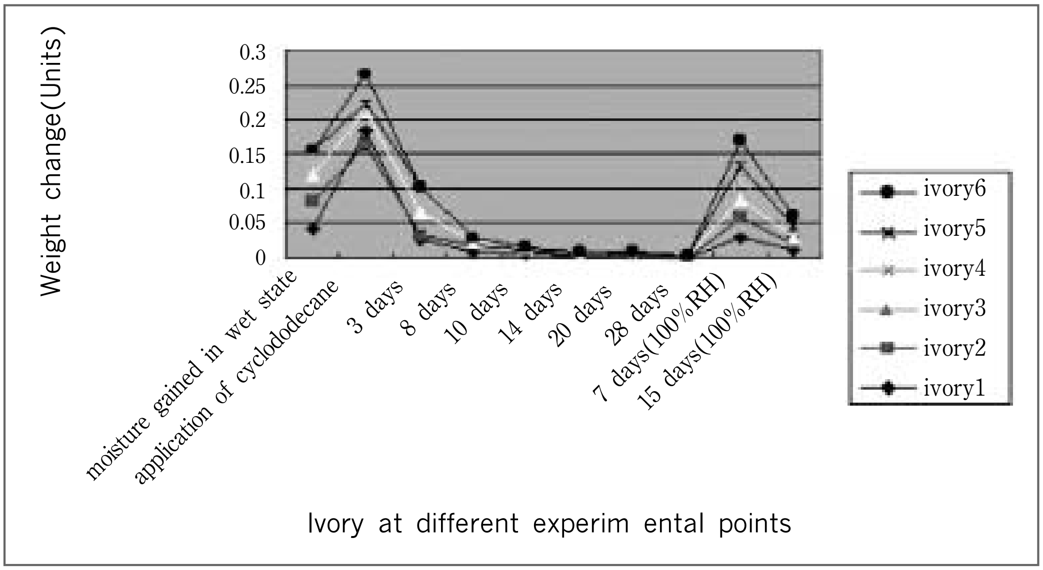

Fig. 3 Weight change over experiment: desorption and re-absorption moisture in wet ivory samples sealed with cyclododecane

Table 2. Measure of the weight of wet bone samples over time

state / samples	dry state	wet state	with cyclododecane coating	3 days (65% RH)	6 days (60% RH)	10 days (60% RH)
bone 1	2.2431	2.3283	2.9873	2.9534	2.9340	2.9190
bone 2	2.3685	2.4412	2.4508	2.4159	2.4050	2.3960
bone 3	0.3020	2.3997	2.4709	2.4098	2.3990	2.3890
bone 4	2.4895	2.5965	-	2.5134	2.5060	2.4990
bone 5	2.8961	-	2.9384	2.9143	2.9060	2.8980
bone 6	4.1891	-	4.2738	4.2624	4.2520	4.2400

state / samples	14 days (60% RH)	20 days (55% RH)	26 days (55% RH)	7 days (100% RH)	15 days (100% RH)	30 days (100% RH)
bone 1	2.9109	2.9006	2.8929	2.9162	2.9257	no mold
bone 2	2.3904	2.3845	2.3806	2.4199	2.4260	mold growth
bone 3	2.3830	2.3764	2.3713	2.4153	2.4228	slightly mold growth
bone 4	2.4949	2.4923	2.4905	2.5392	2.5445	mold growth
bone 5	2.8928	2.8873	2.8837	2.9225	2.9323	mold growth
bone 6	4.2341	4.2264	4.2200	4.2907	4.3162	mold growth

Bone 1 was made wet and sealed with molten cyclododecane.
Bone 2 was made wet and sealed with saturated cyclododecane solution in mineral spirits.
Bone 3 was made wet and sealed with saturated cyclododecane solution in hexane.
Bone 4 was made wet without cyclododecane sealing layers.
Bone 5 was dry and sealed with saturated cyclododecane solution in mineral spirits.
Bone 6 was dry and sealed with saturated cyclododecane solution in hexane.

