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# The Neutralization on Calcium (Ca) Finishing Color Paint Used for the Wall Painting in the Koguryo Tombs

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**Abstract:** A medium substance has not been detected in the wall paintings of the Goguryeo tombs. The most important concern of the world's cement and concrete researchers has been a method for neutralizing lime mortar. The reason is that the naturalization of lime mortar contributes not only to the improvement of strength and the prevention of oxidation, but also to significantly increasing durability. This study was conducted to examine ions in the leachate from the wall paintings of the Goguryeo tombs and to compare and analyze its pH value with one of the calcium (Ca) based finishing layer that was revealed by experiments. The results showed that both of them were neutralized by pH7. The neutralization of lime mortar varies depending on the type of glue, in terms of its functions and performance.

**Key words:** finish layer paint, jeongbun, dog skin glue, pH, neutralization

## 1. Introduction

The wall paintings in the Goguryeo tombs are largely classified into the lime mortar paintings in the early age and the stone-based paintings in the late age. Calcium (Ca), as an active ingredient, was found in the finish layer of the lime mortar wall paintings in the tombs, and it was mostly similar to the stone-based wall paintings in the tombs. there are eight kinds of calcium oxide salts in nature. The main ingredient of the coating (preparation) layer, on which wall paintings are applied, has been identified as Ca. Ca-based material is white in color, so it can be used as a white pigment of the paint layer, as well as for the preparation layer that coats the stone surface.

In nature, there are eight types of materials that are classified as Ca. However, even in UNESCO and in Japan, where Goguryeo mural painting specialists are being trained, they are all lumped in to one material which is Ca. The preceding researchers who have surveyed and analyzed the Twin Column Tomb murals are no exception. Despite being the same subject of study, Ca-based material is described with different name s depending on there searchers, and the same material is sometimes described differently even in papers by the same researcher. Under the circumstance, when a mural is to be preserved or reproduced, it is not easy to determine exactly what type of material it was that there searchers referred to in their papers.

There is no stone-built cultural heritage's thin film coating material that has been nationally and internationally recognized and officially approved. In general, the synthetic resin and its copolymer developed in Europe have been used to restore and conserve the world's stone-built cultural heritage. However, the problem is that both of domestic and European authorities do not have definite guidelines for using the resin, and that their efficiency can be defined only after their use. In Korea, for example, individual authorities and private conservation companies have made many efforts to develop a

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synthetic resin best suited to restoring and conserving our cultural heritage since 1960s.

In Japan, in principle, only the glue has been used for traditional decorative coloring on wooden buildings and artifacts for the purpose of style while there has been an increase in the frequency of using the glue beyond the resin since 1993. The importance of the glue has been emphasized to foster experts in wall paintings after the wall paintings of the Goguryeo tombs were registered as the World Cultural Heritage in UNESCO in 2004. In 2008, Japan Ministry of Education, Science and Culture widely carried out the five-year program of research on the glue in 2008.

Korea's scientific research on the glue was firstly conducted in 2009. Namely, 10 experts in old literature, Ugyo glue manufacturing and experiment and organic material analysis conducted a joint research to examine the mechanism of methods for manufacturing the Ugyo glue that is believed to have been used for Dancheong, Korean traditional decorative coloring on wooden buildings. The importance of the research was that it was firstly conducted in Korea to scientifically study Korean traditional decorative coloring agents. Nevertheless, serious cracks have occurred in the Dancheong of Sungnyemun Gate, conserved on the basis of the results of the research, in just 1 year. In 2017, the Japanese authorities also determined to properly store and manage stone-built cultural heritage while avoiding its conservation treatment after many efforts were made, For this reason, there is an urgent need for more research on the neutralized thin film coating material.

## 2. Objectives and Methodology of Study

This study was conducted (1) to examine the calcium pigment type used for the finish layer of the stone-based wall paintings in the Goguryeo tombs among eight different kinds of oxidized calcium salts, as well as the ingredient kind of medium, and (2) to explore the performance and functions of [White thin film coating material] by investigating a variety of phenomena occurring in manufacturing and drying calcium ingredient paints. Whether they were neutralized or not was determined by analyzing ions in the leachate from the wall paintings and by comparing their pH value with one of specimens that was revealed by experiments. When results were not consistent, also, their reasons were examined.

