Traditional craftwork that can be washed with a dishwasher, "nanocomposite *tamamushi-nuri*"

—Expansion from exhibits to daily necessities—

Takeo Ebina[1*], Midori Saura[2] and Yasukatsu Matsukawa[2]

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We developed highly durable lacquerware by applying a protective layer in which resin and clay were mixed on the surface of the lacquerware. The components of the protective layer were selected from the viewpoints of dispersibility in a solvent, transparency of the layer, and hardness of the layer. It was confirmed that even after repeated washing with a dishwasher, the color, gloss, and surface flatness of the protective layer resisted deterioration. We optimized the paste viscosity, spray blowing pressure, and number of coatings to establish a method of giving a protective layer to products. In addition, we examined designs and productivity, considered user ratings, and created a product that exhibited the above-mentioned superior characteristics.

Keywords **:** Lacquerware, *tamamushi-nuri*, clay, nanocomposite, hard coat

1 Introduction

1.1 Goal of research

The goal of the research is to develop lacquerware with excellent abrasion resistance, UV resistance, and dishwasher resistance and its manufacture method, by adding a protective layer containing clay on top of the *tamamushi-nuri* coat, to improve the durability of *tamamushi-nuri*, a traditional craft. Moreover, the coating method is investigated and a product with the aforementioned excellent characteristics is created.

1.2 Research goal and relationship to society

The *urushi* lacquerware manufacturing technology represents the high level of Japanese manufacturing since ancient times, and is highly evaluated overseas. In general, it involves woodwork and coating with plant-derived resin that requires no heating, and it is also recognized as manufacturing technology with a low environmental load. Lacquerware includes bowls, tableware, and artistic objects, but it is not expected to be used in dishwashers that require durability at a wide temperature range. Lacquerware does not have abrasion resistance, UV resistance, or durability. Therefore, attempts were made to increase the durability by coating and other methods.[1] In this research, the characteristics are enhanced by adding a transparent protective layer containing clay, thereby adding value to the craft.

The *tamamushi-nuri* (jewel beetle coating) is a traditional craft designated by the Miyagi Prefecture.[2] This research aims to develop next-generation lacquerware by matching the traditional *tamamushi-nuri* and clay film, an innovation of AIST. While passing down the Japanese traditional craftwork technology, it also attempts to create innovation through companies that were affected by the earthquake and tsunami of 2011. Also, this research achieves high functionality of a traditional craft, in the field of chemical manufacturing, as high functional materials and parts, and attempts are made to apply the innovative technology to fields and products that were conventionally considered impossible.

2 Scenario for development of high-durability lacquerware

The *tamamushi-nuri* consists of undercoat, midcoat, semitransparent layer containing silver powder, and then a semitransparent topcoat containing dyes (Fig. 1).[3] For undercoat, midcoat, and topcoat, *urushi* (natural resin collected from Japanese lacquer trees), cashew, or urethane coats are used according to the product usage. When incident light passes through the topcoat that contains a dye, light is scattered by silver powder and then passes through the topcoat again, and depending on the type of dye, a characteristic deep appearance is exhibited according to the reflected light with red, green, blue, or black colors. However, lacquerware has low surface hardness, and it is about F in the pencil hardness test[1] (a general hardcoat layer is 3H or higher).

On the other hand, AIST possesses material technologies for mixing organic and inorganic materials such as clay at nanolevel.[4]-[6] In this research, this technology is applied to the surface protective layer, to create traditional craft products with excellent durability. The composition of the proposed new *tamamushi-nuri* is shown in Fig. 1.

1. Research Institute for Chemical Process Technology, AIST 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan ∗ E-mail: takeo-ebina@aist.go.jp, 2. Tohoku Kogei Co., Ltd. 3-3-44 Kamisugi, Aoba-ku, Sendai 980-0011, Japan

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To incorporate the desired function, the following composition can be considered as the fine structure (Fig. 2). With clay being evenly distributed as fine particles in a film, it is possible to make a highly transparent coating film.[7] As for nanocomposite hardcoat agents, it has been reported that abrasion resistance increases when the particle size is 1 μm or less.[8] Also, there is a stabilizing effect for unstable molecules adsorbed on clay crystals.[9] Therefore, we expected that high UV resistance could be achieved by increasing the stability of UV absorbers by adding UV absorbers to the clay.

Tohoku Kogei Co., Ltd. has conventionally used brush-coating on lacquerware, but around 1955, it started using spray-coating for the first time on traditional lacquerware. Currently, it uses spray-coating on products with various shapes such as glass, vase, plate, and others. Expert skill is required to apply even coating to the entire surface of products with complex shapes, and the coating technology based on long experience accumulated by Tohoku Kogei was utilized in this development. This development was achieved after the material composition was ultimately determined for the balance between beauty and coating condition of *tamamushi-nuri*, and after repeated lab investigations at AIST and sample coating at Tohoku Kogei.

3 Development of high-durability lacquerware

3.1 Design of protective layer

As the protective layer of *tamamushi-nuri*, three types were considered including the organic, inorganic, and organic-inorganic composites, and initial evaluations were conducted by selecting candidate materials from each category. When candidates for the organic material including acrylic resin and others were used, we were unable to realize surface hardness of 3H that was our goal, although the paste had excellent long-term stability. Next, silica coating, an inorganic material, was considered, and surface hardness 3H was obtained with room temperature processing only. However, the disadvantage was poor stability of the paste. Therefore, we decided to achieve a protective layer using organic-inorganic composite materials that have the stability of organic materials and high surface hardness of inorganic materials. For organic-inorganic composite materials, high-temperature treatment is normally conducted to increase water resistance. However, some base materials for *tamamushi-nuri* do not have heat resistance, and *tamamushi-nuri* itself is not heat resistant, and therefore the heating process cannot be used. Therefore, we used UV curing resin in which hardness could be attained without heating, and the aim was to obtain high hardness with room temperature processing only by adding clay. The characteristic diagram for the development of high-durability lacquerware is shown in Fig. 3. There was a case in which UV curing resin was used in a polymer clay composite material, but the transparency was reduced when the amount of clay added

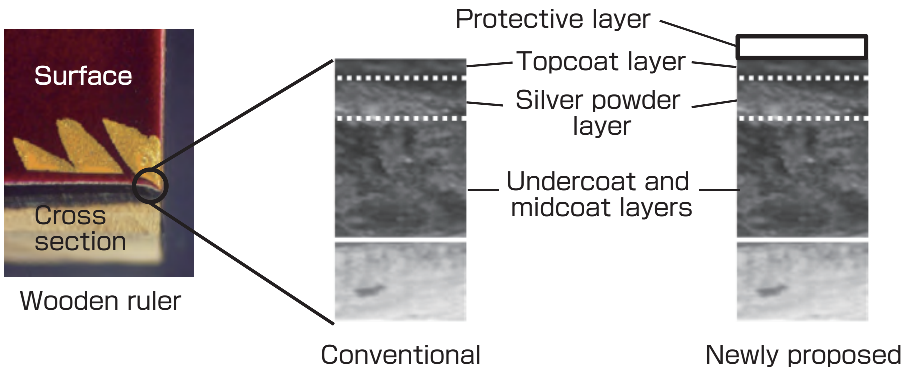


Fig. 1 Structure of conventional *tamamushi-nuri* and structure of newly proposed *tamamushi-nuri*

