건축물 실내 공기질 향상을 위한 광촉매 코팅 효과에 관한 연구

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A Study on the Effect of Photocatalyst Coating to Improve the Indoor Air Quality in Buildings

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Abstract : Sick Building Syndrome (SBS) is an illness symptom such as irritation of eyes, skin eruption and vomit ing in newly constructed buildings. It is mainly due to the harmful gases from the materials installed in building such as Volatile Organic Compounds (VOCs), Semivolatile Organic Compounds (SVOCs), floating bacteria, fungi, fungal spores and viruses, human bioeffluents in many modern buildings. The general ways to improve the Indoor Air Quality (IAQ) are ventilating, utilizing eco-material without harmful gases and reducing or removing harmful gases through additional treatment to the building materials. This study aimed to improve the Indoor Air Quality(IAQ) by applying surface coating on the building materials and to make safe living environments through the analysis of air quality before and after surface coating treatment in buildings.

초 록 : 새건물증후군이란 새로 지은 건물에서 생활하는 사람들에게 눈이 따갑거나 목이나 코가 아프거나, 두통, 구토, 피부발진 등 증상이 나타나는 것을 일컫는 말이다. 새집증후군 원인물질의 주요 성분으로는 건축 자재나 벽지, 페인트, 가구 접착제 등에서 발생되는 포름알데이드(HCHO)와 톨루엔 등 휘발성 유기화합물(VOCs: Volatile Oragnic Compounds), 부유 박테리아, 곰팡이, 바이러스 등이다. 새집증후군을 저감하기 위한 방법으로는 환기에 의한 방법, 오염물질이 없는 친환경 재료의 사용 및 재료위 처리를 통해 오염물질을 저감하거자 제거하는 방법이 있다. 본 연구는 이들 방법 중 건축 재료 위에 표면코팅처리를 함으로써 실내 공기질을 향상시키기 위한 것으로, 건물 내 표면 코팅 전후의 공기질을 분석함으로써 실내 거주환경을 안전하게 조성하는 데 그 목적이 있다.
Key Words : sick building syndrome, VOCs, HCHO, IAQ, ventilation

1. Introduction

Recent buildings have been made airtight through the development of architectural technology, which is efficient from an economic point of view. But this trend causes serious problems with regard to the quality of air. Poor air quality results from not only airtight buildings, but also pollutants from materials. As such, it is necessary to check architectural materials to treat the indoor air quality fundamentally[1,2].

The eco-environmental criteria applied to building materials are being intensified continuously. In Nov. 2004, the Korean Agency for Technology and Standards of the Ministry of Commerce, Industry and Energy stated it was willing to eliminate materials which discharge pollutants such as harmful volatile organic compounds (VOCs) and formaldehyde (HCHO) among twenty-two indoor materials from KS certifi-

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cation. Related government agencies such as the Ministries of Environment, Construction and Transportation, Education, and Health and Welfare are also interested in dealing with harmful substances.

The syndrome caused by newly constructed buildings consists of symptoms such as sore eyes, sore throat, snuffles, headaches, nausea, and whealing[2]. It has been reported that harmful substances are discharged from newly built and rebuilt houses and buildings. The main ingredients of substances causing the sick building syndrome are VOCs like HCHO and toluene, resulting from architectural materials, wallpapers, paints, and adhesives for furniture. These have a more serious effect on the human body when several substances are processed compositively than just as a lone substance. Therefore, large effort has been given to develop efficient air-purifying systems[3]. As the sick building syndrome is now recognized as inner environmental pollution, the Ministry of Environment was obligated to remove substances causing it by carrying out air quality laws in May 2004.

A number of studies have tried to solve the problems of formaldehyde and microorganism in indoor air (Pavlovas, 2004, Sekine and Nishimura, 2001). Pavlovas (2004) found that ventilation requires exhaustive air, resulting in a large amount of heat requirement. Sekine and Nishimura (2001) reported that the lifetime of air purifier with a filter is limited and the air filter accumulates microorganism with time. Thus, an advanced treatment technology is required to remove various organic matters and microorganisms in indoor air.

Photocatalysis is one of the attractive processes to remove formaldehyde and microorganisms. Photocatalytic reactions allow in many cases, a complete degradation of formaldehyde into harmless species without use of any chemicals. This avoids sludge production and its disposal. Titanium dioxide (TiO_2) catalyzed photocatalysis is broadly used because of its capability in removing a wide range of pollutant and disinfection. The photochemical stability, low toxicity and low cost are the other advantages.