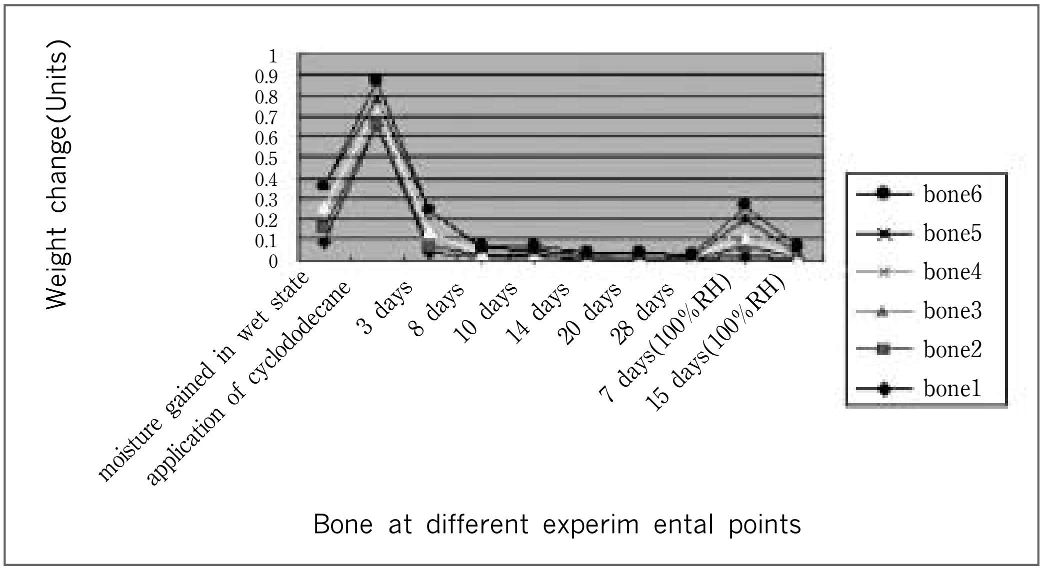

Fig. 4 Weight change over experiment: desorption and re-absorption moisture in wet bone samples sealed with cyclododecane

1.3. Protection of a cyclododecane sealing layer on painted and stained ivory

Ivory samples sealed with saturated cyclododecane solution in mineral spirits were excluded from these experiments because of the poor coating of the layers on the highly polished ivory samples. In order to assess the efficiency of cyclododecane sealing on ivory, more aggressive treatments were performed than would be ordinary treatments, in this case poulticing with 1% (w/w) Triton X-100 solution in deionized water for five days.

1.3.1. Cotton swab poulticing with acetone

Cyclododecane is known to be easily soluble in non-polar and aromatic solvents, and is almost insoluble in polar solvents, such as acetone, ethanol, and water. After poulticing with acetone for 15 minutes, the cyclododecane sealing layers were melted down. Cyclododecane sealing layers formed by saturated solution in hexane were melted more by acetone than the sealing layers formed by molten cyclododecane. Acrylic paints on ivory samples were slightly damaged as the sealing layers formed by saturated cyclododecane solution in hexane were melted in acetone. Recrystallization of cyclododecane melted in acetone was clearly shown on mylar. The natural and artificial stains on the ivory were not removed.

1.3.2. Cotton swab poulticing with ethanol

The cyclododecane sealing layers appeared to be stable against ethanol, but the stains on the ivory were not removed.

1.3.3. Laponite poulticing with 1% (w/w) Triton X-100 solution in deionized water

After poulticing with 1% (w/w) Triton X-100 solution in deionized water for five days (including slow drying periods), the natural and artificial stains were all removed. However, the sealing layer formed with only molten cyclododecane removed some of the watercolor painting (Color plate 2). The sealing layer formed with only saturated cyclododecane solution in hexane did not completely protect the painted area from water. Some of the watercolor painting was removed. The sealing formed with two different layers, in which saturated cyclododecane solution in hexane was applied initially and then molten cyclododecane was applied over the first layer, securely protected the painted area. The first sealing layer formed by saturated cyclododecane solution in hexane may have penetrated more deeply into the surface of the ivory sample and secured the second sealing layer formed by molten cyclododecane, so that the two layers did not come off under the extreme moisture treatment. The upper sealing layer formed by molten cyclododecane certainly offered a better barrier effect to the under sealing layer. In this experiment, the ivory samples were highly polished so that the coating layer of saturated cyclododecane solution in mineral spirits was not properly formed. If the samples were not highly polished, the sealing layer formed only by the molten cyclododecane might not have come off after poulticing with the water-based cleaning system and might have completely protected the painted area. Also the sealing layer formed only by the molten cyclododecane might not have come off if ordinary treatments were performed, for example a short term poulticing. No tide lines were observed after removing the natural and artificial stains.

