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Effects of Viscosity on Dispersion Stability of Nano $CoAl_2O_4$ Ceramic Ink

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ABSTRACT

Inkjet printing is a widespread technology, offering advantages such as high-quality decoration, a continuous process, and the accurate direct reproduction of patterns or pictures. In inkjet printing technology, the dispersion stability of ceramic ink is one of the most important factors. In this study, the dispersion stability of blue $CoAl_2O_4$ ink for ceramic inkjet printing is systematically investigated. Blue $CoAl_2O_4$ pigment was synthesized by a solid-state reaction and then milled to less than 300nm in size. In order to investigate the influence of the viscosity on the dispersion stability, two types of $CoAl_2O_4$ ceramic inks (termed here Blue L and Blue H) were prepared using different volume ratios of ethylene glycol and ethanol. The Blue L and Blue H ink solutions contained cetyltrimethylammonium bromide(CTAB) as a dispersive agent. The viscosity, surface tension and jetting stability of the $CoAl_2O_4$ ceramic inks were analyzed using a rheometer, a surface tension meter and a dropwatcher. The dispersion stability of the $CoAl_2O_4$ ceramic ink was investigated by a multiple light-scattering method. Blue H, a ceramic ink with higher viscosity, showed much better dispersion stability than the Blue L ceramic ink.

Key words : Blue ceramic ink, $CoAl_2O_4$, Dispersion stability, Viscosity, Multiple light scattering, Raw material

1.Introduction

In the construction ceramic tile industry, a change in paradigm is occurring from producer-oriented development of tile products to buyer-oriented one since ceramic inkjet printing equipment of mass-production (single pass) type was incorporated in the early 2000's. Due to an ease of changes in the desired image and design, securing of semi-permanent durability of the products by high-temperature heat treatment, and high ink efficiencies, eco-friendly work environments can be realized by inkjet printing ceramic tiles.[1-4] Because of such advantages, the share of inkjet printing systems are expected to increase from 30% in 2013 to 70% in 2017 in the construction ceramic tie industry.[5]

In general, ceramic inkjet printers have a nozzle of a few ten µm in size, and the ceramic ink should have fine particles of less than 300 nm in size for suppression of nozzle blockage phenomenon as well as for smooth jetting. Ceramic nano particles not only are thermodynamically unstable and have an increased friction between particles due to high specific surface areas but also have a high tendency for agglomeration among particles due to low solubilities in the solvent.[6] Also, the ceramic ink is a very complicated system consisting of substances such as particles as a dispersed phase, dispersion medium as a continuous phase, surfactant added to improve dispersion stability of the ink and diversified additives for control of viscosity and surface tension, etc. In such thermodynamically unstable ceramic inks with a complicated configuration, precipitation of particles and agglomeration phenomenon among particles become active during a distribution process and a storage period. Such phenomenon causes the problems of nozzle blockage upon inkjet printing and a poor coloring properties due to reduction in concentrations, with such problems being directly connected to quality degradation of printing products. To avoid such problems, securing of dispersion stability for the ceramic ink is very important.

Dispersion behavior of ceramic suspensions such as a ceramic ink may be represented by the following Stokes's law,

$$U_S = \frac{2gd_{50}(\rho_p - \rho_f)}{g_{\eta_f}}$$

where g is the gavitational acceleration, d_{50} the average diameter of particles, η_f the viscosity of fluid, and ρ_p and ρ_f the densities of particle and fluid, respectively. From the above equation, the precipitation rate (U) allowing evaluation of the dispersion stability of ceramic inks depends on the average diameter and the viscosity of particles.[7]

In the present study, confirmation was made on the dispersion stability of blue $CoAl_2O_4$ ceramic ink as one of the colors used most frequently for ceramic tile products produced by inkjet printing. The $CoAl_2O_4$ ceramic pigment sta-

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ble at high temperatures above 1000°C was prepared by solid state reaction method, followed by atomization to a size less than 300 nm using attrition milling. For ink preparation, the pulverized $CoAl_2O_4$ ceramic pigment was added to the mixed solvent of ethylene glycol and ethanol, and a cationic surfactant was added as dispersant.[8,9] To check for dispersion stabilities as a function of surfactant, particle movement and agglomeration phenomena of the ceramic inks as a function of time were comparatively analyzed by using multiple light scattering method after preparation of two types of $CoAl_2O_4$ ceramic inks with different viscosities.

