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Preparation of environmental-friendly lime paints from hydrated lime and hydrated light burned dolomite

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Abstract−Environment-friendly lime paints were prepared from 38 wt% slurries of hydrated lime ($Ca(OH)_2$) and hydrated light burned dolomite ($Ca(OH)_2\cdot Mg(OH)_2$). These materials and the resulting paints' antibacterial and anti-mold properties were investigated. The hydrated lime used in this study contained 97 wt% $Ca(OH)_2$, which implies a 71.85 wt% equivalence of CaO. This 71.85 wt% CaO content was responsible for the antibacterial and anti-mold characteristics. The antibacterial and anti-mold characteristics of the hydrated light burned dolomite were attributed to its 56 wt% CaO and 44 wt% MgO contents. The antibacterial-reducing activities of 38 wt% hydrated lime and hydrated light burned dolomite slurries were found to be 99%. Their anti-mold activities against mixed strains were outstanding. Lime paints produced from the slurries and various additives also showed 99% antibacterial activity and outstanding anti-mold activity. The paints' low total volatile organic compounds (TVOCs) releases were graded as excellent. Their formaldehyde (HCHO) releases were classed as best through excellent, indicating their suitability as environment-friendly building materials.

Key words: Hydrated Lime, Hydrated Light Burned Dolomite, Anti-bacterial, Anti-mold, Total Volatile Organic Compounds/Formaldehyde

INTRODUCTION

Currently used oil-based paints perform poorly in proofing against and absorbing moisture. Thus, in winter they are liable to produce dew on heated interior walls, which can lead to black molds or bacteria. Hazardous TVOCs and HCHO that are emitted indoors due to the use of chemically synthesized volatile solvents can cause skin disease. These environmental problems of oil-based paints fuel create a demand for water-based paints that lack organic solvents and have improved environmental properties [1-7].

Functional materials are being considered to fill this demand, with studies reporting the anti-bacterial characteristics of CaO and MgO produced from limestone and dolomite. These materials radiate heat during rapid hydration in atmospheric conditions, leading to $Ca(OH)_2$ and $Mg(OH)_2$, which have been tested for use in water-based paints [8]. Inorganic antimicrobial agents are of interest for controlling microbes because of their safety and stability [9].

The majority of antibacterial inorganic materials are ceramics with immobilized antimicrobial metals such as Ag and Cu [10,11]. Hence, the antibacterial activities of ceramics have been studied [12,13].

Twenty-six ceramic powders have been reported to demonstrate antibacterial activity, ten of which were confirmed to inhibit bacterial growth. MgO, CaO, and ZnO have demonstrated strong antibacterial activity [14-19]. ZnO can act as a bacteriostatic agent; it showed stronger activity against gram-positive than gram-negative bacteria. The antibacterial activities of metal oxides such as MgO, CaO, and ZnO were measured by direct [20] and indirect [21] conductometric assays [22-26]. However, ZnO is too expensive to be used as an antibacterial inorganic material. Although ZnO, Ag and Cu are impregnated into zeolite and used as antibacterial inorganic materials, they are still expensive. On the other hand, CuO and MgO based materials are cheap and can be used as antibacterial inorganic materials for water-based paints. These materials can also act as extenders in paints with high whiteness, and opacity.

Previous works have focused on uses of CaO and $CaO\cdot MgO$ as extenders for paints [27]. However, the rapid exothermic reactions during hydration of CaO and $CaO\cdot MgO$ inhibit direct uses as extenders. In this study, our aim was to investigate possibilities of $Ca(OH)_2$ and $Ca(OH)_2\cdot Mg(OH)_2$ slurries as principal ingredients, not as extenders for paints.

This work reports the antibacterial and anti-mold characteristics of hydrated lime produced by the hydration of CaO from calcined limestone, and hydrated MgO produced by the hydration of MgO from calcined dolomite. These materials' antibacterial and anti-mold properties were also assessed when formed into paints with SB-latex or acrylic resin binders and other additives and without organic solvents. TVOCs and HCHO releases, responsible for sick building syndrome, were assessed and the physical properties of the result-

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ing water-based paint were characterized.