2. SEM images

SEM images show uneven coating of cyclododecane on ivory (fig. 6). A thin layer of cyclododecane penetrating the surface of ivory was shown in the pictures.

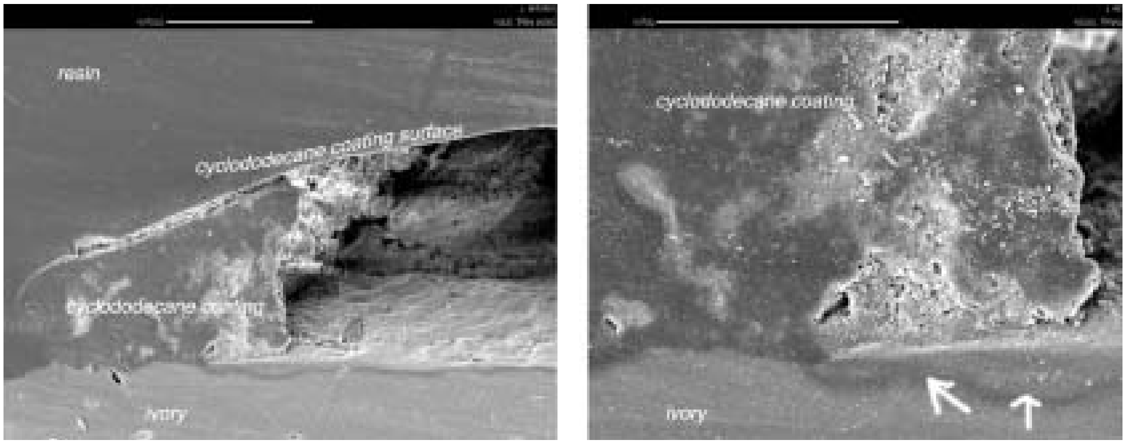

Fig. 5 SEM images of cross sectional molten cyclododecane coating on ivory sample. 300x (left) and 1000x (right). Two white arrows point out the cyclododecane penetrating the ivory sample.

Chapter Ⅳ: Conclusions

Molten cyclododecane formed dense and more even layers on ivory than saturated cyclododecane solution in hexane or saturated cyclododecane solution in mineral spirits. Saturated cyclododecane solution in mineral spirits could not form sealing layers on highly polished ivory samples. Neither the sealing layers formed by molten cyclododecane nor by saturated cyclododecane solution in hexane did form a secure contact with the surface of the highly polished ivory. After poulticing with a 1% (w/w) Triton X-100 solution in deionized water, the sealing layer formed with only molten cyclododecane came off along with some of the watercolor paint. The sealing layer formed with only saturated cyclododecane solution in hexane did not completely protect the painted area from water. The watercolor painting was damaged. The sealing formed with two different layers, in which saturated cyclododecane solution in hexane was applied initially and then molten cyclododecane was applied over the first layer, was found to securely protect the painted area. The first sealing layer formed by the saturated cyclododecane solution in hexane may have penetrated the surface of the ivory sample more deeply and secured the second sealing layer formed by the molten cyclododecane. The upper sealing layer formed by the molten cyclododecane certainly offered a better barrier effect to the under sealing layer so that the two layers did not come off under the extreme moisture treatment.

Cyclododecane is known to be easily soluble in non-polar and aromatic solvents, and is almost insoluble in polar solvents, such as acetone, ethanol, and water. After poulticing with acetone for 15 minutes, however, the cyclododecane sealing layers were melted down. The acrylic paint was damaged. The cyclododecane sealing layers appeared to be stable against ethanol.