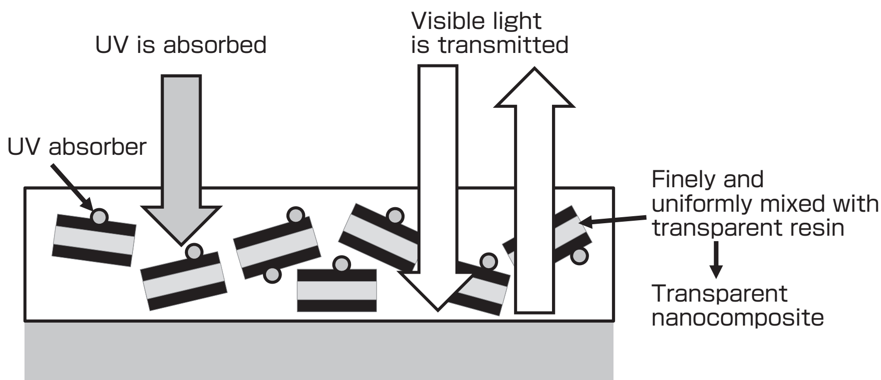


Fig. 2 Expected internal structure of protective film and its optical property

Table 1. Organoclay and organification agents used

Clay (product name)	Organification agent	
	Component name	Carbon number
SPN	Polyoxypropylene methyldiethyl ammonium chloride	75
STN	Methyltrioctyl ammonium	8
SAN	Dimethyldistearyl ammonium	18
SAN316	Dimethyldistearyl ammonium	18

increased to 5 wt%.[10] It was found that high transparency could not be obtained unless the solvent, clay, and resin were carefully selected and an optimal combination was found. To form a coating that adhered firmly to the *tamamushi-nuri* surface without peeling off, a solvent, clay, and resin were selected, the mixture ratio was optimized, and the mixing method was investigated.

3.2 Selection of the nanocomposite protective layer ingredient

For even distribution of clay in resin, organification is conducted in which sodium ions between the clay layers are replaced by organic cations.[11] Since dispersibility in resin changes according to the type of organic cations used, the selection of organic cations is important. Here, we investigated four types of organoclay using different organic cations (Table 1). First, four types of organoclay were dispersed in toluene, an organic solvent that was initially considered, and the dispersibility was evaluated. The solid to liquid ratio of the toluene dispersion was 0.1 wt%. The particle size distribution was measured using a fiber-optical dynamic light scattering spectrophotometer (FDLS-2000; Ohtsuka Electronics Co., Ltd.). The result is shown in Table 2. In the histogram analysis, the average values of SPN and STN were small, while those of SAN and SAN316 were large.

Table 2. Average values of the particle size of organoclay in organic solvent and haze value of glass coat samples

Clay	Average value [nm]	Standard deviation [nm]	Haze value [%]
Glass plate	–	–	0.41
SPN	8.8×10^2	9.2×10^2	21.3
STN	1.1×10^3	6.4×10^2	68.6
SAN	1.9×10^4	2.9×10^4	42.3
SAN316	1.9×10^4	3.4×10^4	23.4

(Particle size is from histogram analysis; thickness of glass plate is 1 mm.)

Next, about 0.3 g of toluene dispersion of four types of synthetic clay (5 wt%) was placed on a glass plate with thickness of about 1 mm, the dispersion was spread out to about 3 × 3 cm in size, and this was dried at room temperature. The haze values of the dried glass plates were measured using a haze meter (NDH5000; Nippon Denshoku

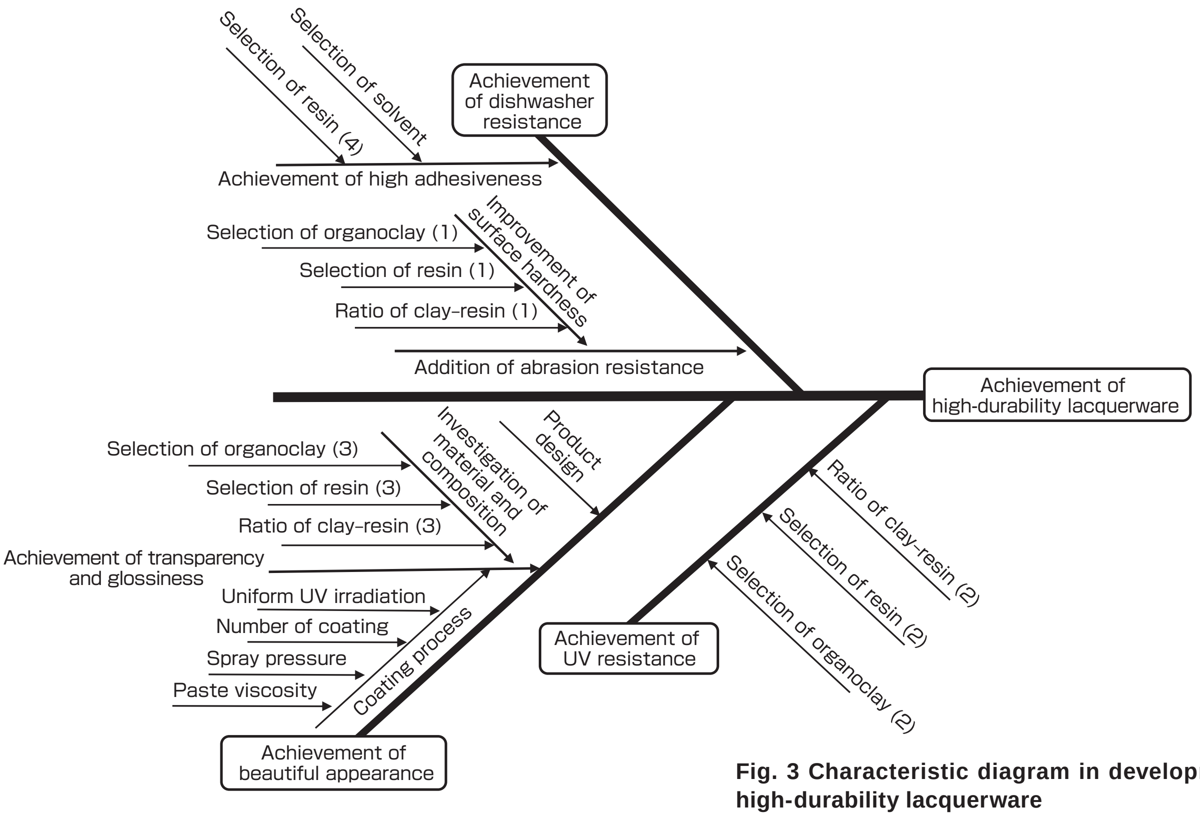


Fig. 3 Characteristic diagram in development of high-durability lacquerware

Industries Co., Ltd.). The haze values were small in the order of SPN, SAN316, SAN, and STN. A small haze value indicates that the light does not scatter and the appearance is clear, and this is desirable.

From the above result, it was found that SPN that had the most carbon number among the organification agents dispersed most finely in the dispersing liquid and haze was low for the glass coated film. Therefore, we decided to use SPN as the clay.