## 3. Conditions and Methods of Study for Fabricating Specimens

1) The paints used for the study are [pigment + vehicle] and [pigment + adjuvant + vehicle].
2) The fabricated specimens include those with good coloring dependent upon the blending ratio of paints, and those with poor concealment force.
3) White is proposed for clear discrimination of the binding conditions of the [stone base] and the [paint layer].
4) Photos of the specimens and those taken after artificial weathering are compared with the color chart of KODAK. Three specimens of good coloring are selected, and machined with sandpaper until any scratches become invisible.
5) The thickness of the sectional structure and the surface structure were photographed using a Digital Microscopy (Scalar, Co, Japan), and the scale bar of the microscope photo by the Kodak Gray Scale (Licensed Product). The production of calcium carbonate was measured with an X-ray diffraction analyzer (XRD).
6) Colors were measured using the KURABO Color-7X for searching the CIE 1976 Lab color system, Nickerson color system, Hunter lab color system, and Munsel color system as well as the spectral reflection factor.

## 4. Theoretical Basis and Selection of Materials

### *4.1 Stone Base: Granite*

The Goguryeo Mural Tomb is divided into early lime mortar tombs and late stone graves. This study is

limited to later stone-based tombs. The walls are built of a single stone and a combination of pieces of stone, but the material is commonly used granite.

*4.2 Finish Layer Pigments; $Ca(OH)_2$, Aragonite, Jungbun*

Eight types of minerals with calcium oxide bases are found in nature, all of which can be converted into $CaCO_3$ by a chemical reaction. Lime is converted into CaO and $Ca(OH)_2$ by firing. CaO is excluded from the experiments, since the target of the study is dry wall prints. $CaCO_3$ is classified into calcite, vaterite, and aragonite depending on the crystal structure. These minerals are difficult to use in wall printing in tombs, as they consist of partly-altered $CaCO_3$ from lime stone. The same goes for dolomite [$CaMg(CO_3)_2$]. Gypsum ($CaSO_4$) is a commonly used material; however, it is altered physiochemically over time and turns darker. Hobun is very soluble in water; while aragonite is soluble in acid. Based on the aforementioned conditions, the author of this study selected $Ca(OH)_2$, aragonite and hobun as the pigments for the experiments on the finish layer of wall prints in the Koguryo Period

*4.3 Bases for Selecting Vehicle: Animal Glue, Perilla Oil*

4.3.1 Literature Materials

Inorganic pigments painted on the finishing layers of murals require a glue, because they are different. In Nihon Shoki, it is written that carbon black and glue were used together. On the other hand, Joseon silrok record that 80% of perilla oil and 20% of perilla oil which is boiled with Pyrolusite stone is used as a glue to fix the pigment on the finishing layer of Dancheong.

4.3.2 Glue, Perilla Experiment

1) Processing of animal glue in 2004. Copy of a part of the ceiling prints in the dance tomb. 2) Experiments of dog glues, Fe2O3 with Yamauchi Akira (山内章) in the coloring data recovery room, Cultural Asset Research Center of Wonhung Temple in Japan in 2006. 3) Sientific study of cow glue Korea in 2009 (Exhibited in the National Science Museum). 4) Experiments on color with pigments of known origin macro-molecule cow glue, perilla oil and polyzol. Measurement of absorbtion force. Experiments on glues from Korea, China and Japan.

## 5. Considerations and Conclusions

Among ten kinds of finish coating specimens, [jeongbun+glue solution] is the best suited paint for the stone-based wall paintings in the Goguryeo tombs. jeongbun easily melts in glue solution while manufacturing paint, and physical and chemical reactions occurring in drying show the following characteristics.

When results were not consistent, also, their reasons were examined. The main substance of the glue is mostly composed of amino acid molecule of protein and gelatin. Its general physical properties are about 1.35 specific gravity, 7-8 H coating strength, high refractive index and high intermolecular attractive force. When the glue contains about 70-90% water, the solidification phenomena occur at temperature below 20°C. If the water content is less than 20%, the glue turns into a gel and becomes stiff. As a water-soluble chemical material, the glue features the quick dispersion drying in the painting. Namely, solvency, dissolution velocity and drying characteristics are essentially required to make well paintings.