After coating with saturated cyclododecane solution in mineral spirits, the wet ivory sample actually lost weight, indicating the loss of moisture during application of the sealing layers. Sealing with even layers, such as the molten cyclododecane sealing layers, gave better stabilization to the wet ivory and bone samples. However, the sealing layers formed by the molten cyclododecane did not completely prevent the loss of moisture form the wet ivory and bone samples. Moisture seemed to be slowly driven off from the wet ivory and bone samples as the cyclododecane sealing sublimed. Experiments showed that larger wet objects would show better stabilization effects when they were sealed with cyclododecane.

When the samples were kept in 100% RH environments, active mold growths were observed except in the samples sealed with molten cyclododecane. It is possible that an even layer of cyclododecane on the samples prevented mold from getting into the samples. The pores present in the sealing layer, which allowed moisture to escape continuously, were so small that spores of the mold might have not entered the sample.

Cyclododecane was an efficient hydrophobic sealing agent to protect painting area while cleaning stains on ivory. It also prevented mold growing on wet ivory and wet bone. The sealing formed with two different layers, in which saturated cyclododecane solution in hexane is applied initially and then molten cyclododecane is applied over the first layer, might be used to prevent mold growing on archaeological wet ivory or wet bone.

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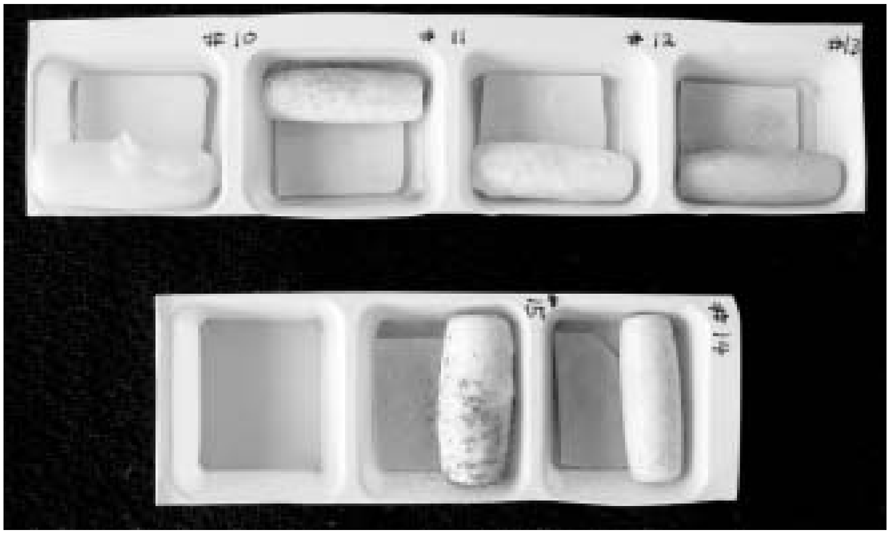
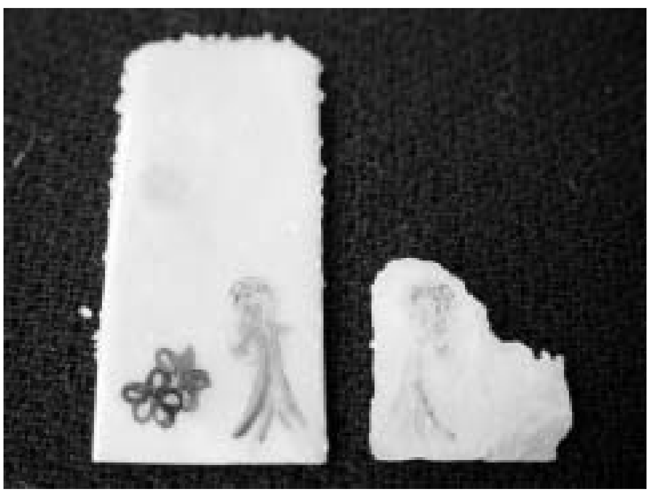


Color plate 1 Wet ivory and wet bone samples showing mold except those sealed with molten cyclododecane. Green and brown molds were appeared.