For UV curing resin, we selected three candidates, UV-7605B, UV-7640B, and UV-1700B (all of The Nippon Synthetic Chemical Industry Co., Ltd.) that have catalog value pencil hardness of 3H or more that was the goal value of this research. These are urethane acrylate resin, and the molecular weight/number of oligomer functional group for UV-7605B, UV-7640B, and UV-1700B are 1100/6, 1500/6-7, and 2000/10, respectively. The method for adding the protective layer using these types of resin is shown in Fig. 4. This involved mixing UV curing resin, toluene, clay, and a photopolymerization initiator at a certain ratio into a paste, applying an even paste to a glass slide or to *tamamushi-nuri* using a bar coater, and allowing polymerization to take place in the UV curing device.

For the solvent, toluene was used since it was suitable for the selected SPN. Here, the weight ratio of resin and toluene was unified to 30:70. Since clay thickened the paste, coating was not possible if there was excessive clay, as that increased viscosity. Therefore, we studied the relationship between the amount of clay that could be added to the paste and the viscosity of liquid. Specifically, the paste viscosity was studied by changing the amount of organoclay added to UV-7605B, and the procedures were as follows. First, 30 g of resin was dispersed in 70 g of toluene. Then, a weighed amount of SPN was put into a screw cap bottle, and the bottle was shaken until the clay was dispersed. When the paste was made using the above method, we could make the mixture only up to 25 g of added SPN, and the liquid became immobile when the amount of SPN reached 30 g (Fig. 5). Since UV-7605B had the lowest molecular weight among the three types of resin, it was thought to have low viscosity. Therefore, it was found that the percentage of additive organoclay that could be shaken was up to 25 g for 30 g of resin and 70 g of toluene. Here, from the perspective of ease of handling, the paste was made with 21 g of SPN added.

The UV visible absorption spectra of the protective layers on the glass slides are shown in Fig. 6. It was found that the protective layers had no absorption in the visible light range. Also, it was confirmed that when resin and clay coexisted, the absorption peak of the UV absorber shifted remarkably to the long wavelength side. This is a phenomenon that is observed when the concentration of the UV absorber is high, and it indicates that the UV absorber was concentrated and attached onto the clay surface. Also, as the absorption shifted to the long wavelength side, the UV blocking effect of the protective layer increased, and increased UV resistance of the lacquerware was expected.

In the hardening experiment of the protective layer on a glass slide, it was confirmed that UV curing occurred even when the solvent was toluene or a thinner (mixture of toluene, xylene, and others) used at Tohoku Kogei (dried thickness of about 10 μm). At Tohoku Kogei, an *urushi* bath[12] is used for drying, and it was checked whether drying was possible without heat. An *urushi* bath is a wooden shelf with no particular temperature control. *Urushi* lackerwares gradually dry and harden as they are placed in the *urushi* bath. According to the experiment at AIST, the drying process that normally took 3 min at 60 ºC could be replaced by 1 hour at

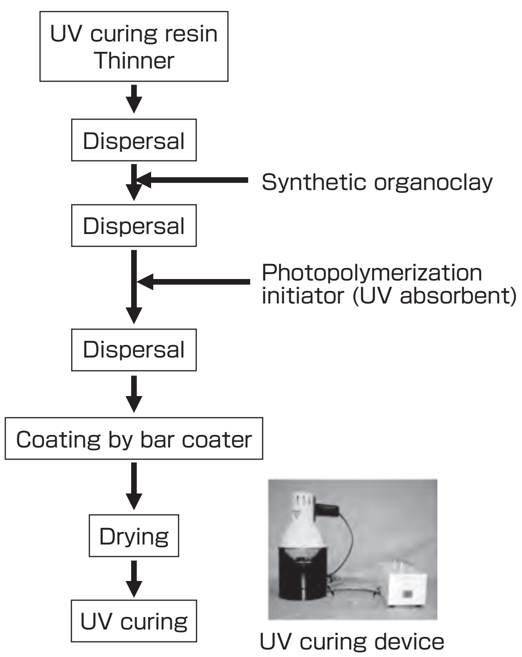


Fig. 4 Preparation procedure of protective layer

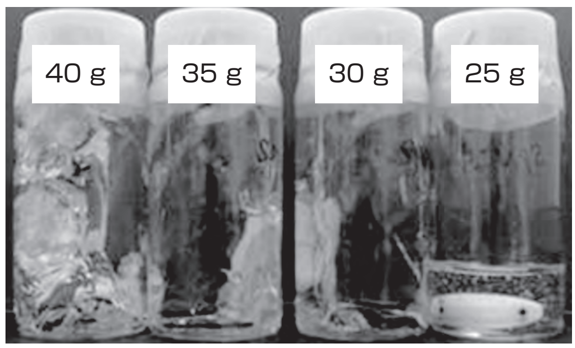


Fig. 5 Amount of organoclay added and the condition of liquid
The numbers in the figure show the amount of SPN added to 30 g. of resin. *From Abstracts of 58th Annual Meeting of the Clay Science Society of Japan,* A6 (2014).

room temperature. Through this finding, it became possible to conduct drying by placing the products in an *urushi* bath within a clean environment, without taking them to a drying oven outside the clean environment where spray-coating was done, and dust adherence could be avoided.

3.3 Evaluation method and results

3.3.1 Evaluation of transparency

With the configuration of 30 g of resin, 70 g of toluene, 0 to 40 g of SPN, and 6 g of initiator, the protective layer was applied to a glass slide with a bar coater, and the transparency was evaluated. Cissing occurred in the coats that did not contain SPN, and samples could not be made. The total light transmittance and haze of the film applied to the glass were measured (Figs. 7 and 8). In Fig. 7, it is shown that the total light transmittance of the film surpassed 90 %, which was our target value, regardless of the amount of added clay, and the transparency was sufficient. In Fig. 8, it is shown that haze was 0.6 or higher and 1.8 or lower, and the lowest value was obtained when the amount of clay added was between 20 to 30 g.[13] From this result, it was shown that sufficiently high total light transmittance could be obtained when the amount of clay added was in the range of 5 to 40g.