The glue from the animal skin is a functional group featuring a sufficient amount of reactivity, due to carbon-oxygen double bonds resulting from polyunsaturated fatty acids among monounsaturated fatty acids. In particular, phosphoric acid plays a role in separating two electrodes and transporting hydrogen ions. Like Seokbinggo (stone ice storage), the Goguryeo tomb with wall paintings is a low-temperature space. While the general glue usually coagulates immediately after coming into contact with the side of a wall, the glue from the dog skin does not coagulate even in winter and thus is best suited to the conservation of the stone-built cultural heritage. The

body fat or protein in dog can be used in many different ways, according to methods for concentrating and processing them.

The sample protein molecular volume can be predicted by the travel distance of protein molecular weight markers. As a result of protein molecular volume electrophoresis analysis, the powdered glue has a protein aspect similar to a manufactured glue. However, the manufactured glue shows a band at around level 50 kDa, and the powdered glue at level 75 kDa, respectively. It means that the manufactured glue contains more protein molecular volume than the powdered glue. That is, the size of the protein molecular weight varies depending on the processing method of the glue.

As a result of infrared spectroscopy analysis (FT-IR) on the powdered glue, it seems that a wider band formed at around level 3500-3300 $cm^{-1}$ is the band of primary amine N-H stretch band. Both bands formed at around level 1650 and 1420 are assumed to be the powdered glue & manufactured glue bands of carboxylate(-COO-) symmetric & asymmetric stretch band (Table 2). It indicates that the peptide bond of partial protein is dissolved and exists in a form of amino acid, and that it exists in a form of carboxylate, due to metal.

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**Table 1 Types of calcium oxide bases, and selected pigments.**

| | Mineral | Chemical formula | Selection |
|---|---|---|---|
| Types of minerals with calcium oxide bases | Calcium hydroxide | $Ca(OH)_2$ | ○ |
| | Quick lime | CaO | × |
| | Aragonite | $CaCO_3$ | ○ |
| | jeongbun | $CaCO_3$ | ○ |
| | Calcite | $CaCO_3$ | × |
| | Dolomite | $CaMg(CO_3)_2$ | × |
| | Vaterite | $CaCO_3$ | × |
| | Gypsum | $CaSO_4$ | × |

**Table 2 Types [Ca pigment+medium] used for test.**

| | Components of pigment + medium |
|---|---|
| Types of test specimens | $Ca(OH)_2$+glue solution |
| | $Ca(OH)_2$+jeongbun+glue solution |
| | jeongbun+glue solution |
| | Aragonite+glue solution |
| | Aragonite+jeongbun+glue solution |
| | $Ca(OH)_2$+perilla oil |
| | jeongbun+perilla oil |
| | $Ca(OH)_2$+jeongbun+perilla oil |
| | Aragonite+perilla oil |
| | Aragonite+jeongbun+perilla oil |

The feature of the glue from the dogs skin is that it is shown to decrease immediately at pH9 or more when measured after opening a sealed bottle (Fig. 1 and Fig. 2). In addition, [jeongbun+Glue solution] was shown to be neutral pH7 after drying. The glue ion may be hydrophilic. The powder detergent is also a hydrophilic pigment so that it can become the same molecule as the glue. When the powder detergent and the glue water molecule with increased reaction efficiency become ions after melting, they react with each other so that they can be neutralized (Fig. 3).

National Research Institute of Cultural Heritage, Republic of Korea, examined and analyzed the leachate coming from 8 tombs with wall paintings by means of ion chromatography. The analytic results of $Ca^{2+}$ ion mostly showed pH7. The acidity of the leachate is consistent with the pH7 as shown in the analytic results.


