Preparation of Functional Antibiotic and Deodorization Pigments Using Surface Modification Method for Special Papermaking

Jun-Hyung Cho*, Yong-Won Lee†, and Dong-Jin Min‡

* Professor, †Doctor's course, ‡ Researcher
Department of Paper Science & Engineering, Kangwon National University, Chunchon-si, 200-701, Korea
jhcho@kangwon.ac.kr

ABSTRACT

In this study, colloidal Ag solution was spouted on the surface of the inorganic pigment using the hybridizer system and the spray nozzle. Then, the surface of the inorganic pigment was modified by titanium dioxide in order to possess antibacterial ability. Nano-sized colloidal Ag was made by using a seed sol method in this study. It was confirmed that the size of particle per unit weight becomes enlarged, as the addition of $AgNO_3$ increased, and as the time of reaction increased, in the manufacturing process of nano-sized colloidal Ag. The antibacterial measurement of the inorganic pigment showed that the growth of fungus was reduced as the reaction time increased. It was measured that the antibacterial activity was excellent at fixed time frame, after the antibacterial ability appeared in 5~7 hours of the antibacterial inoculation experiment. The experiment of titanium dioxide's Photocatalyst effect showed 60~70 % efficiency in about 80 minute reaction time of the dissolution results regarding measurements of benzene. It was shown that more than 90% of the dissolution efficiency was achieved in the reaction time of about 30 minute.

INTRODUCTION

A well-being trend, which people pursue cleanness and amenities, shows up as a societal phenomenon, thanks to recent improvements in the levels and environments of lives. Societal moods when antibiotic products are favorable may be closely relevant to recent pursuit of amenities in accordance to improvement of economical environments surrounding the public. Even if the products containing antibiotic functions are favored, the development of antibiotics in domestic markets is at initial stage yet so that many researches about antibiotics are being actively conducted recently. The utilization of organic antibiotics occupies 80% of domestic consumption. The level of recent state-of- art technology is a development of the inorganic antibiotics as the micro-powder type. Metal ions such as Ag and Zn characterized by excellent antibiosis are combined mechanically and chemically through inorganic carriers such as zeolite and phosphate.

Many researches have conducted to solve this problem. One of solution methods is to use metals holding antibiosis against microbe known from long term experiences. Inorganic antibiotics are, in terms of stability or antibiosis, better than organic antibiotics, but inorganic antibiotics also have several problems in terms of price, colors, and applications. It is the valuable metals and very expensive. Its color can not be controlled because of plasma effect that its color is regressed into the original colors of metals. It is a power type so that it causes a problem of its addition to stock.

This study intended to develop the new functional pigments with environmentally-friendliness for papermaking industries. To do this, we tried to manufacture natural pulps and nano-particles of silver (Ag) and titanium dioxide (TiO_2), which is featured by its environment friendly and excellent antibiosis, deodorization, and electric functions. The functional pigments were manufactured through a method that the surfaces of low-cost inorganic filters are modified with functional nanoparticles. The manufacturing of functional pigments may help making progresses in various high-value products such as life sanitary papers for babies and females, air purification filtering paper for homes and automobiles, wall papers with antibiosis and photocatalyst, and electric beam screen paper for cell phones, TV Braun tubes, wrapping paper etc. Those technological developments of paper production are expected to have a great effect on the creation of new demands and profit improvements in papermaking industries in response to a recent trade-reverse phenomenon due to the current tax-free imports and exports and Chinese recent fast progresses made in papermaking industry.

Experimental

Manufacturing of nano-sized Ag particles

In the process of the manufacture of nano-sized Ag (Silver), $AgNO_3$ solution was used as a starting material. A seed addition method was used to mix $AgNO_3$ with H_2O, and then an agitation was conducted. After the agitation, sodium citrate was added. Several minutes later, $NaBH_4$ was added. Then, it was agitated so that manufactured seed solution is used to produce a nano-sized colloidal Ag.

Hybridization system

The surface modification systems, which make it possible to combine fine powders in dry condition, using physical methods are classified into O.M.dizers and hybridizers. The core and fine particles input into an O.M.dizer forms the arranged mixture that the fine particles cover the core particles by mixed dispersion action, and then a certain quantity of the mixture is collected into the hybridizer. Then, the hybridizer gives mechanical thermal energy with shock power that does not destroy the particles by dispersing the mixture into the air. The principle in this process is that the modified powders are rapidly recollected into a collector right after composition or micro capsulation within a short time. In reality, it is the generated power in the space between rotor and stator that modifies find particles (Fig. 1).