3.3.2 Evaluation of surface hardness

The protective layer made from the samples of aforementioned paste applied to glass with a bar coater was evaluated for abrasion resistance using the pencil hardness test (JIS K5600). As a result, UV1700B failed to reach 3H that was our target. On the other hand, it was found that UV7640B and UV7605B achieved hardness of 3H or higher.[13] It is thought that resin gains higher hardness with more oligomer functional groups, but in the clay-resin mixture, it is thought that there is an optimal molecular weight as well as amount of oligomer

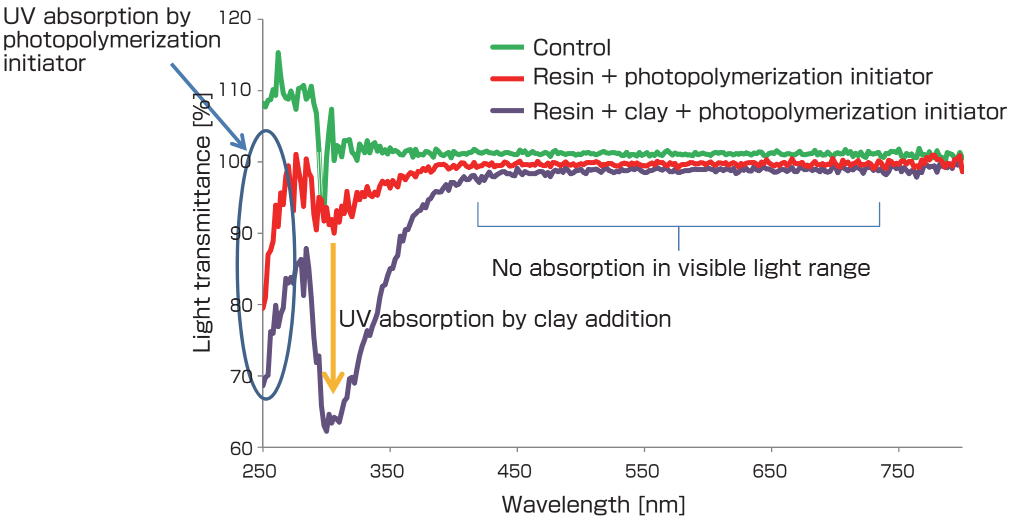


Fig. 6 UV-visible absorption spectra of protective film

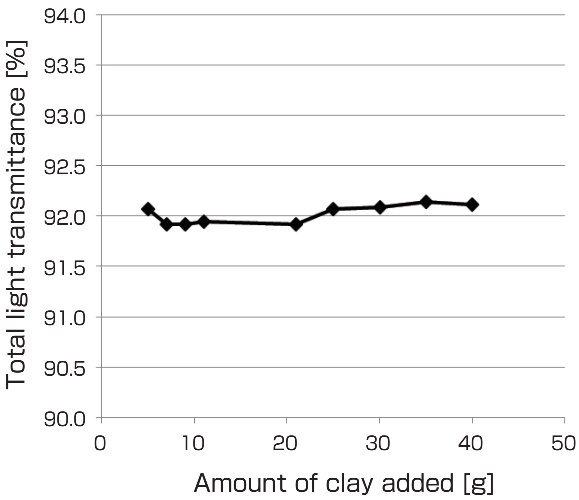


Fig. 7 Relationship between amount of clay added and total light transmittance

From *Abstracts of 58th Annual Meeting of the Clay Science Society of Japan*, A6 (2014).

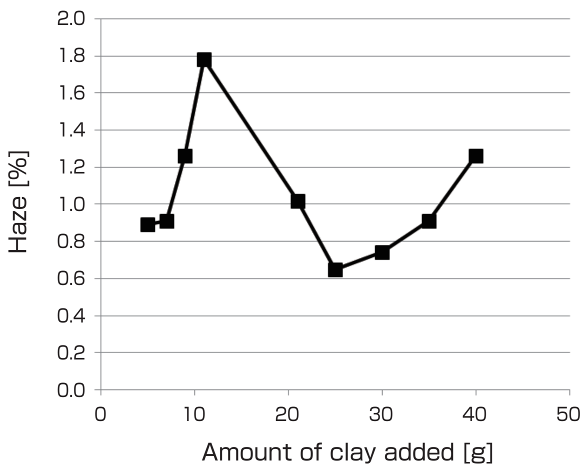


Fig. 8 Relationship between amount of clay added and haze

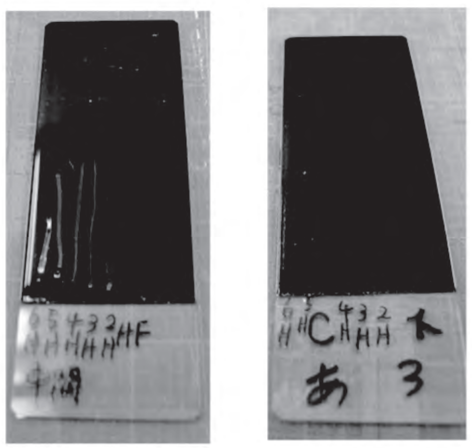
From *Abstracts of 58th Annual Meeting of the Clay Science Society of Japan*, A6 (2014).

function groups. The amount of the initiator was set at 6 g that allowed sufficient hardness. For resin, since the viscosity of UV7640B was much higher than that of UV7605B, and there was the problem that UV7640B had to be diluted with more solvent during spray coating, we decided to use UV7605B.

While no problem was encountered during film forming with a bar coater, we were unable to obtain sufficient gloss when a solvent was added for the purpose of decreasing viscosity during spray-coating. This occurred as unevenness formed on the surface due to low leveling of paste with high clay content. It was possible to decrease the viscosity by reducing the amount of clay added, and the amount of 7 g, 3 g, and 1.5 g of added clay were investigated, and it was confirmed that the leveling property improved with those compared to 21 g.

The organoclay was selected from the haze value and dispersibility. The relationship between viscosity and amount of added organoclay was checked, and the visible light absorption property, transparency, spray-coatability, and leveling property were evaluated. In the subsequent film forming evaluation, we used the evaluation with 3 g of added clay (for 30 g of resin).

In the case in which 3 g of SPN was added to 30 g of resin, the result of evaluation using pencil hardness as surface hardness is shown in Fig. 9. The samples are all black *tamamushi* layers (urethane resin) on glass slides spray-coated with the protective layer. Pencil hardness was from 4H to 5H, and sufficient surface hardness of 3H or higher that was our target value was obtained (Fig. 9 right). On the other hand, the black *tamamushi* surface with no protective layer had pencil hardness F (Fig. 9 left). As shown above, sufficient improvement in abrasion resistance was seen by applying the protective layer. Coats of *tamamushi-nuri* use cashew or urethane in most cases. Since urethane was already evaluated for the black color, we conducted tests for the samples in which cashew resin (red color) was coated on the glass slide. The pencil hardness of cashew resin was determined to be HB, and it was somewhat softer compared to pencil hardness F of urethane (Fig. 9 left). When a protective layer equivalent to Fig. 9 was applied to cashew resin, it was confirmed that the surface hardness improved to 3H. It was found that the protective layer increased the hardness of both the urethane and cashew surfaces.



No protective layer; F   With protective layer; 4H

Fig. 9 Result of pencil hardness test

3.3.3 Evaluation of dishwasher resistance

There was no standard method for evaluating dishwater resistance. Therefore, washing using a dishwasher was repeated a set number of times, evaluation test was done before and after, and the goal was to find the least change. The evaluated items were color, gloss, and surface flatness.