This study examines its physical and chemical characteristics by manufacturing a photo catalyst including a high-efficiency corpuscle dioxide titan and checks its applicability as an indoor environment purification material by examining the effect of removing substances causing the sick building syndrome after coating a photo catalyst in newly built apartments, classrooms, and offices.

2. Standards on indoor air quality

A cause of indoor air pollution is classified according to air pollution around or caused by buildings. Air pollution results from gas: automobile exhaust fumes, burning gas for heating, factories, and power plants. Pollutants include carbonic acid gas, steam, body odor discharged from residents, architectural materials, furniture, and office utensils. Table 1 is a list of criteria by the WHO, which regulates permissible concentration according to kinds of VOCs. TVOCs concentration is regulated as $0.3 mg/m^3$.

In several countries, architectural materials like insulating materials have been used for the purpose of energy saving since the 1970's, and buildings have

Table 1. Permissible concentration of VOCs (WHO)

VOCs	Concentration (mg/m^3)
alkane	0.1
aromatic hydrocarbon	0.05
delpene	0.03
hydrocarbon	0.03
ester	0.02
aldehyde ketone	0.02
etc.	0.05
TVOCs	0.30

Table 2. Criteria for HCHO by countries

Country, Organization	Criteria Concentration (ppm)	Country, Organization	Criteria Concentration (ppm)
Norway	0.05	USA	0.1(EPA)
WHO	0.08	Italy	0.1
Japan	0.08	Sweden	0.11
Austria	0.08	Denmark	0.13
Canada	0.05	Finland	0.13
Australia	0.10	Switzerland	0.2
Germany	0.10	Spain	0.4

Table 3. Recommended criteria for indoor air quality in Korea

Items / Multi utilization facilities	VOC ($\mu g/m^3$)	HCHO (ppm)
underground stations, subway stores, waiting rooms of bus or train stations(total area $2000m^2$ or more), waiting rooms in flight facilities(total area 1500 m^2 or more), waiting rooms of harbor facilities (total area $5000m^2$ or more), libraries, museums, art galleries(total area $3000m^2$ or more), funeral homes and saunas(total area $1000m^2$ or more), large scale stores	500 or below	0.10 or below
medical facilities(total area more than $2000m^2$ or 100 or more beds), national or civil nursery facilities(total area $1000m^2$ or more), national or civil senior citizens' recuperation facilities and special hospitals(total area $1000m^2$ or more)	400 or below	0.10 or below
indoor parking facilities(total area $2000m^2$ or more)	1000 or below	0.10 or below

been made airtight. As a result, several pollutants are discharged into indoor air, and problems in indoor pollution increased as a social concern as sick building syndrome. Before 1980, indoor air quality was recognized as a developed kind of new environment issue in western countries and Japan and a studies on indoor pollution were in achieve progress.

In Korea, the Ministry of Environment revised a law on indoor air quality to maintain and manage indoor air quality of multi-utilization facilities and newly built apartment complexes. The maintenance and recommended standards of indoor air quality are presented in Table 3. The maintenance standards regarding PM_{10}, CO_2, HCHO, total floating bacteria, and CO and the recommended standards NO_2, Rn, VOC, asbestos, and ozone were enacted. Most facilities such as underground railroad stations among multi-utilization facilities are regulated to require VOCs to be under $0.5mg/m^3$ and HCHO below 0.10ppm.

3. Experiment and Method

3.1. Photocatalytic raw material composition and properties

In 1972, after Hujishima and Honda of Tokyo University in Japan arranged platinum to the cathode and TiO_2 to the anode, they started an investigation in relation to photocatalysts by decomposing water into hydrogen and oxygen. Photo catalysts, which consist of TiO_2 as a main component, tend to decompose organic matters according to the photo-oxygenation reciprocal action by the reflected UV on the surface. From photo catalysts, electrons appear on the surface by the reflected UV, and when holes take place at the position of electrons, these electrons and holes have strong deoxidation and oxygenation. At that time, the OH radical forms by oxygenating water in the air. OH radical shave stronger oxygenation than hydrogen peroxide, chlorine, and ozone, so they decompose molecule combination of organic substances easily.

The used photo catalytic sol in this experiment, LT-1, is manufactured from reagents like titanium aldrich and nitric acid. After the titanium is dropped into distilled water and a mineral acid is added, the solution is stirred under room temperature. The final solvent is manufactured by reacting as water heating composition over six hours. The crystal structure, particle size, and surface area of manufactured photocatalysts are examined through XRD (Rigaku D/MAX-1200) pattern, TEM (JEOL, EIM-2000FXII: Korea Basic Science Institude/Gwangju Branch) photo, and nitrogen absorption experiment, which are powder obtained after drying photo catalytic sol at one hundred degrees. In the present experiment, the character of manufactured photocatalysts is compared with a common photo catalytic powder, P-25 (Dequssa, Germany).