**Fig. 1 Korea, China, Japan glue types and transparency.**

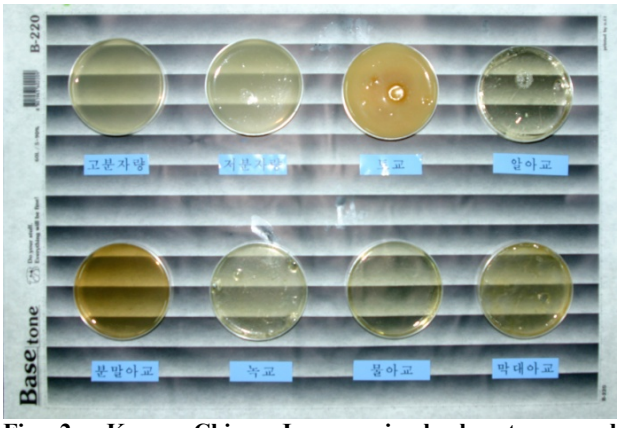



**Fig. 2 Korea, China, Japan animal glue types and concentration.**

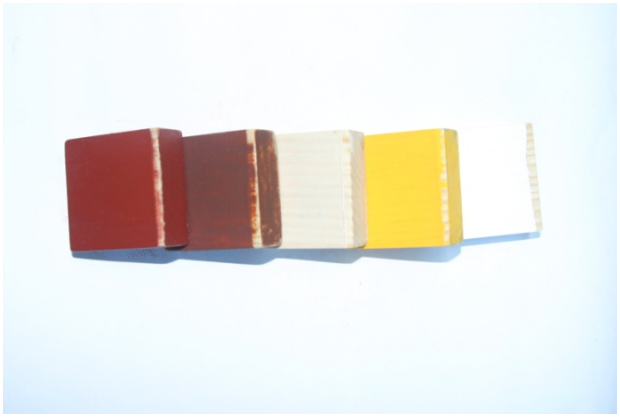


**Fig. 3 Absorption rate measurement.**

**Fig. 4 [Jeongbun + glue solution] 3years.**

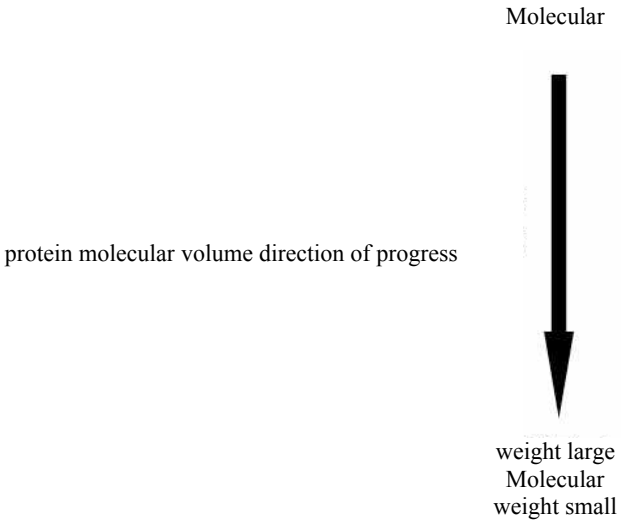
**Fig. 5 National science museum, danchung exhibition.**

**Fig. 6 Mural copy of ceiling wall painting in the chum(dance) tomb.**

It seems, namely, that the glue from the dog skin was used as a coloring agent for the tombs with wall paintings and that from the beginning it was planned and designed for the neutrality of pH7. The leachate of $Ca^{2+}$ ion from the eight tombs with wall paintings was shown in the following order: Susanri tomb (Yeondo, 183.6) → Gangseodae tomb (67.26) → 1st Jinpari tomb (52.96) → 3rd Anak tomb (41.63) → 4th Jinpari tomb (15.50) → Susanri tomb (Hyeonsil, 9.56) → Honamrisasin tomb (8.87) → Gangseojung tomb

(2.67). It was shown, therefore, that the Susanri tomb (Yeondo)'s leachate of $Ca^{2+}$ ion was 183.6 which was highest, while the Gangseodae tomb showed 67.26 in spite of its stone floor. These figures indicates a serious situation, in addition to the Yeondo of Susanri tomb. It seems that based on the importance of the wall paintings, it is urgently required to eliminate the mound soil of the Gangseodae tomb, as well as the Yeondo of the Susanri tomb with wall paintings.

The Goguryeo tombs with wall paintings were neutralized when they were built, namely, the strong alkali of burial mound made from cement or newly coated mortar seem to be the direct cause of damage to the wall painting. The leachate from the Gangseojung tomb was 2.67 which was lowest. It seems that the Gangseojung tomb has been maintained in good condition because people have been not allowed to enter the tomb since the Japanese colonial period. Except the staff, nobody is allowed to enter the Goguryeo tomb with wall paintings that is a sealed dark space. The old tomb will be quickly weathered and damaged by environmental change if people are allowed to enter the tomb.