First, a dishwasher (NP-TR6; Panasonic Corporation) was set in the AIST lab. Washing was done in a standard course, including sterilizing mist, washing, and rinsing processes. To reduce time, drying was not done. The washing temperature was set to about 70 ºC. The washing time per cycle was about 30 min. The detergent used was Charmy Crysta Clear Gel (Lion Corporation). A sample was made by applying black *tamamushi* and others on a glass, and then spray-coating a protective layer consisting of 30 g of resin, 70 g of toluene, 3 g of SPN, and 6 g of initiator (there were three *tamamushi-nuri* thicknesses: thin, medium, and thick). These were placed in the dishwasher 20, 60, and 100 times, the samples were taken out, and changes in color compared to the start were measured using a color difference meter (Fig. 10). A smaller figure for color difference ΔE*ab showed that the before-after color difference was small. When there was no protective layer, the color difference after 100 wash cycles was on average 0.97, and with a protective layer, it was 0.76. The figure 0.97 is categorized as AA level tolerance[14] or the “level in which some color difference can be seen in side-by-side color comparison.” On the other hand, 0.76 is AAA level tolerance or the “limit at which strict color tolerance can be set from the viewpoint of reproducibility of visual determination.” After 100 wash cycles, there was no case

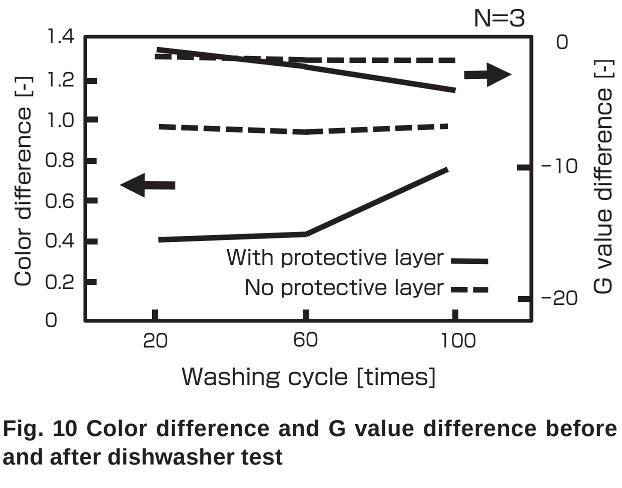


Fig. 10 Color difference and G value difference before and after dishwasher test

where the color difference was 1.6 or higher, that is, a level tolerance or the "level in which one can hardly detect any difference in color comparison from a distance." From this result, it was found that the protective layer did not undergo discoloration even with repeated washing with a dishwasher.

"G value" that is the measurement of "gloss" was evaluated as part of the evaluation of appearance. G value is calculated by subtracting the value of specular component exclude (SCE), that does not include specular reflection light, from the value of specular component include (SCI) that includes specular reflection light.[15] Larger value indicates higher gloss. The G value was measured with a spectrophotometer (CM-2600d; Konica Minolta Japan, Inc.). The angle of incidence was 8 degrees. The measurement values of samples with a protective layer added to black *tamamushi* were between 98 and 99. When the G value is around 100, it is equivalent to glossy plastic, and it was found that the surface was shiny. The changes in G value were measured before and after the dishwasher test. All samples showed a trend of slight reduction in G values after dishwashing. In the case without the protective layer, the difference was 2, and in the case with the protective layer, the difference was 4 (Fig. 10). Although the value was slightly larger when there was a protective layer, the change was almost unnoticeable in terms of appearance.

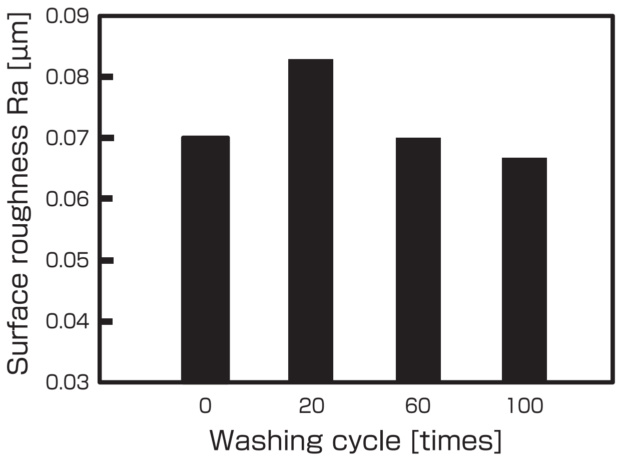


Fig. 11 Relationship between washing cycle and surface roughness

Next, the surface roughness Ra value was measured using a laser microscope (Keyence Violet Laser Color 3D Profile Microscope VK-9500; Keyence Corporation). Figure 11 shows the relationship between the number of wash cycles and surface roughness. The surface roughness ΔRa of the coating layer before washing was between 0.07 and 0.08 µm, and it was between 0.09 and 0.06 µm after washing. The increase in surface roughness by washing was not confirmed. As seen above, by the addition of the protective layer, it was confirmed that there was almost no deterioration of color, gloss, or surface evenness.

3.3.4 Evaluation of UV resistance

For UV irradiation, Handy Cure Lab (HLR100T-2; Sen Lights Co., Ltd.) was used (intensity 12,000 µW/cm^2, wavelength 365 nm). Setting the distance from the light source to the sample at about 10 cm, irradiation was done for 1 to 5 hours, and the color change in the sample was evaluated using a color difference meter. From the illumination measured using an illuminometer under this condition and the annual average value of irradiation in Tsukuba,[16] it was calculated that one hour irradiation was comparable to the irradiation dose for 2.6 years in a room.

Samples consisted of three types of *tamamushi-nuri* postcards: no protective layer; protective layer with SPN; and protective layer without SPN. These were irradiated with the UV light at the same time, left overnight, and the color change was measured. The color change increased in the order of no protective layer > protective layer without SPN > protective layer with SPN, and the effect of clay addition was confirmed (Fig. 12). The color change was large in the order of blue > green > red.

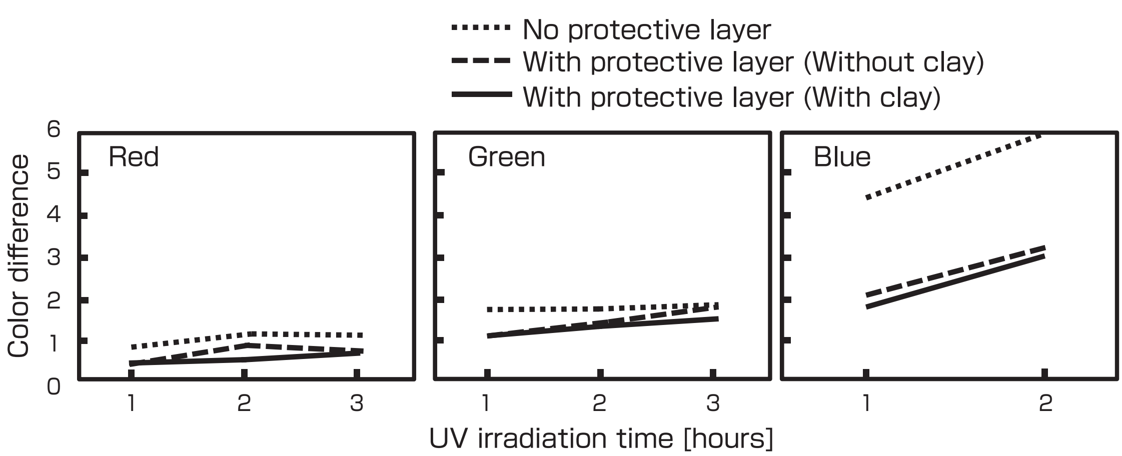


Fig. 12 Relationship between UV irradiation time on postcard samples and color difference

For blue, in addition to the postcards, evaluation for glass substrates was conducted. Samples consisted of three types: no protective layer; protective layer without SPN; and protective layer with SPN. These were irradiated with the UV light at the same time, and the color change was measured. As a result, the ΔE*ab of no protective layer, protective layer without SPN, and protective layer with SPN after 1 hour irradiation were 3.6, 0.7, and 0.5, respectively. The color change of the sample with protective layer that includes SPN was the smallest, and the effect of clay addition was confirmed.