2. Experimental Procedure

2.1. Preparation of $CoAl_2O_4$ ceramic ink

$CoAl_2O_4$ ceramic ink was prepared by using solid state reaction method. As the starting raw material, $CoAl_2O_4$ ceramic pigment was synthesized by mixing 1 mol of CoO(325mesh, Aldrich) and 1mol of Al_2O_3(0.3um, Sumitomo) by wet milling for 3 h followed by heat treatment at 1200°C for 1 h. To atomize the $CoAl_2O_4$ ceramic pigment prepared by such solid state reaction method into a particle size of less than 300 nm suitable for inkjet printing, particle refinement process was implemented by using an attrition mill(KMD-1S, developed by Korea Material Development Co.). For the milling process, zirconia balls of 1 mm in diameter were employed, and wet milling was conducted for 3 h together with ethanol under the BPR (Ball to Powder Ratio) condition of 100:1.

To make into an ink the $CoAl_2O_4$ ceramic nano pigment having undergone refinement process, the pigment was dispersed in the mixed liquid of ethanol and ethylene glycol (99.5%, Samchun), and CTAB(cetyltrimethylammonium bromide) was added as a cationic surfactant to obtain stable dispersibility.

2.2. Characteristics analysis for $CoAl_2O_4$ ceramic ink

To analyze particle shapes and sizes of the synthesized $CoAl_2O_4$ ceramic ink, Transmission Electron Microscope(TEM, Tecnai G2 F30 S-Twin) was employed. To check for viscosities of the ink, Rheometer(Hakke mars III, Thermo scientific) was used, and surface tension was measured by using Tensiometer (DST60, Surface electro optics). To check for the high-temperature stability, white porcelain specimens were coated with the ceramic ink and maintained for 1 h after temperatures were raised to 1250°C at a rate of 5°C/min. Printability of the ceramic ink were checked by observing formation status of spherical-shaped single droplets required for inkjet printing by using Dropwatcher(Cera DW, STI). For evaluation of dispersion stabilities of the ink, the changes of particles dispersed within the sample were analyzed as a function of time by employing Turbiscan(Turbiscan LAB, Formulaction) which uses multiple light scattering method(MLS). Measurements were made at an interval of 4 h for 1 day, and acceleration tests were conducted under the condition of 45°C for prediction of a long-term dispersion stability.

3. Results and Discussion

3.1. Characteristics analysis for $CoAl_2O_4$ ceramic ink

Discharge aspects of the ink in ceramic inkjet printing are greatly affected by particle size, solvent, additives such as surfactant, and physicochemical characteristics such as viscosity and surface tension. Fig. 1 shows TEM observation results for $CoAl_2O_4$ ceramic ink particles atomized after preparation by solid state reaction method. The atomized ink particles had a mixed form of square and hexagonal particles in shape, and were affirmed to have a variety of sizes less than 300 nm, while deformation and dislocations due to the loads applied to particles while undergoing high-energy milling could be observed.

Since the ceramic ink is applied to ceramic products fired at high temperatures, forming the colors intrinsic to the ink without discoloration even at high temperatures may be considered as an essential element. Fig. 2 shows the result of application of $CoAl_2O_4$ ceramic ink to ceramic tile and holding the general firing temperature for ceramic products of 1250°C for 1 h. The $CoAl_2O_4$ ceramic ink showed results

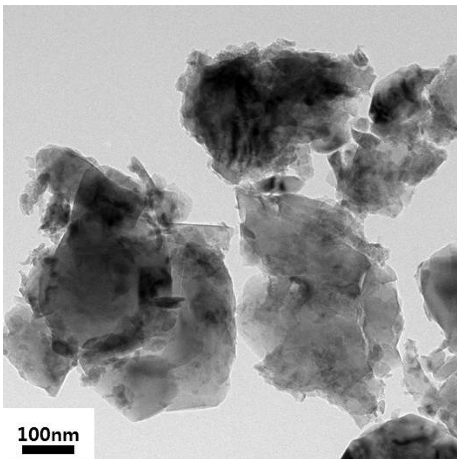

Fig. 1. TEM image of blue $CoAl_2O_4$ ceramic ink.