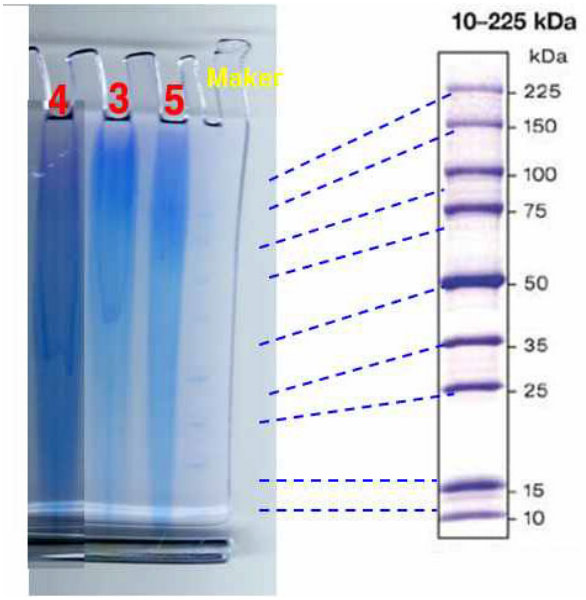




**Fig. 7 Size of protein molecular weight of glue and powder glue.**

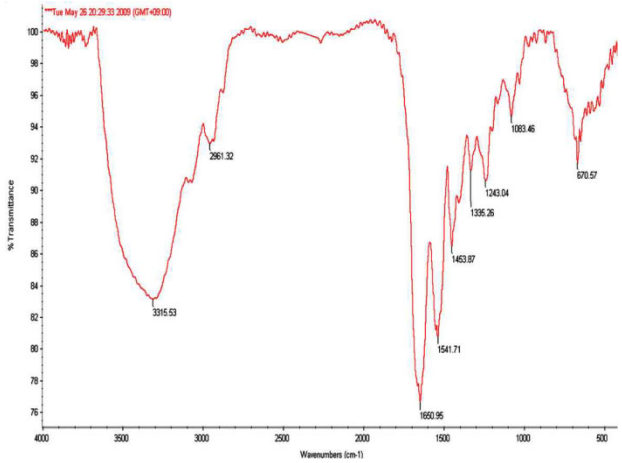



**Fig. 8 Powdered glue FT-IR spectrum.**

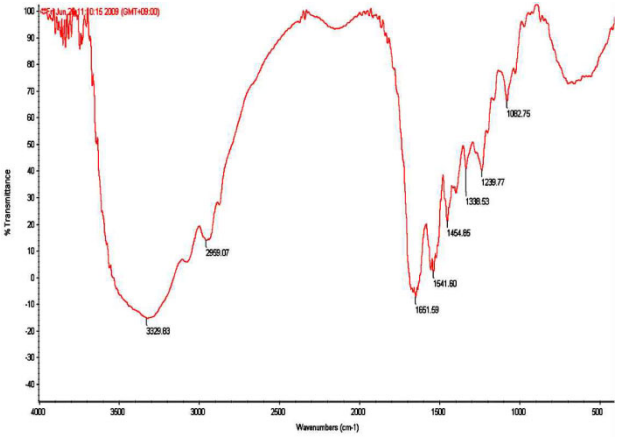



**Fig. 9 Manufactured glue FT-IR spectrum.**

The Goguryeo tombs with wall paintings were neutralized when they were built, namely, the strong

alkali of burial mound made from cement or newly coated mortar seem to be the direct cause of damage to the wall painting. The leachate from the Gangseojung tomb was 2.67 which was lowest. It seems that the Gangseojung tomb has been maintained in good condition because people have been not allowed to enter the tomb since the Japanese colonial period. Nevertheless, the Gangseojung Tomb requires the technology to carbonate leachate annually.

Except the caretaker, nobody is allowed to enter the Goguryeo tomb with wall paintings that is a sealed dark space. The old tomb will be quickly weathered and damaged by environmental change if people are allowed to enter the tomb. The raw materials, production techniques and color expression techniques of the tombs of Goguryeo are revealed and the organic study of inside and outside of the tomb is most important. and the best way to keep the circle is to keep the environment in its original state.

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