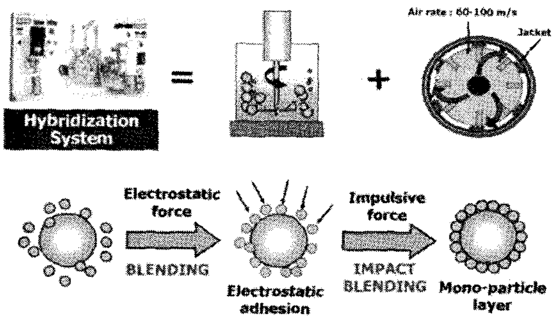

Fig. 1, Mechanism of hybridizer.

Spray coating method

The spray coating systems that coat sample surface make the produced liquid materials were installed in the hybridizer. The average atomizing angle of installed nozzle falls in the range of 60~85°. An employed mechanism is that the Ag (silver) solution is dry coated on the surface of the core particles, by the high speed of steam (15,000 rpm) due to the revolution of the rotor in the hybridizer, and by the thermal winds from a stator exceeding 60℃ of temperature. The quantity of spouted liquid is 1mL per 2minutes, and the injection on the core particles was conducted five times. This resulted in the manufacture of functional silver particles with environmentally friendliness (Fig. 2).

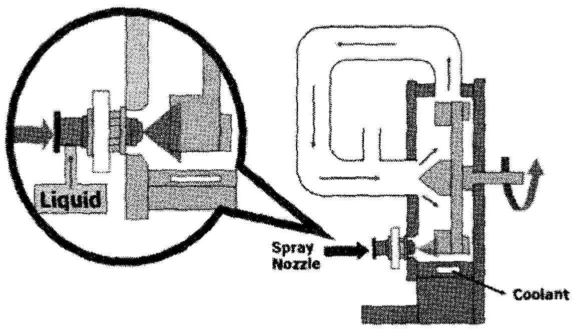

Fig. 2, Mechanism of spray coating.

Materials & titanium dioxide surface modify-cation of Ag coated inorganic pigment

In this experiment, the nano-sized particles of functional antibiotic Ag was, through a vapor spray method, coated on the surfaces of various inorganic pigments for paper, and then functional inorganic pigments were manufactured through a surface modification method with titanium dioxide. Titanium dioxide makes it possible to remove various volatile organic compounds (V.O.C). The properties of core particles and fine particles used for the surface modifications are as follows (Table 1). The added quantity for the surface modification was calculated by retrieving the ratio between the specific gravity and the size particles of core particles and fine particles used in the experiments (Table 2). Titanium dioxide, through vapor spray method, modifies the surface of Ag coated inorganic pigments for paper-making. The required addition quantity calculated through the equation, is spouted to the hybridization system, and the surface modification, by titanium dioxide for inorganic pigments, has been conducted at 9,000rpm of speed for 4 minutes.

Table 1, Properties of Materials.

Powder	Species	Size(um)	Gravity[-]
Clay no.1	Ultra gloss E10®(Engel Hard, U.S.A)	1.8um	2.60
Clay no.2	Ultra gloss KL®(Engel Hard, U.S.A)	1.8um	2.60
Talc	Hydro gloss LV®(Huber, U.S.A)	2.1um	2.85
PCC	HIT-1000®(Baek Kwang, Korea)	1.2um	2.55
TiO_2	P-25®(Degusa, Germany)	0.025um	3.80
Ag	Sarpu™-2KW®(Nano Tech, Korea)	0.015um	-

Table 2, Core particle and titanium dioxide's ratio.

Core Particle : Titanium dioxide	Compound Ratio
Clay no.1 : Titanium dioxide	93:7
Clay no.2 : Titanium dioxide	93:7
Talc : Titanium dioxide	92:8
$CaCO_3$: Titanium dioxide	88:12

Evaluation of antibiosis characteristics of inorganic pigment of which surface modified

The antibiosis measurement of manufactured functional inorganic pigments allows us to test the inhabitation efficiency of fungi. In this study, an inhibition growth test was conducted by using the MIC (minimal inhibitory concentration) bio-screen C. After the fungi have been inoculated and cultured in the materials for 24 hours, the control degree of fungi growth is measured by investigating the 600nm of wavelength light. This makes it possible to estimate the quality and quantity of strains by evaluating the light extinction in respect to the growth of fungi. The microorganisms used for antibiotic activity searching in this experiment are as follows.