3.3.5 Evaluation of adhesiveness

A tape peel test (JIS K5600) was conducted for the protective layer applied using a bar coater and spray, with the composition of 30 g of resin, 70 g of toluene, 3 or 0 g of SPN, and 6 g of initiator. No peeling of the protective layer was observed. Also, a cross-cut tape test (JIS K5600) was conducted for the same sample. No peeling was observed, and all 25 test areas that were set as goals were categorized as Category 0 where there was no peeling, and sufficient adhesiveness was confirmed. Furthermore, concerning samples of wood molded plate and aluminum surface to which the same protective layer was applied, the results were Category 0, and sufficient adhesiveness was confirmed.

3.4 Establishment of coating method

The above investigations were evaluations of planar samples. However, actual products are 3D, and it was necessary to add the protective layer to 3D surfaces. Therefore, coating was conducted with a spray rather than a bar coater. Due to the viscosity property of the paste liquid, it was important whether it was possible to add a protective layer of even and sufficient thickness. Therefore, the developed paste was spray-coated at the Tohoku Kogei studio to seek optimal conditions that allowed transparent, even, and highly artistic coating on the lacquerware surface. Specifically, optimization was done for paste viscosity through solvent addition, spraying pressure, and number of coats, to investigate the coating method to obtain a high-quality coating layer.

3.4.1 Spraying condition with high evenness

In *tamamushi-nuri*, there is optimal paste viscosity according to the shape of the product to be coated. Specifically, between products with numerous sides and those with numerous flat surfaces, the viscosity is lower for the latter, and even for the same flat surfaces, the larger the surface the viscosity is reduced. In the newly developed paste, a urethane thinner (Strone Thinner; Cashew Co., Ltd.) was used as an additional solvent, and it was confirmed that the viscosity could be adjusted by changing the amount. Optimal paste viscosity was confirmed for application to ten types of products, including regular products [bookmarker, tumbler, rocks glass, and wine cup (two types)] and prototypes (*sake* cup, lipped bowl, small plate, square bowl, and plate). From the above findings, appropriate amount of solvent to be added was obtained per product shape.

In the *tamamushi-nuri* that uses spray-coating, the spraying speed is adjusted by air pressure. In the usual *tamamushi-nuri* coating, the optimal pressure is around 0.2 to 0.4 MPa. However, when the newly developed paste was sprayed at this pressure, an “orange peel” surface or unevenness appeared, and the glossiness that characterized the *tamamushi-nuri* disappeared. As a result of study, it was found that the optimal pressure for this paste was 0.15 MPa.

3.4.2 Number of coats

In this research, high transparency was mandatory for the protective layer since it was added as the finishing coat of *tamamushi-nuri*. It was confirmed that transparency of the protective layer was obtained, and the brightness and glossiness were not lost through the additional number of coats. Specifically, the content of SPN was adjusted finely, and we found the combination that did not alter the appearance compared to products without the protective layer (i.e. a regular *tamamushi-nuri* product). The process of UV irradiation after coating with the protective layer was done with the utmost care to avoid adhesion of dust. For UV irradiation, a special box was created so that sufficient intensity of UV can be irradiated from the sides as well as the top. This box was set in the room where topcoat spraying was done, and a series of processes of UV drying could be completed in that room. The original device was made by using a light-reflecting aluminum plate with a rotary table.

3.4.3 Reproducibility by difference in shapes

As mentioned above, the viscosity of the coating paste is controlled according to the shapes of the *tamamushi-nuri* products. In one of the prototypes that was manufactured this time, we were able to obtain almost the same appearance as Tohoku Kogei’s regular *tamamushi-nuri* products and parts. Also, we were able to reproduce the *tamamushi-nuri* appearance equivalent to the regular products from materials that were already used such as wood, resin (acrylic, ABS), and glass, as well as ceramics that is expected to be used in the future.

3.5 Establishment of product specification

3.5.1 Manufacture of prototypes, evaluation test, and surveys at exhibitions

G value measurement and a monitor evaluation questionnaire were conducted for *sake* cups that were spray-coated with four types of paste, in which the amount of clay added was changed from 1.5 to 7.0 g for 30 g of resin.

A total of five types of *sake* cups, consisting of a regular *tamamushi-nuri sake* cup (no protective layer) and four types of *sake* cups which were spray-coated at the studio with varying ratio of clay in UV curing resin, were shown at exhibitions, and questionnaires were given to the visitors (Fig. 13). They were asked to select the cup that was closest in appearance to the one without the protective layer. The questionnaire was given to 91 people. The *sake* cup that was considered the most similar was the one with 1.5 g, the least amount of clay added, and it was over 60 percent of the total response. As seen in Fig. 14, as a result of evaluation using the glass plate samples, there is a tendency that the G value increased as the amount of clay loaded decreased (Fig. 14). The result of the questionnaire matched the relationship of the amount of clay loaded and G value as shown in Fig. 14.

3.5.2 Monitor survey at restaurants

In the next step, in addition to the *sake* cup, prototypes were manufactured using the developed paste for six product types including lipped cup, tumbler, rocks glass, ceramic plate, and ceramic small bowl. Some of the products were evaluated at restaurants A, B, and C. At a kaiseki restaurant A, a product was used as a cup for local Japanese *sake* and explanation was provided about the product. We received comments that it was good, and it could be used as PR for tourists and other people who wish to enjoy the local cuisine. Restaurant B was a French restaurant where there was a sommelier with knowledge of French cuisine and wine, and the sommelier was actually the owner of the restaurant. Wine cups were used, and although there was no problem about durability, it was indicated that the color of wine could not be seen through the cup, and we reconsidered the shape of the glass so that the wine color would show. Restaurant C was an Italian restaurant, and plates and wine cups were used (Fig. 15). The plates with and without protective layer were used, and after washing in the dishwater, it was confirmed that there were less scratches on plates with the protective layer.

The user evaluation was positive, and we received comments that the overall design and usability were good, and people said they wished to purchase them when the products became commercially available.

3.5.3 Product realization

When creating a product, it is necessary to sell a certain number of products, and though we initially considered various products, we decided to select final candidates. When we asked the restaurants that actually used the products as well as people of various fields, we were told that wine cups could be used as souvenirs overseas and could be used for a

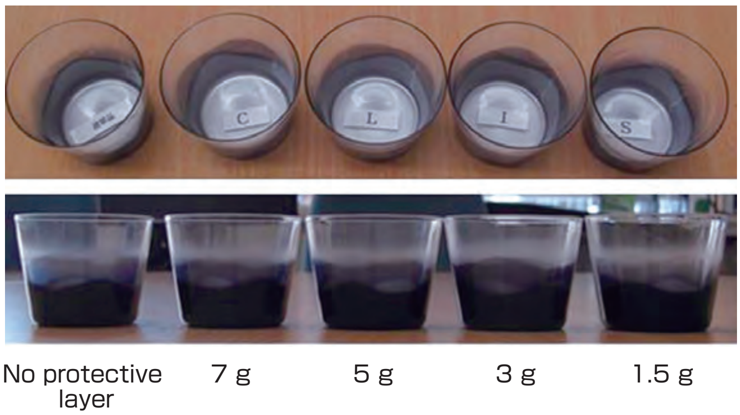


Fig. 13 Appearance of sake cup sample used in user evaluation
Numbers indicate the amount of clay added to 30 g of resin.