EXPERIMENTAL

1. Materials and Lime Paint Mixing

The major ingredients of the lime paints were hydrated lime ($Ca(OH)_2$, BeakKwang Mineral Product Co. Ltd., Korea) or light burned dolomite (CaO·MgO, DS MDI Co. Ltd., Korea). SB-Latex 27 wt% (solid 49-51 wt%, Hansol Chemical Co., Ltd.) was used as a binder and AP-3960 27 wt% (solid 49-51 wt%, APEC Co., Ltd.) was used as an acrylic resin. Other additives were dolomite (DS MDI Co., Ltd., 325 mesh), EVA (Ethylenevinylalcohol, OCI Company, Korea), TiO (COSMO Chemical Co., Ltd., Korea), super-plasticizer (ISOCA Korea Co., Ltd.), antifoaming agent (ISOCA Korea Co., Ltd.) and wetting agent (ISOCA Korea Co., Ltd.).

Hydrated lime was produced as 38 wt% slurry by bead agitation for 1 hour at room temperature. Light burned dolomite was produced first as hydrated light burned dolomite (380 g/L) by agitation and then as 38 wt% slurry after desiccation. The 38 wt% slurries were investigated for antibacterial and anti-mold properties.

The lime paints were mixed as follows:

Lime paint I was produced by bead agitating 38 wt% hydrated lime slurry with 27 wt% SB-Latex (solid 49-51 wt%), 14.25 wt% EVA, 17.25 wt% dolomite, 8 wt% TiO, 5 wt% super-plasticizer, 2 wt% antifoaming agent, and 2 wt% wetting agent for 1 hour at room temperature.

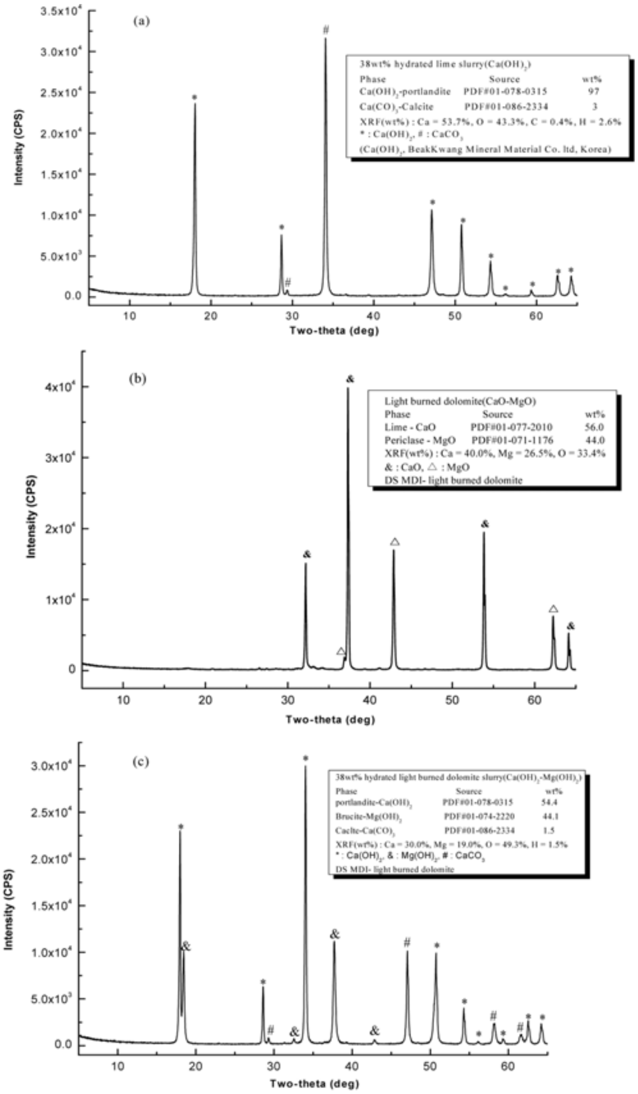

Fig. 1. XRD patterns of (a) hydrate lime, (b) light burned dolomite, and (c) hydrated light burned dolomite.