Measurement of the removal efficiency of volatile organic compounds (V.O.C)

In the degradation of the volatile organic compounds (V.O.C) that is recently socially issued as a serious problem, the deodorization of V.O.C was measured by using the GC (gas chromatograph; Hewlett Packard, HP6890, U.S.A). It allows us to measure the efficiency of titanium dioxide photocatalyst that are used as core particles for the surface modification. 1000ppm of benzene gas as one of V.O.Cs was manufactured, and then after it was tinned into 10ppm with air gas, the photolysis efficiency was measured by reacting it with photocatalyst.

Evaluation of antibiosis characteristics of inorganic pigment of which surface modified

The antibiosis measurement of manufactured functional inorganic pigments allows us to test the inhabitation efficiency of fungi. In this study, an inhibition growth test was conducted by using the MIC (minimal inhibitory concentration) bio screen C. After the fungi have been inoculated and cultured in the materials for 24 hours, the control degree of fungi growth is measured by investtigating the 600nm of wavelength light. This makes it possible to estimate the quality and quantity of strains by evaluating the light extinction in respect to the growth of fungi. The microorganisms used for antibiotic activity searching in this experiment are as follows.

Table 3, List of microorganism and media used for antibiotic experiment.

Microorganisms	Media
Escherichia coli K-12IFO3301	Tryptic soy broth and agar (Difco, USA)
Listeria monocytogenes ATCC 19111	
Staphylococcus aureus IFO 13867	

Results and discussion

Evaluation of optical characteristics of inorganic pigment of surface modified.

The variations in respect to the sprayed Ag and titanium dioxide on the surface of inorganic pigments used as core particles via surface modifications are measured by using FE-SEM and TEM. It allows us to observe the surface shapes of inorganic pigments of which surface were modified. Figs 3~4 are pictures of TEM taken after moisture coating Ag nano-sized particles on the surface of inorganic pigments through a vapor spray method. The black spots on the surface of inorganic pigments show that Ag particles are well distributed. SEM pictures are presented in Figs 5~6 after a surface modification of the moisture coated inorganic pigments for paper making with titanium dioxide. As shown in Figs 5~6, a surface modification of treated pigment was accomplished better than that of primary samples, and titanium dioxide is overall well distributed.

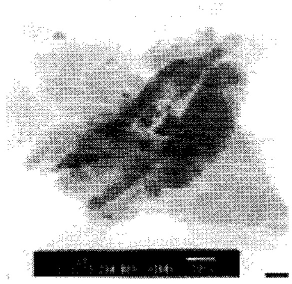

Fig. 3, TEM of modified clay no.1 with nano Ag.

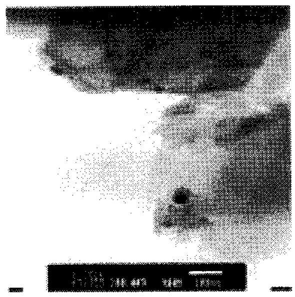

Fig. 4, TEM of modified talc with nano Ag.

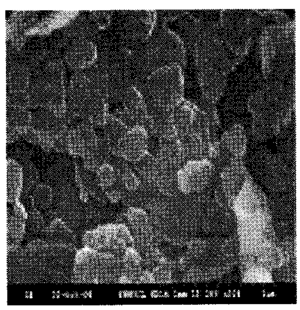

Fig. 5, SEM of clay no.1.

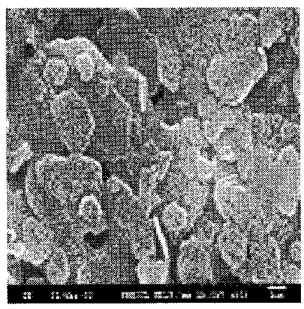

Fig. 6, SEM of modified clay no.1 with Titanium dioxide.

Antibacterial measurement of inorganic pigment of which surface modified

An antibacterial measurement of manufactured functional inorganic pigments is a method to check the efficiency of its inhibiting the survival of fungi. In this study, an inhibition growth test using MIC bio screen C was employed. The degree of rearing suppression is observed by investigating 600nm of wavelength light 24 hours after fungi is inoculated and cultured into the materials. This test is to evaluate the extinction of light in response to the growth of fungi.

Fig. 7 shows the Ag concentration in respect to the active exertion of optimal antibiosis against fungi. As shown in Fig. 7, when 200-300ppm of tinned solution for each fungus is moisture-coated on the surface of the inorganic pigments for papermaking as a vapor spray method, the most excellent antibiosis was exerted. Based on the optimal antibiotic activity test for each fungus, the antibiosis for each fungus is presented as Fig. 8-9.