The organic degradation efficiency evaluation of photo catalytic sol progresses by measuring concentration changes of an interaction and a product with FT-IR in a reactor filling formaldehyde by about 7000ppm after coating 30mL of photocatalysts on the 10 by 30 wallpaper with low pressure coating equipment (spray nozzle diameter: 0.5nm) of HVLP-type. The sterilization power of photo catalytic sol progresses at the raiser equipped with three fluorescent lamps after painting over E-Coli (coliform bacteria) at a badge and photo catalytic sol. And the changing number of colonies according to the research time of fluorescent lamps is measured. The sterilizing power of the corona-virus PEDV and TGEV of photocatalysts is also examined.

3.2. Photocatalytic indoor coating and effect

Amounts of photo catalytic indoor coating of newly built apartments are controlled to about 30-35mL/m^2 by using the low pressure coating equipment.

Measuring indoor air quality is executed under a standard condition presented by the Ministry of Environment. The openings (windows and doors, gates, ventilation panels) next to the outside, indoor gates and doors of furniture are opened for over thirty minutes, and then the air-flow is blocked by closing the openings (windows and doors, gates, ventilation panels) next to the external air for over five hours. Doors and furniture are opened to move air between the rooms. A sample extraction is selected in principle over one meter from the inside wall, ceiling, and flat surface, and progressed twice for thirty minutes in the range of 1.2～1.5 meters from the flat surface. In the case of a natural ventilating opening and machinery ventilating system, these are measured by closing and stopping operation.

The formaldehyde and TVOC is measured by using Z-300P (Environmental Sensors Co.) and IAQRAE (RAE System, Inc.),and floating bacteria in the air is examined by measuring the number of bacteria culturing at 37 degrees after installing BHIV badge at Air Sampler (M.A.Q.S.II, OXOID Co.) and inhaling air for a regular period of time. Measuring floating bacteria is averaged by two measurements at the same place.

4. Results and Analysis

4.1. Character and property of raw materials of photocatalysts

Fig. 1 shows powder obtained through plasticity, drying manufactured LT-1 and X-ray diffraction patterns of TiO_2 powder, P-25. The photo catalyst, P-25, shows diffraction peaks at 25, 38, and 48 degree of anatase, and rutile diffraction peaks at 27, 36, and 41 degrees. Rutile content is about 20% from the peak area of XRD diffraction patterns. On the other hand, the photo catalyst obtained from LT-1 raw materials shows only a diffraction peak of anatase. Generally, it is reported that Titan-CO_2 of anatase structure has higher activity than rutile structure. As such it is expected that the photo catalyst, LT-1, has higher activity than the photo catalyst, P-25.

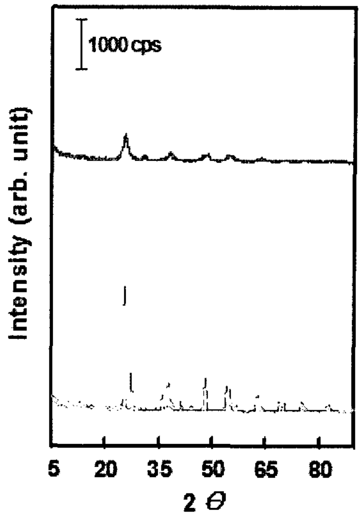

Fig. 1. XRD patterns of photocatalysts.

Fig. 2 is the TEM photo compared with the size and shape of photo catalytic raw materials. From the result of analyzing the TEM photo, P-25 is a 20～25nm particle of unequal shape, but LT-1 consists of equal particles that have a pyramid shape, which is 20nm on the long side and 5nm on the short side.

Fig. 3 shows that the nitrogen absorption experiment progresses to check the surface area of photocatalytic raw materials. The rate of particular holes of P-25 seems low in comparison with the nitrogen absorption isothermal line, but the existence of particular holes at a photocatalyst, LT-1, is analogized. The surface area of P-25 calculated from the result of experiments is about 50m^2/g, yet the surface area of LT-1 is about 200m^2/g, which indicates high photocatalytic activity is expected.