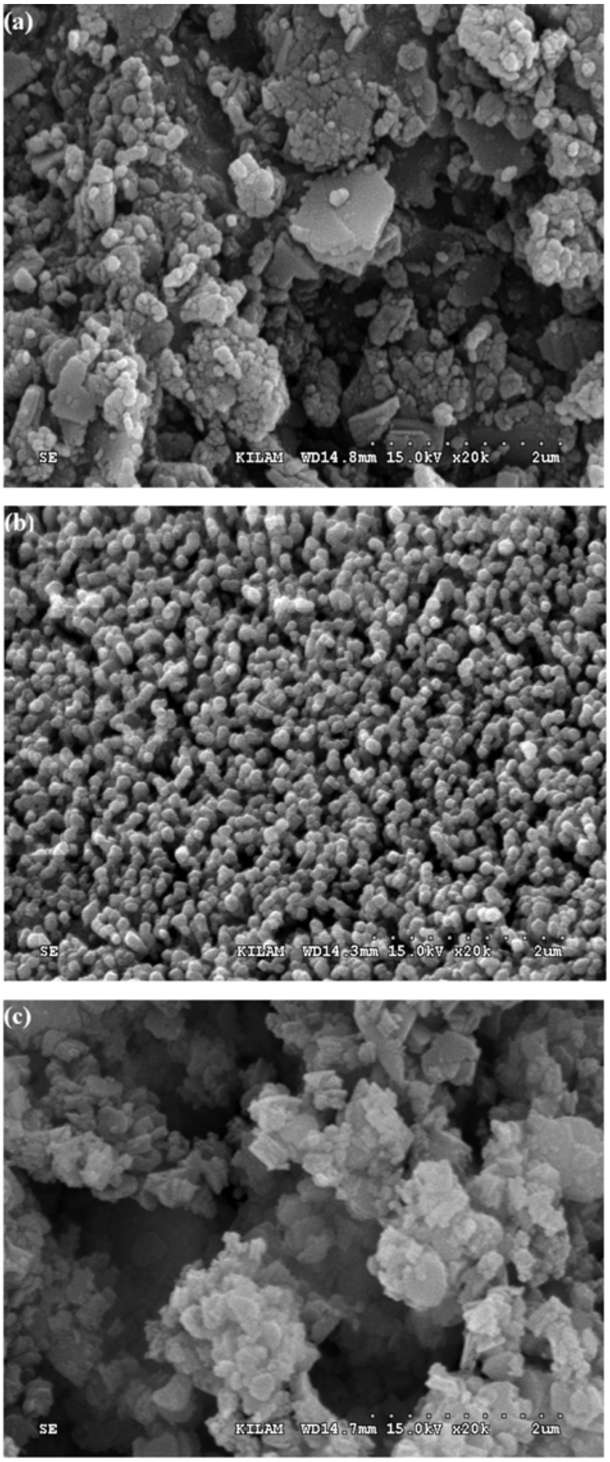

Fig. 2. SEM images of (a) hydrate lime, (b) light burned dolomite, and (c) hydrated light burned dolomite.

Lime paint II was produced similarly to lime paint I but with 27 wt% AP-3960 (solid 49-51 wt%) used as an acrylic resin in place of SB-Latex.

Lime paint III was produced similarly to lime paint I but with 38 wt% hydrated light burned dolomite slurry rather than hydrated lime slurry.

Lime paint IV was produced similarly to lime paint III but with AP-3960 (solid 49-51 wt%) 27 wt% added as an acrylic resin instead of SB-Latex.

2. Characterization and Analysis

2-1. XRD Analysis and SEM Images Analysis

Desiccated, additive-free slurries were observed by XRD (Rigaku D-MAX 2500V). Their surfaces were observed by FE-SEM (field emission-scanning electron microscopy, S-4300, Hitachi, Japan). Hardened surfaces of the four lime paints were also analyzed by FE-SEM.

2-2. Antibacterial Testing

The slurries' and paints' antibacterial properties were tested by the Korea Conformity Laboratories according to KCIM-FIR-1002:2009 (Shake flask method) standard against *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 15442.

2-3. Anti-mold Testing

The slurries' and paints' anti-mold characteristics were tested by Korea Conformity Laboratories according to ASTM G-21:2009 standard against a mixture of five strains (*Aspergillus niger* ATCC 9642, *Penicillium pinophilum* ATCC 11797, *Chaetomium globosum* ATCC 6205, *Gliocladium virens* ATCC 9645, and *Aureobasidium pullulans* ATCC 15233).