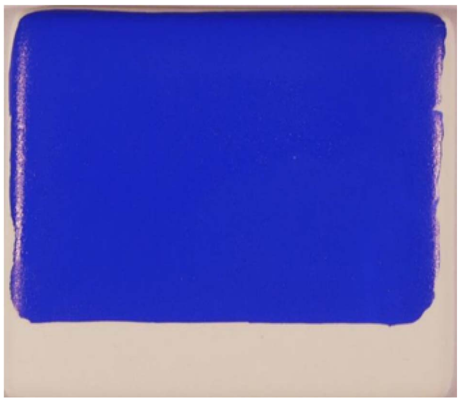

Fig. 2. Thermal stability of blue $CoAl_2O_4$ ceramic ink at 1250°C.

Table 1. Physical Properties of Blue L and Blue H Ceramic Ink

	Blue L	Blue H
Viscosity (cps)	15.58	22.52
Surface tension (mN/m)	28.40	26.47

suitable for a ceramic ink by forming a blue color without discoloration even after firing at a high temperature.

Table 1 shows viscosity and surface tension of the $CoAl_2O_4$ ceramic ink with adjustment of the ratio between ethylene glycol and ethanol. In general, when viscosity of the ink is too high, flows of the ink within a channel of the inkjet head, jetting rates of droplets and refilling rates of the ink within the channel slow down. And excessively high surface tension can make droplet formation of the ink difficult and cause formation of satellite droplets where the droplet is divided into more than two droplets rather than being formed as a single spherical droplet. On the other hand, when surface tension of the ink is too low, ink wetting phenomenon occurs on the surfaces around the nozzle, where the wet inks can cause undesirable ink flow due to gravity at jetting nozzle. Also, it is difficult to guarantee stability when the droplet is falling onto a substrate after being jetted from the nozzle. Viscosity values of the ceramic ink required for an inkjet printer to prevent such problems are known to be in the range of 4-40cps, and surface tension values in the range of 20 - 45 mN/m.[3] As shown in Table 1, the viscosity values of $CoAl_2O_4$ ceramic inks with different ratios of ethylene glycol and ethanol (Blue L, Blue H) are 15.58 cps and 22.52 cps, respectively, showing the range of viscosity values required for inkjet printing, while the surface tension values are shown to be similar at 28.40 mN/m and 26.47 mN/m, respectively.

Forms of ink droplets jetted from the ceramic inkjet printing nozzle have a very large effect on the quality of printed pictures or patterns. Fig. 3 shows the result as to whether jetting of the ink is smoothly realized upon jetting of each ink from the inkjet head and appropriate droplets of the ink are formed upon jetting. Both inks have a suitable viscosity for inkjet printing, with jetting of droplets through the dropwatcher being smoothly realized also. Satellite droplets with the droplet being divided into more than two were not observed due to formation of a long tail from the droplet, and it was considered suitable for inkjet printing since straightness without showing the phenomenon of being bent into other directions was observed while the droplet was falling.

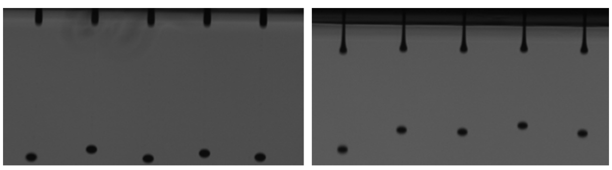

Fig. 3. Jetting stability of (a) blue L and (b) blue H ceramic ink.