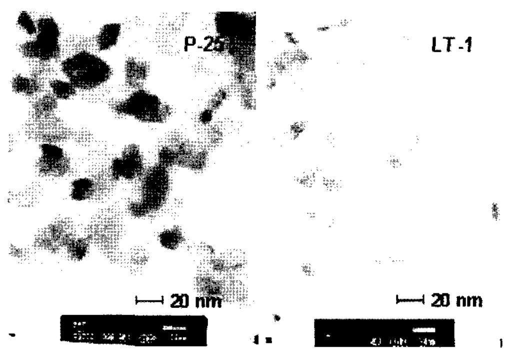

Fig. 2. TEM images of photocatalysts.

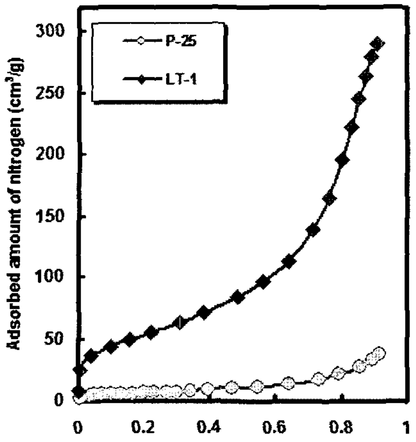

Fig. 3. N_2 absorption isotherms of photocatalysts.

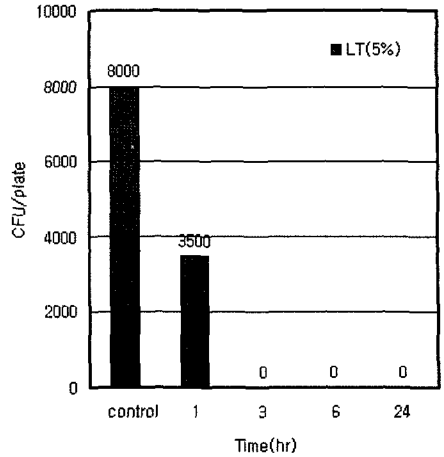

Fig. 5. Photocatalytic bactericidal effect on E-coli of LT-1 photocatalyst.

Fig. 4 shows the result of the formaldehyde sterilization experiment of LT-1. As time passes, amounts of formaldehyde are reduced and amounts of carbon dioxide (CO_2) are increased. Formaldehyde over 90% is dissolved by lighting ultraviolet rays for 100 minutes.

Fig. 5 shows the result of the E-coli sterilization experiment of LT-1. The number of coliform bacteria is 8000 early, but reduced to 3500 after lighting a fluorescent lamp for an hour and completely sterilized after lighting for 3 hours. The sample in which photocatalysts are unused is checked so that a number of coliform bacteria are not reduced just by lighting a fluorescent lamp.

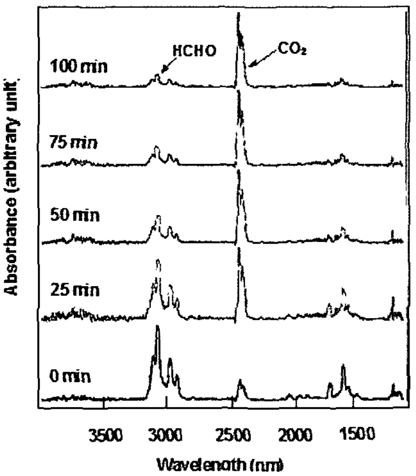

Fig. 4. Photocatalytic degradation of formaldehyde on LT-1 coated sample.

Table. 4. Result of sterilization of manufactured photocatalytic raw materials

Bacteria/Virus		Bactericidal Ratio
E-coli		< 99.999%
Virus	PEDV*	< 99.99%
	TGEV**	< 99.9%

*PEDV: Porcine Epidemic Diarrhea Virus
**TGEV: Transmissible Gastroenteritis Virus

The results of the coliform-bacteria and corona-viruses sterilization experiments are arranged together in Table 4. High sterilization power of the photocatalyst, LT-1, can be checked by having sterilization power over 99.9% for corona-viruses PEDV and TGEV.

4.2. Indoor air quality changes after photocatalyst coating

The air quality changes before and after coating is examined. Several spaces like newly built and remodeling apartments which cause seriously sick building syndrome are selected. Table 5 shows the result of measurements. There are comparisons between formaldehyde 0.1ppm and TVOC 0.5ppm according to the recommended criteria of the Korea Air-Quality Administration Law.