2-4. TVOCs and HCHO Testing

TVOCs and HCHO released from the lime paints were analyzed by Korea Conformity Laboratories following the indoor air quality process testing standard. The testing chamber conditions were as follows: load rate 0.4 m^2/m^3, dry paint thickness 60 μm, applied amount 146 g/m^2, drying time 30 minutes, ventilation restoration 0.5 cycles/hour, relative humidity 48-52%, and test period (time in chamber) 7 days.

2-5. Synthetic Resin Emulsion Paint Testing

Lime paint I was tested as a synthetic resin interior emulsion paint through analysis of its consistency (K.U), nonvolatile content (%), drying time (min), diffuse reflectance (45°), gloss (85°), hiding power, washability resistance, low temperature stability, condition in container, alkali proof, odor, storage stability and fungus resistance by the KS M 6010 : 2009 testing standard.

RESULTS AND DISCUSSION

1. XRD and SEM Analyses of $Ca(OH)_2$ and $Ca(OH)_2 \cdot Mg(OH)_2$ Slurries

The major components of the lime paints, hydrated lime, light burned dolomite, and hydrated light burned dolomite, were quantitatively and qualitatively analyzed by XRD (Fig. 1).

The 38 wt% hydrated lime slurry consisted of 97 wt% $Ca(OH)_2$ with 3 wt% $CaCO_3$ from unburned limestone in the shaft kiln (Fig. 1(a)). The light burned dolomite consisted of 56 wt% CaO and 44 wt% MgO (Fig. 1(b)). The hydrated light burned dolomite was 54.4 wt% $Ca(OH)_2$, 44.1 wt% $Mg(OH)_2$, and 1.5 wt% $CaCO_3$ (Fig. 1(c)).

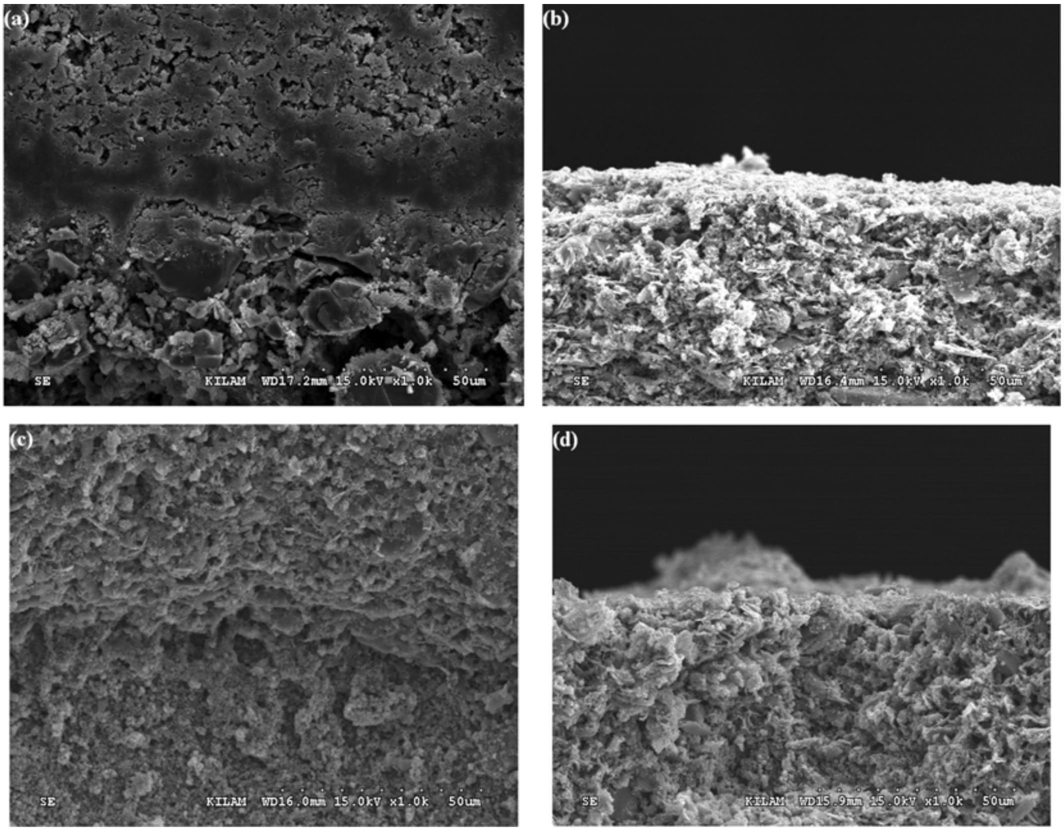

Fig. 3. The SEM images of hardened lime paints (a) I, (b) II, (c) III, (d) IV coating objects.