Fig 8 shows the quantity of light absorbance in respect to time passing, when *Listeria monocytogenes* was inoculated and cultured into untreated pigments. Overall, it is concluded that the growth of fungi is made according to the results that the absorbance of all samples increases with increasing time. As shown in Fig. 9, however, the absorbance decreases with increasing time for each fungus, resulting in a suppression of fungi growth. The antibiosis was exerted within 5~7 hours after antibiotic inoculation test, which means the antibiosis is the most excellent within a certain time range. In addition, in the comparative antibiotic activity test of each manufactured functional inorganic pigment, the case of clay shows more enhanced antibiosis than those of talc or PCC.

Based on these results, it is also speculated that the small diameters and plate shape of clay particles more actively respond to fungi, resulting in the more enhanced self-antibiosis of clay than that of talc.

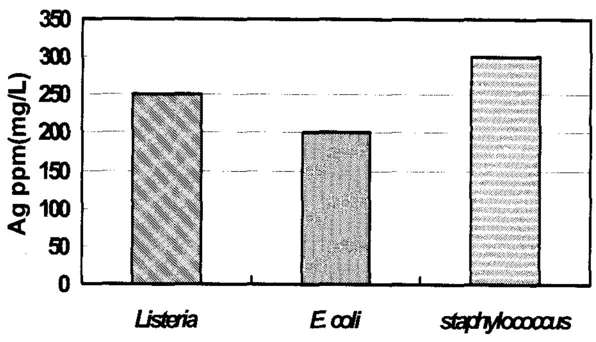

Fig. 7, Optimum antibiotic active test.

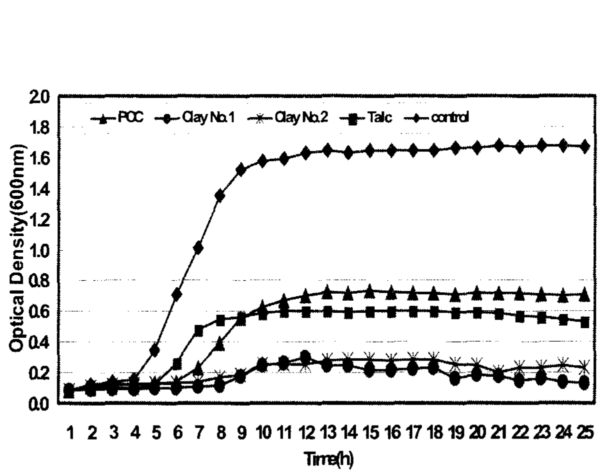

Fig. 8, Raw material antibiotic test of *Listeria.*

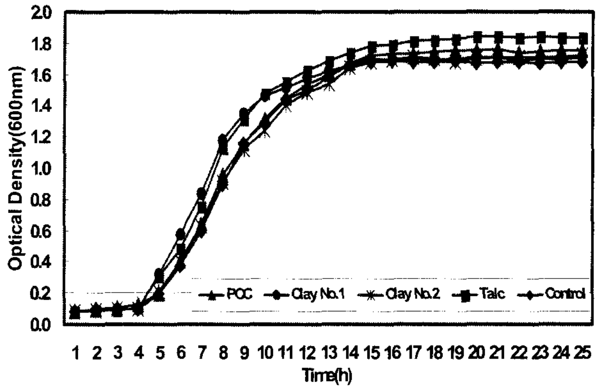

Fig. 9, Antibiotic test of *Listeria (Ag Liquid 250ppm).*

Measurement of the removal efficiency of volatile organic compounds (V.O.C)

This study intended to test the efficiency of titanium dioxide employed as a photocatalyst of core particles on the surface modification related to recently socially issued decomposition of volatile organic compounds. As shown in the photolysis efficiency test of benzene in Fig. 10, it is found that 60~70% of efficiency lasted for 80 minutes of reaction time, and 90% of attained resolution was reached at approximately 30minutes of response time. In addition, 40minutes later, the variation of decomposition reaction showed a weak exponent shape curve, probably following the Langmuir-Hinshelwood Kinetics. According to the equation, the velocity of its reaction depends on the concentration. The reaction speed is proportional to the material concentration, but if the resolution rate approached to its maximum, the speed of absorption is faster than the photolysis, implying that the speed of reaction in the air does not depend on the concentration of materials. In other words, in the latter part of decomposition efficiency curve, the photolysis efficiency curve appears to be parallel to increasing time. This pattern may show, because photocatalyst remains around coated powders after initially spouted benzene is decomposed into CO_2 and H_2O, and because later spouted benzene contact but does not react with photocatalyst.