The result of measuring the indoor formaldehyde and TVOCs concentrations before coating catalysts is higher than recommended values at most of the newly

Table 5. Result of removing organic substances of photocatalytic indoor coating

Building		Formaldehyde (ppm)		TVOC (ppm)	
		before	after	before	after
D apartment (new)		0.25	> 0.01	0.65	0.07
K apartment (remodel)		12.25	0.44	5	> 0.01
C apartment (New)		0.65	> 0.01	-	-
K lawyer's office (New)		0.8	> 0.01	-	-
G government office (New)		0.15	> 0.01	0.93	0.04
C office (Old, smoke room)		0.47	> 0.01	0.07	> 0.01
H piano school		0.8	0.18	0.68	0.31
K accountant office		1.2	0.12	0.57	> 0.01
W apartment		0.48	> 0.05	-	-
L apartment		0.35	> 0.01	-	-
H apartment	Living room	12.15	0.17	1.04	0.22
	Bedroom1	13.68	0.16	1.57	0.23
	Bedroom2	4.57	0.01	1.07	0.19
	Bedroom3	3.54	0.19	0.87	0.17
	Bedroom4	3.9	0.13	0.83	0.11
Recommended value		0.1		0.5	

built buildings. In particular, remodeling K-apartment shows the concentration of TVOCs and formaldehyde over 10～100 times. K-apartment is largely made of timber. At this time, using an excess of formalin or adhesives for timber to prevent timber from decay is regarded as the main cause. In Table 5, D-apartment and G-office among newly built buildings show half the figure in comparison with standards over one year after complete construction. Generally, it is known that substances causing the new house syndrome in the case of newly built buildings decreased under standards after two years. However, the concentration of formaldehyde is highly detected in the smoking area of an old building (C-office) due to the influence of cigarette nicotine (tar).

The result of examining the indoor formaldehyde and TVOCs concentrations a day after coating the photocatalyst, LT-1, shows that the formaldehyde concentration is under recommended concentration values at all spaces except the K-apartment. Indicating the concentration of formaldehyde and TVOCs as under 0.01ppm means the concentration is below the analysis limit of the analyzing equipment. In the case of the K-apartment, the TVOCs concentration is under the recommended values. This result means that it is possible to remove the formaldehyde and TVOCs of newly built buildings by coating a photocatalyst, LT-1.

In the case of buildings over 2 years after construction and remodeling, it is not necessary to worry about the formaldehyde and TVOC, but pollution problems are considered with floating bacteria in the case of facilities used by many people. To check the effect of sterilization of bacteria in the air by photocatalytic coating,amounts of floating bacteria before and after photocatalytic coating in the Gwangju S-high school classroom is measured.

The result of measuring the floating bacteria of a classroom before coating shows that a corridor side is 58cfu/plate and a window side (space B) is 36cfu/

Table 6. Result of the sterilization experiment of photocatalytic coating

Measurement	Floating Bacteria (cfu/plate)	
	A-1	B-1
1st (before coating)	58	36
2nd (one day after coating)	31	14
3rd (26 days after coating)	29	11
Recommended value	50	

* A-1: toward corridor, B-1: toward windows

plate. In other words, the concentration of floating bacteria of a corridor side is higher than that of a window side. The result of measurement after a day and 26 days after coating photocatalysts shows that the concentration of floating bacteria is considerably reduced. The reducing degree of a window side is bigger than that of a corridor side. It is regarded that the property of photocatalysts is more active by the sunlight.

The formaldehyde, TVOCs substance removal, and sterilization effect according to examined photocatalytic coating are influenced by the inside structure, temperature, and humidity. Also, the property of photocatalysts is determined by the light, so it is influenced directly by the kinds of indoor lighting, the intensity of radiation, and degree of lighting strength coming from the outside. And it is necessary to be concerned about indoor lighting to maximize the effect of photocatalysts.

5. Conclusions

In this study, in order to seek alternatives to remove substances causing sick building syndrome, raw materials are manufactured by water heating composition. The results from this study are as follows:

1) Manufactured LT-1 photocatalyst's physical and chemical properties were examined by nitrogen absorption, XRD, and the TEM technique. This contains higher anatase than the photocatalyst P-25, and particles are uniform and four times bigger.

2) Formaldehyde in materials coated with LT-1 was removed for two hours over 90%, and colon bacteria and corona viruses were checked to eliminate them over 99.9%.

3) Coating LT-1 photocatalysts to the inside of newly built buildings is checked to remove substances like formaldehyde, VOC, and floating bacteria in the air. As a result, the substances were decreased under the limit of criteria. This shows that photocatalysts are likely to be used widely to improve our living environments.

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