Table 1. Antibacterial characteristics of slurries

Test item		Test result			Test method
		Initial concentration (CFU/ml)	After 24 hr the concentration (CFU/ml)	Germ rate (%)	
By *Escherichia coli*, antibacterial test	Blank	1.3×10^4	4.2×10^4	-	KCIM-FIR-1002:2009
	Hydrated lime	1.3×10^4	<10	99.9	
	Blank	1.3×10^4	4.3×10^4	-	
	Hydrated light burned dolomite	1.3×10^4	<10	99.9	
By *Pseudomonas aeruginosa*, antibacterial test	Blank	1.6×10^4	4.7×10^4	-	
	Hydrated lime	1.6×10^4	<10	99.9	
	Blank	1.6×10^4	4.8×10^4	-	
	Hydrated light burned dolomite	1.6×10^4	<10	99.9	

Used strain: *Escherichia coli ATCC 25922*
Pseudomonas aeruginosa ATCC 15442
Starter culture bacteria concentration (CFU/mL): *Escherichia coli ATCC 25922*: 1.4×10^6
Pseudomonas aeruginosa ATCC 15442: 1.6×10^6
Sample weight: 4 g
CFU: colony forming unit

Table 2. Anti-mold test results of slurries

Test item	Anti-mold test			
	Initial concentration			
	After 1 weeks	After 2 weeks	After 3 weeks	After 4 weeks
Test result	0	0	0	0
Test method	ASTM G-21 : 2009			

Traces of unburned $CaCO_3$ were not observed in the XRD pattern of light burned dolomite. The materials' SEM images show that the hydrated lime and the hydrated light burned dolomite were amorphous and that the light burned dolomite was composed of nearly spherical particles after molding at 1,000 °C for 1 to 2 hours in a shaft kiln (Fig. 2).

The paints' microscopic structures after one application to cement by a paint brush were analyzed by FE-SEM (Fig. 3). The applied lime paints showed sturdy structures after hardening.

2. Antibacterial and Anti-mold Properties of $Ca(OH)_2$ and $Ca(OH)_2\cdot Mg(OH)_2$ Slurries

The 38 wt% hydrated lime slurry and 38 wt% hydrated light burned dolomite slurry were tested for antibacterial activities by the KCIM-FIR-1002:2009 standard method. The antibacterial activity of 38 wt% hydrated lime slurry against *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 15442 was assessed through comparison of the bacteria after incubation for 24 hours in the presence and absence of slurry. There is a visible reduction of bacterial growth in the samples that contained slurry. The 38 wt% hydrated light burned dolomite slurry demonstrated similar antibacterial characteristics. Both 38 wt% hydrated lime and hydrated light burned dolomite slurries showed 99.9% bacteria reductions against both test strains (Table 1). The slurries' anti-mold characteristics were assessed by the ASTM G-21:2009 standard method, which involved growing five molds for four weeks (Table 2). No growth of the tested mold strains was detected in four weeks.

The antibacterial and anti-mold properties of ceramic powders are affected by cations eluted from the powder, mechanical destruction of cell membranes, active oxygen generated from the powder, and pH. However, Sawai et al. [14-19] reported that the antibacterial and anti-mold characteristics of ceramics powders were not affected by eluted cations or cell membranes' mechanical destruction. They reported that active oxygen generation and pH were important factors. Elsewhere [20-26], they reported that bactericidal effects increased with increasing pH and that in the alkali region the bactericidal effects of CaO against *Staphylococcu aureusn* were different from those of NaOH solution, suggesting that antibacterial activity is affected by factors in addition to pH. They found that super-oxide, O_2^-, generated on the surfaces of CaO and MgO affected the inhibition of bacterial growth. They also reported that increasing CaO content in CaO·MgO powders increased pH and superoxide generation, and thus improved bactericidal activity [13-18, 21-25].