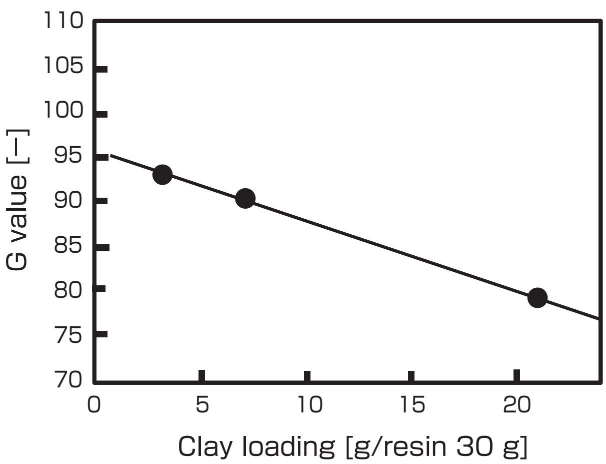


Fig. 14 Relationship between clay loading and G value

Fig. 15 User evaluation at a restaurant

wide range of beverages. Therefore, we commercialized the wine cups in two colors in April 2015 (Fig. 16). The wine cups were used as souvenirs at the G7 Finance Ministers and Central Bank Governors Meeting held in Sendai on May 2016.

After achieving product realization, the product received the Minister of Economy, Trade and Industry Award of the 6th Monodukuri Japan Award. It was also listed in the Monodukuri White Paper and selected as Miyagi Sugure MONO (Excellent Products of Miyagi). Support was obtained from the City of Sendai, Miyagi Prefecture, METI, Reconstruction Agency, and others. An NHK TV documentary “Ippin” that featured this product was received with such enthusiasm that it was re-aired four times, and the product became known throughout Japan. In NHK World’s “Science View,” it was aired internationally. There was also coverage by various newspapers and magazines, and the product continues to be taken up in product reviews. As of February 2018, for the wine cups, there is a waiting period of three months from order to delivery.

4 Summary and future prospect

For the protective layer, we achieved the goal for appearance, abrasion resistance, UV resistance, and others. The process of applying this to a product was established and the product was commercialized. In the future, we hope to enhance the durability of *tamamushi-nuri* itself. Also, since the newly developed protective layer can be applied to a wide range of plastic products with soft surfaces, it can be expanded to use other than lacquerware.

Appendix: Collaboration and cooperation of traditional craft and advanced technology

The efforts for the development of high-durability lacquerware was started when a worker saw an exhibit in the “Exhibition Room for Craft Prototypes”[2] that was established in the first floor of Building C at AIST Tohoku, from 2004 to 2011, under the supervision of Akiko Shoji, Honorary Professor, Tohoku Institute of Technology. The National Institute of Industrial Art (NIIA), which was the predecessor of AIST Tohoku, was established for the purpose of promoting the industries of Tohoku, and prototypes of the craft of the Tohoku Branch of the Industrial Art Institute and NIIA were stored and exhibited there. Since AIST Tohoku was set in the area where there were many natural smectite mines, it succeeded in the industrialization of synthetic smectite in cooperation with smectite companies.[17] The clay material used in this research is the organified product of synthetic smectite. Moreover, clay film is a material that takes advantage of the characteristic that “high film formability” of synthetic smectite. Since both *tamamushi-nuri* and clay film are coating materials, the idea of merging the technology developed at AIST Tohoku with lacquerware led to this collaboration.

Fig. 16 Commercialized a pair of wine cups
About 6 cm in diameter, about 15 cm in height.

While in general, collaboration of materials development and craft is difficult, the respective fields worked closely together for collaboration and cooperation. Feedback was applied to results of investigation, improvements were made, and we believe the collaboration of industry-academia-government was conducted effectively. We think this is largely due to Tohoku Kogei’s stance of incorporating new things while carrying on the tradition.

Through the collaboration with companies that supply the clay material, we were able to create the flow of product supply from paste to lacquerware production, and we believe it is an excellent example of integrated development.[18]

The development of high-durability lacquerware was conducted within the Revitalization Promotion Program of the Japan Science and Technology Agency after the Great East Japan Earthquake. With the support toward commercialization by a JST coordinator, it was evaluated highly as an industry-academia-government collaboration product along with AIST Tohoku and members of Tohoku Kogei.

In December 2017, Tohoku Kogei was selected as the “Company that Leads the Region to the Future” by METI, and by government-civilian collaboration, the brand was established for high-durability lacquerware and nanocomposites. In the future, we hope this will lead to participation by different industries and products to generate new values. With the history of Sendai from which modern craft was started and the technique of *tamamushi-nuri* that was born from industry-academia-government collaboration, we shall continue this collaboration to pass on this technique to the future.

Acknowledgement

Parts of this research were conducted under the Japan Science and Technology Agency (JST) Revitalization

Program A-STEP Seeds Actualization Type "Development of high-durability lacquerware with added protective layer containing clay"; the JST A-STEP High Risk Challenge Type (Revitalization Promotion) "Development of High-Durability Surface Treatment Technology by Inorganic-Organic Nanocomposites and Its Application to *Tamamushi-nuri*, a Traditional Craft of Miyagi"; and the Grant for Product Development by Small to Medium-sized Manufacturing Companies of Sendai "Application of High-Durability Surface Treatment Technology by Inorganic-Organic Nanocomposites to *Tamamushi-nuri*, a Traditional Craft Designated by Miyagi Prefecture." We would like to thank the following people who were involved in this development: Professor Akiko Shoji (Tohoku Institute of Technology); Mr. Jun'ichi Isoe (JST); Mr. Noriyuki Kuwanaga, Mr. Yukiteru Sato, and Mr. Mitsuhiro Endo (Bureau of Industry, Sendai City); Mr. Tatsuji Hajimesawa (K.K. Sendai Yamarai); Mr. Yasuhiro Saura and Mr. Shinsuke Kimura (Tohoku Kogei Co., Ltd.); Mr. Shin'ichi Iwata and Ms. Rie Tanaka (AIST at the time): Ms. Asami Suzuki, Ms. Emiko Tomon, Dr. Hiroshi Nanjo, Dr. Ryo Ishii, Dr. Hiromichi Hayashi, Dr. Takafumi Aizawa, Dr. Yoshito Wakui, Dr. Takashi Nakamura, and Mr. Masayuki Abe (AIST); and many others.

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Authors

Takeo Ebina

Completed the doctor's course at the Graduate School of Engineering, Tohoku University in 1993. Joined the Government Industrial Research Institute, Tohoku, Agency of Industrial Science and Technology, Ministry of International Trade and Industry. Visited the University of California at Santa Barbara twice to study functional materials including clay. Currently, Prime Senior Researcher, Research Institute for Chemical Process Technology, AIST. Started the development of film materials with clay as main component in 2004. Conducted wide-ranging research from synthesis of clay materials to mass production of application products. Use of clay-based films include transparent film using synthetic clay and electronic device that employs the film. In this paper, was in charge of the materials development for protective layer and its evaluation.