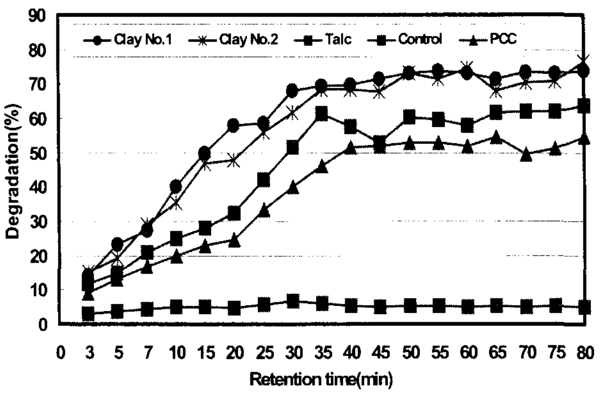

Fig. 10, Degradation efficiency of the benzene at 10ppm.

Conclusion

In this study, functional inorganic pigments were manufactured through a surface modification by Ag solution and titanium dioxide, which provide the functions of antibiosis and photocatalyst deodorization to the surfaces of inorganic pigments. The characteristics of the functional inorganic pigments are summarized as follows.

(1) The absorption rate increases with increased quantity of $AgNO_3$ and lapse time after adding $AgNO_3$ in manufacturing of nano-sized colloidal Ag, indicating that the size of particles per unit weight increases.

(2) From the observation about the surface particle shape of surface modified inorganic pigments for paper-making, it was found that the surface modification with Ag and titanium dioxide are more enhanced than original materials, and that overall Ag and titanium dioxide are evenly well distributed.

(3) In the antibiosis test of manufactured functional inorganic pigments against fungi in respect to time passing, it is found that the growth of fungi is restricted. Within 5~7 hours, antibiosis occurred and, the antibiosis is maximized in a consistent time range.

(4) The photocatalyst effect test of titanium dioxide used as core particles shows that in 80minutes of response time, the efficiency of benzene photolysis approached to 60~70%, In addition, more than 90% of the dissolution efficiency reached the reaction time of about 30 minute.

References

1. Ohashi, S., Yamamoto, K., Aono, M., Kobuko, T. and Yamachi, I., Antibacterial activity of silver ion implanted into silver filler, **Dent. Res. J.** 74(3):968 (1995).

2. Honda, H., Preparations of composite and encapsulated powder particles by dry impact blending, **Research Paper** 18(2):96 (1992).

3. Honda, F., Honda, H. and Koishi, M., Application of non-porous silica ultra micro spheres to high-performance liquid chromatographic column pickings, **Journal of Chromatography** 609:49 (1992)

4. Ishizaka, T., Honda, H. and Koishi, M, Drug Dissolution from starch Hybrid Powders Prepared by the dry Impact Blending Method, **Journal of Chromatography** 26:82 (1992).

5. Cho. J.H., Min, D.J., Surface Modification of pigment for papermaking by hybridizer, **Theories and Applications of Chem. Eng** 6(2):3569, (2000).

6. Cho, J.H., Min, D.J., Lee, J.M. and Hmamda, K., Fluidity consideration by surface modification of inorganic pigment, **Theories and Applications of Chem. Eng** 19(2):13, (2001).

7. Cho, J.H., Min, D.J., Ushijima, Y. and Yoo, T.I., Powder surface modification technology, **Workshop Series of Chem. Eng** (2): 86, (2001).

8. Willets, W.R, Bingham, R.T and Maechetti, F.R. Paper Coating Pigments, **TAPPI Monograph** (20):211 (1958)

9. 室井宗一, 紙塗工, 高分子ラテックスの應用, 高分子刊行會, 弟Ｖ章, 弟Ⅷ章

10. Pertti Ahonen, Talc as a coating pigment in lightweight coated papers, **TAPPI J** 68(11):235 (1985).

11. 小石眞純, Mechanochemical法を利用した粉體/粉體系複合素材の調製, **粉體工學會誌** 24(1):18 (2000).

12. Powder surface modification. **NARA MACHINEY CO., LTD.**

13. Zhao, J. and Yang, X., Photocatalytic oxidation for indoor air purification, literature review, **Building and Environment** 38:645 (2003).