The hydrated lime used in this study contained 97 wt% $Ca(OH)_2$, which implies a 71.85 wt% equivalence of CaO from the conversion: 1.35 ((100.0869 g-$CaCO_3$/mol)/(74.093 g-$Ca(OH)_2$/mol)) (Fig. 1(a)). This 71.85 wt% CaO content was responsible for the antibacterial and anti-mold characteristics. The antibacterial and anti-mold characteristics of the hydrated light burned dolomite were attributed to its 56 wt% CaO and 44 wt% MgO contents (Fig. 1(b)). Therefore, the 38 wt% slurries were expected to be effective bases for environment-friendly lime paints.

Table 3. Antibacterial characteristics of lime paints

Test item		Test result			Test method
		Initial concentration (CFU/ml)	After 24 hr the concentration (CFU/ml)	Germ rate (%)	
By *Escherichia coli*, antibacterial test	Blank	1.3×10^4	4.3×10^4	-	KCIM-FIR-1002:2009
	Lime paint I	1.3×10^4	<10	99.9	
	Blank	1.3×10^4	4.3×10^4	-	
	Lime paint II	1.3×10^4	<10	99.9	
	Blank	1.3×10^4	4.3×10^4	-	
	Lime paint III	1.3×10^4	<10	99.9	
	Blank	1.3×10^4	4.3×10^4	-	
	Lime paint IV	1.3×10^4	<10	99.9	
By *Pseudomonas aeruginosa*, antibacterial test	Blank	1.6×10^4	4.8×10^4	-	
	Lime paint I	1.6×10^4	<10	99.9	
	Blank	1.6×10^4	4.8×10^4	-	
	Lime paint II	1.6×10^4	<10	99.9	
	Blank	1.6×10^4	4.8×10^4	-	
	Lime paint III	1.6×10^4	<10	99.9	
	Blank	1.6×10^4	4.8×10^4	-	
	Lime paint IV	1.6×10^4	<10	99.9	

Used strain: *Escherichia coli ATCC 25922*
Pseudomonas aeruginosa ATCC 15442
Starter culture bacteria concentration (CFU/mL): *Escherichia coli ATCC 25922*: 1.4×10^6
Pseudomonas aeruginosa ATCC 15442: 1.6×10^6
Sample weight: 4 g
CFU: colony forming unit

Table 4. Anti-mold test results of lime paints

Test item	Anti -mold test			
	Initial concentration			
	After 1 weeks	After 2 weeks	After 3 weeks	After 4 weeks
Test result	0	0	0	0
Test method	ASTM G-21 : 2009			

3. Antibacterial and Anti-mold Characteristics of Lime Paints

Lime paints were produced by mixing bead agitating additives into pastes of the 38 wt% hydrated lime and hydrated light burned dolomite slurries.

Lime paint I, characterized by the addition of 27 wt% SB-Latex (solid 49-51 wt%) to 38 wt% hydrated lime slurry paste. Lime paint II was similar, though with 27 wt% AP-3960 (solid 49-51 wt%) acrylic resin replacing the SB-Latex to assess the effects of SB-Latex, which has been reported to give hydrated lime sustained antibacterial performance effective for ten years [28]. Lime paints III and IV were similar to lime paints I and II, respectively, with the only difference being their 38 wt% hydrated light burned dolomite slurry base, rather than 38 wt% hydrated lime slurry. These paints were produced to assess effects attributable to the paints' bases.

The paints' antibacterial characteristics were tested by the KCIM-FIR-1002: 2009 standard method.

Each paint showed distinct bacterial reduction compared with blank samples after 24 hour exposure. Both of the tested bacterial strains, *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 15442, were reduced by 99.9% for each paint (Table 3).

The paints' anti-mold characteristics were analyzed by the ASTM G-21:2009 standard method (Table 4). The paints allowed no growth after spawn fostering for four weeks with five mold strains.

The paint testing showed that the slurries' antibacterial and anti-mold properties were retained by the resulting paints and that these properties were unaffected by the choice of binder.