3.2. Dispersion stability of $CoAl_2O_4$ ceramic ink

To analyze precipitation and agglomeration behaviors of particles within the ceramic ink which occur during storage, dispersion stabilities of the ink were observed by using MLS method. Samples were inserted in the analyzing instrument, and measurements were started after 30 minutes considering the time to reach the set temperature of 45°C. Based on the changed amount of measured values for transmission and backscattering as a function of time with the starting value of initial measurement (0 : 00 : 00) as the reference, relative analysis was made on the blue L and blue H samples of $CoAl_2O_4$ ceramic ink. Fig. 4 and 5 show the backscattering profiles for two samples (Blue L, Blue H) of the $CoAl_2O_4$ ceramic ink. In the case of measurement of backscattering values, changes within the sample were analyzed by arbitrarily dividing the measurement cell into upper layer (35 - 43 mm), middle layer (15 - 25 mm), lower layer (0 - 5 mm) parts to observe behaviors of the particles as a function of height. In the upper layer part of the blue L sample having a relatively low viscosity value, the backscattering value was reduced by about 26% in comparison with the reference value of measurement start as the time elapsed. Here, the backscattering values were reduced since scatter-

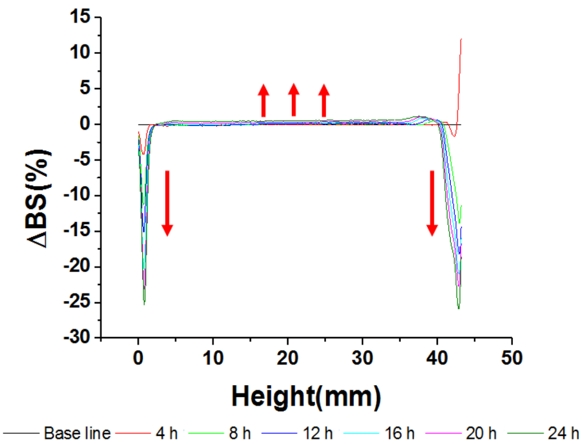

Fig. 4. Backscattering profile of blue L ceramic ink.

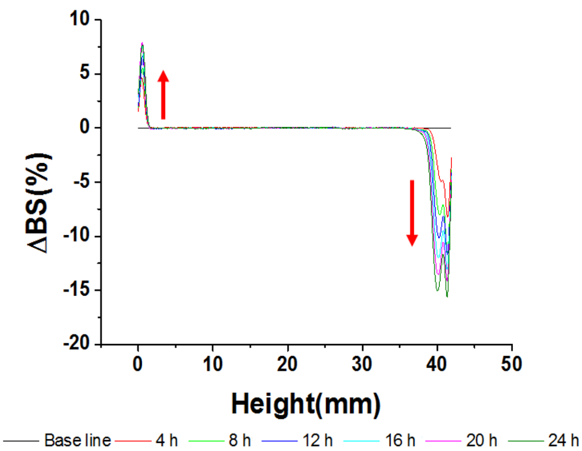

Fig. 5. Backscattering profile of blue H ceramic ink.

ing probabilities between light and particles were lowered as the distance between particles was increased with a reduction in concentration of the upper layer part when the relatively large particles distributed within the sample were precipitated at the lower layer part of the sample due to gravity. On the other hand, there was a change where the backscattering value in the middle part of the sample was increased by about 1%. This is attributed to an increase in the backscattering values since the particle sizes were increased due to particle agglomeration and the scattering probabilities between light and particles were increased. In view of such analysis results, agglomeration phenomenon can be seen to occur among the inorganic particles within the sample of low-viscosity ceramic ink (blue L). In the lower layer part of the sample, the backscattering values reduced by about 25% were observed as compared with the reference value of measurement start. Since destructive interference of scattered light due to adjacent particles occurred as the distance between particles became very close while the dispersed phase particles were precipitated by more than the saturated concentration in the lower layer part of the sample, the backscattering values for the lower layer part of the sample were shown to be reduced.