Sample # 10 Wet samples sealed with molten cyclododecane, showing clean sealing layers (No mold)
Sample # 11 Wet samples sealed with saturated cyclododecane solution in mineral spirits (Mold growth)
Sample # 12 Wet samples sealed with saturated cyclododecane solution in hexane (Mold growth)
Sample # 13 Wet samples without sealing cyclododecane (Mold growth)
Sample # 14 Dry samples sealed with saturated cyclododecane solution in mineral spirits (Mold growth)
Sample # 15 Dry samples sealed with saturated cyclododecane solution in hexane (Mold growth)



Color plate 2 Disengaged sealing layer formed by molten cyclododecane from ivory sample, removing some of watercolor painting

사이클로도데칸을 사용한 상아와 뼈로된 예술품 및 발굴품의 세척, 처리 및 보존

이 현 숙

상아로 이루어진 예술품과 출토 유물 상에 발생된 얼룩이나 오염물질을 제거하는 것은 오랫동안 보존과학 분야에서 바람직하지 못한 보존처리로 간주되어왔다. 왜냐하면 상아는 그 특성상 흡습성(hygroscopic) 이며 異方性(anisotropic) 이기 때문에 동일한 상아질 안에서도 다른 방향으로 서로 다른 물리적 특성을 보이기 때문이다. 실온에서 승화하는 사이클로도데칸은 1995년 이래 보존과학 분야에서 복구 가능한 임시적 강화제 (consolidant), 밀봉제 (sealing agent) 또는 코팅제, 방수제, 및 barrier layer로서의 사용이 연구되어 왔다. 본 연구논문은 상아 표면에 발생한 얼룩 또는 오염물질을 제거하기 위해 메탄올, 아세톤 또는 수성 세척제계 (aqueous cleaning system)를 사용하는 동안 얼룩이나 오염물질이 없는 부위나 장식용으로 채색된 부위를 임시적으로 밀봉하고 보호하기 위해 사이클로도데칸을 소수성(hydrophobic) 밀봉제로 사용하는 처리 방법에 관한 것이다. 또한 본 연구는 출토 시 젖어있는 상태의 상아나 뼈에 대한 보존 처리로서 사이클로도데칸이 안전하고 효과적으로 사용될 수 있는지에 관한 연구이다. 용융된 사이클로도데칸 및 mineral sprit 또는 hexane에 용해된 사이클로도데칸 포화용액이 상아로 이루어진 샘플들에 적용되었다. 적용 방법, 상아 샘플 상에서의 사이클로도데칸의 작용성 및 젖어있는 유물의 수분 함량에 대한 사이클로도데칸의 코팅 효과의 관계 등이 연구되었다.

용융된 사이클로도데칸, 또는 mineral spirit 또는 hexane에 각각 용해시킨 사이클로도데칸 포화용액을 한가지씩만 사용하여 형성된 도포막은 보호하고자 하는 상아의 부분을 완벽하게는 보호하지 못하였다. 하지만, 헥산에서의 사이클로도데칸 포화용액을 보호하고자 하는 페인팅 부위에 먼저 도포하고 그 위에 다시 용융 사이클로도데칸을 덧발라 도포하면 페인팅 부위를 수성세척제계로부터 확실히 보호할 수 있는 것을 알 수 있었다. 발굴된 상아나 뼈를 보존하기 위한 사이클로도데칸의 사용 가능성 여부를 알아보기 위하여, 젖어있는 상아 및 뼈의 샘플에 용융 사이클로도데칸, 또는 mineral sprit 또는 hexane에 용해된 사이클로도데칸 포화용액을 각각 도포시키고 한 달 가량 실온에서 방치하였다. 그 결과, 용융 사이클로도데칸으로 밀봉된 상아 및 뼈의 샘플을 제외하고는 모든 샘플에 곰팡이가 번성한 것을 알 수 있었다. 이는 용융 사이클로도데칸이 발굴된 상아나 뼈를 실온에서 임시로 안전하게 보존하는데 사용될 수 있는 가능성을 제시한다. 상아 샘플 상에 도포된 사이클로도데칸 필름의 두께에 대한 균일성이 UV상에서 관찰되었다. 분석 방법으로는 가시적 관찰, 편광 현미경 및 Scanning Electron Microscope (SEM)이 사용되었다.

〔Key word〕 상아, 뼈, 사이클로도데칸, 처리, 보존