4. Releases of TVOCs and HCHO from Lime Paints

TVOCs/HCHO releases were assessed for the lime paints using an indoor air quality testing standard (Table 5). Lime paint I released TVOCs at 0.108 mg/m^2·hr and HCHO at 0.008 mg/m^2·hr. Considering environment-friendly building materials' certification levels (Table 6), the release of TVOCs was graded excellent; that of HCHO, best. Lime paint II showed respective releases of 0.145 mg/m^2·hr and 0.034 mg/m^2·hr, both of which were graded excellent. Lime paint III showed releases of 0.245 mg/m^2·hr (good) and 0.009 mg/m^2·hr (best). Lime paint IV showed releases of 0.186 mg/m^2·hr (good)

Table 5. TVOCs/HCHO releases form lime paints

Test item		Test result (mg/m^{2}hr)	Test method
Lime paint I	TVOCs	0.108	Indoor air quality process test method
	HCHO	0.008	
Lime paint II	TVOCs	0.145	
	HCHO	0.034	
Lime paint III	TVOCs	0.245	
	HCHO	0.009	
Lime paint IV	TVOCs	0.186	
	HCHO	0.026	

Table 6. Certification levels of environment-friendly building materials

Classification		Paints (mg/m^{2}hr)
Best	TVOCs	Less than 0.10
	HCHO	Less than 0.03
Excellence	TVOCs	More than 0.10~less than 0.20
	HCHO	More than 0.03~less than 0.05
Good	TVOCs	More than 0.20~less than 0.40
	HCHO	More than 0.05~less than 0.12
General I	TVOCs	More than 0.40~less than 2.00
	HCHO	More than 0.12~less than 0.60
General II	TVOCs	More than 2.00~less than 4.00
	HCHO	More than 0.60~less than 1.25

and 0.026 mg/m^2·hr (best).

The various additives were responsible for the paints' releases of TVOCs/HCHO.

5. Water Paint Test

Lime paint I was tested as a water-based paint for indoor use (Table 7). Eleven of the 13 tested properties of the paint were satisfactory for indoor use class I. The failures were hiding power and washability resistance. Hiding power scored 84 against an acceptable level of 92 for class I standard. This was attributed to the low TiO_2 content and the relatively low whiteness of hydrated lime (85) compared with TiO_2 (94). Class I washability resistance standard requires paint to show no sign of color change after 500 washing cycles. The paint's failure was attributed to the SB-latex binder, which contained 13.5 wt% SB-latex, lower than the required 49-51 wt%/H_2O-L.

CONCLUSIONS

Environment-friendly lime paints were prepared from 38 wt% slurries of hydrated lime ($Ca(OH)_2$) and hydrated light burned dolomite ($Ca(OH)_2 \cdot Mg(OH)_2$). The hydrated lime used in this study contained 97 wt% $Ca(OH)_2$, which implies a 71.85 wt% equivalence of CaO. This 71.85 wt% CaO content was responsible for the antibacterial and anti-mold characteristics. The antibacterial and anti-mold characteristics of the hydrated light burned dolomite were attributed to its 56 wt% CaO and 44 wt% MgO content. The antibacterial-reducing activities of 38 wt% hydrated lime and hydrated light burned dolomite slurries were found to be 99%. Their anti-mold activities against mixed strains were outstanding.

Lime paints produced from the slurries and various additives also showed 99% antibacterial activity and outstanding anti-mold activity. Low releases of TVOCs from paints were graded as excellent. HCHO releases were classed as best through excellent, indicating their suitability as environment-friendly building materials.

Overall the lime paints were highly suitable for use as environmentally-friendly functional materials with high antibacterial and anti-mold characteristics and low releases of indoor air pollutants.

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Table 7. Characteristics of synthetic resin emulsion paints (water-based paint - interior first grade) - lime paint I

Test item	Test result	Interior first grade	Test method
Consistency (K.U)	85	82~110	KS M 6010 : 2009
Nonvolatile content (%)	55	More than 50	
Drying time (min)	20	Within 60	
Diffuse reflectance (45°)	86	More than 82	
Gloss (85°)	2	Under 10	
Hiding power	84	More than 92	
Washability resistance	200	More than 500	
Low temperature stability	None	None (consistency change: 3K.U)	
Condition in container	None	None	
Alkali proof	None	None	
Odor	None	None	
Storage stability	None	None	
Fungus resistance	8	More than 6	

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