In the case of Blue H having a relatively high viscosity, a reduction width of about 16% was observed in the upper layer part as compared with the reference value of initial measurement start. This is attributable to the fact that the probabilities of scattering between light and particles were lowered as the distance between particles was increased because of a reduced concentration due to precipitation of relatively large particles as with the Blue L sample measured earlier. Since the backscattering values in the middle part of Blue H sample showed no changes of increase nor decrease, no agglomeration was shown to have occurred during precipitation although overall precipitation of particles did occur. An increase width of about 8% in the backscattering values was observed in the lower layer part of the sample, which is attributed to an increase only in the backscattering probabilities as a result of an increase in the number of particles since it failed to reach the saturated concentration unlike with blue L, although an increase in concentrations due to precipitation did occur in the lower layer part of the sample.[10]

For evaluation of stability of the ceramic ink, Turbiscan Stability Index(TSI) values were calculated on the basis of backscattering data of the samples. TSI allows evaluation of dispersion stability for the entire samples based on the average values for precipitation and agglomeration phenomena, etc. occurring within the sample.

$$d_i = \frac{\Sigma_h |scam_i(h) - scam_{i-1}(h)|}{H}$$

TSI shown in the above equation is a distance(d_i) between each profile measured as a function of time at the sample height (H), and given as an absolute value by addition of all differences between $scan_i$ and $scan_{i-1}$. It is always increased in the positive direction, and the dispersion stability is degraded, the larger the TSI values.[11]

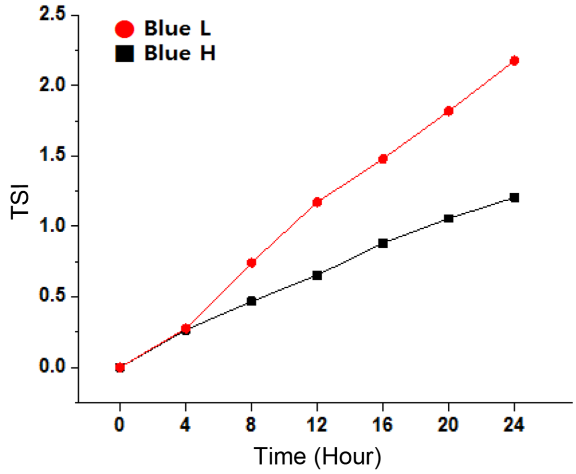

Fig. 6. Global destabilization kinetics of blue L and blue H ceramic ink.

Figure 6 shows the change in TSI as a function of time elapse for two samples(Blue L, Blue H) of $CoAl_2O_4$ ceramic ink. Although there was little difference between the two samples of blue L, blue H up to 4 h after measurement start, the blue L with a relatively lower viscosity showed a higher TSI value than the blue H with a relatively higher viscosity after 4 h, indicating that the dispersion stability was degraded as a result. This shows the result in a good agreement with the equation of Stokes's law introduced earlier.[12]

4. Conclusions

In the present study, $CoAl_2O_4$ ceramic ink was synthesized to check for the changes in dispersion stability as a function of viscosity of inks for inkjet printing. The $CoAl_2O_4$ ceramic ink prepared by solid-state reaction method was atomized to a particle size of less than 300 nm for application to inkjet printers, and particle shapes showed a mixed form of square and hexagonal column-shaped particles. To check for dispersion stabilities as a function of viscosity, two types of samples of blue L and blue H with different viscosities were prepared, where the viscosities were shown to be 15.58 cps and 22.52 cps, respectively, and the surface tensions 28.40 mN/m and 26.47 mN/m, respectively. Also, in ink jetting experiments through dropwatcher, both blue L and blue H samples showed formation of spherical single droplets, and were thereby affirmed to be an ink suitable for inkjet printing. For evaluation of dispersion stabilities of blue L and blue H samples with different viscosities, the two inks were compared by using multiple light scattering method. As shown by the Stokes's law, the blue H samples having a higher viscosity were affirmed to exhibit an excellent dispersion stability when compared with the blue L samples having a low viscosity.

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