Midori Saura

Graduated from the Faculty of Law, Tohoku Gakuin

University in 1991. Joined a bank, and then joined Tohoku Kogei Co., Ltd. in 1996. Currently, Managing Director, Tohoku Kogei. In charge of sales and product planning. In this paper, was in charge of relaying information about coating properties, user evaluation, and product realization.

Yasukatsu MATSUKAWA
Graduated from Tohoku High School in 1981, and joined Tohoku Kogei Co., Ltd. in 1981. Currently, Plant Manager, Tohoku Kogei. In charge of production and control of the products. In this paper, established spray-coating method and method to add protective layer to products.

Discussions with Reviewers

1 Overall

Comment (Shigeki Naito and Akira Kageyama; AIST)

This paper describes the technologies for *tamamushi-nuri*, which is lacquerware with distinctive appearance and ways of producing it invented by the National Institute of Industrial Art, Ministry of Commerce and Industry (current METI) that was established in 1928 to vitalize the industry after the Great Depression. It also describes the new technology that was developed through collaboration of Tohoku Kogei that nurtured the *tamamushi-nuri* into a craft that characterizes Sendai, and AIST Tohoku that succeeded in the commercialization of synthetic smectite and was seeking usage of this product. It explains the course of technological development and the results obtained to significantly improve abrasion resistance that was a disadvantage of lacquerware, while maintaining the excellent appearance of *tamamushi-nuri*.

It is a valuable case study when it was thought difficult to generate new values for society through collaboration of traditional craft and advanced science and technology, by overcoming the weaknesses and barriers of the conventional products. As this may provide guidance to other fields, I think this paper is appropriate for publication in *Synthesiology*.

2 Overall picture of the elemental technologies

Question (Akira Kageyama)

In this technology, I think the overall optimization technology is important for the following issues: (1) indices to provide the product performance (transparency, surface hardness, abrasion resistance, UV resistance, dishwasher resistance, adhesiveness, etc.); (2) parameters when designing protective layer materials (organoclay, UV curing resin, solvent, composition of clay ingredient, dispersed particle size, etc.); and (3) issues in setting coating conditions (suitable viscosity, paste dilution technique according to the shape of object to be coated, avoidance of orange peel, hardening at room temperature, etc.). However, I think it is difficult for the reader to understand since there is no diagram that shows the overall picture. Can you show the overall picture by using a characteristic diagram, for example, a fishbone diagram or a table?

Answer (Takeo Ebina)

As you pointed out, there are many indices that represent product performance. Also, since the indices are correlated, I decided to show the cause-and-effect relationship using a fishbone diagram. I added Fig. 3.

Comment (Akira Kageyama)

Since you added Fig. 3, now the overall picture of the elemental technologies can be understood easily. I think the major characteristic of this technological development is to maintain the “beautiful appearance,” and it is necessary to investigate from both the material composition side as well as the coating process side. Therefore, if you create a characteristic diagram showing the two sides, I think people would better understand the contribution of Tohoku Kogei.

Answer (Takeo Ebina)

Thank you for your comment. By remaking the diagram as you pointed out, the contribution of Tohoku Kogei became clearer. I also added the “achievement of transparency and gloss” within the frame of “beautiful appearance,” and it is shown that the two major categories, investigation of materials and composition and investigation of coating process, were needed to solve this issue, and the various listed factors are shown in the next layer.

3 Reinforcement of data that show the result of R&D

Comment (Shigeki Naito)

In the abrasion resistance evaluation, you mention that the UV curing resin was selected according to pencil hardness, and that UV7605B was selected considering viscosity. I think you should show the outline of the chemical structure of UV curing resin and the scientific reasoning behind it.

Answer (Takeo Ebina)

I think your comment is valid. Therefore, I added the scientific explanation, not only the phenomenal description. Specifically, I added the description that the UV curing resin investigated is a urethane acrylate resin, and the molecular weight/oligomer functional group number for UV-7605B, UV-7640B, and UV-1700B are 1100/6, 1500/6-7, and 2000/10, respectively, to show the chemical properties of the resin. Since UV-7605B has the smallest molecular weight among the three types of resin, it has low viscosity, and it is thought that the hardness increases as the number of oligomer functional group increases. However, in the clay-resin composite, it is thought that there is an optimal molecular weight and an optimal number of oligomer functional groups.

Comment (Akira Kageyama)

I think you should add a bit more data as figures or tables, about optimization of materials technology, in addition to the text, to clarify the basis of your decisions. Also, you evaluate SPN, STN, SAN, and SAN316, I think these were treated by quaternary ammonium salts with different chemical structures, as the organification agents for the organoclay. Can you show the outline of their chemical structures?

Answer (Takeo Ebina)

As you pointed out, I added Figs. 5, 7, 8, and 14 to show that the decisions were made based on the data. The four types of organoclay were treated by different quaternary ammonium salts, and I added Table 1 showing the organification agents and their carbon number.

4 Division of role between AIST and Tohoku Kogei

Comment (Akira Kageyama)

I believe there were elements that could not have been achieved without the participation by Tohoku Kogei. Can you highlight those elements more? One is the realm of art of *tamamushi-nuri* (lacquerware) including a sense of beauty such as coloring, depth of color, gloss and others. Second is the realm of craftsmanship. Both are difficult to quantify, but weren’t there decisions made about the materials composition to strike a balance between the coating condition and the total beauty of *tamamushi-*

nuri? If there were such situations, I think you should give some cases to show the close collaboration between the organizations that have different strengths.

Answer (Midori Saura and Takeo Ebina)

As you pointed out, this development was only possible through AIST’s strength in material development and Tohoku Kogei’s design and craftsmanship. There wasn’t enough focus on this point. Therefore, the following text was added to “2 Scenario of development of high-durability lacquerware.”

“Tohoku Kogei Co., Ltd. has conventionally used brush-coating on lacquerware, but around 1955, it started using spray-coating for the first time on traditional lacquerware. Currently, it uses spray-coating on products with various shapes such as glass, vase, plate, and others. Expert skill is required to apply even coating to the entire surface of products with complex shapes, and the coating technology based on long experience accumulated by Tohoku Kogei was utilized in this development. This development was achieved after the material composition was ultimately determined for the balance between beauty and coating conditions of *tamamushi-nuri*, and after repeated lab investigations at AIST and sample coating at Tohoku Kogei.”

5 Chapter for collaboration and cooperation of traditional craft and advanced technology

Comment (Shigeki Naito)

I think it is a good attempt to present the uniqueness of this paper by introducing this perspective, but I feel it is somewhat out-of-place within the paper. Therefore, how about placing this part outside the text, and putting it in an appropriate place as “Appendix”? Also, please revise it so the text can be more easily understood.

Answer (Takeo Ebina)

As you advised, I detached this part from the main text of the paper, and I made an Appendix of this content in front of Acknowledgements and References. Also, expressions that might be difficult to understand were revised.