CHAPTER III

EXPERIMENTAL

3.1 Materials

(1) Epoxy resin-based coating was supplied by S.B. United Co., Ltd., (Taiwan). Epoxy resin is a bisphenol-A type unmodified solid epoxy resin that can be softened at high room temperature. The chemical structure of epoxy resin is shown below.

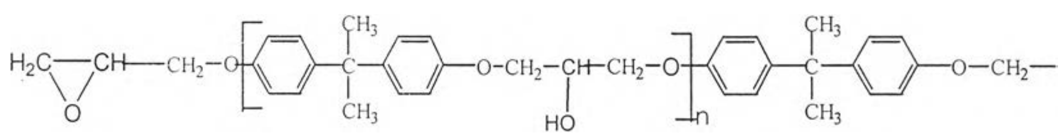

Table 3.1 Typical properties of epoxy resin-based coating

Properties	Typical Value
Appearance	Clear transparent yellowish solid
Epoxy equivalent weight (g/eq)	450 – 500
Viscosity (at 25 $^{\circ}$C, cps)	6,800 – 14,000
Specific gravity	1.10
Color (Gardner)	1.0 Max
Flash Point ($^{\circ}$C)	60 – 70

(2) Epoxy resin-based flooring was supplied by S.B. United Co., Ltd.,(Taiwan). Epoxy resin is a liquid resin, which is manufactured from bisphenol–A and ephichlorohydrin. The chemical structure of epoxy resin is shown below.

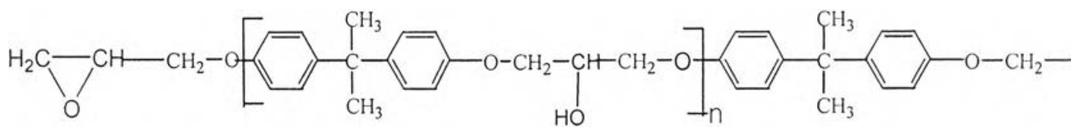

Table 3.2 Typical properties of epoxy resin-based flooring

Properties	Typical Value
Appearance	Clear liquid
Epoxy equivalent weight (g/eq)	184 – 190
Viscosity (at 25 °C, cps)	12,000 – 15,000
Specific gravity	1.16
Color (Gardner)	1.0 Max
Flash Point (°C)	150

(3) Poly(amide amine) used in this experiment was supplied by Sanwa Chemical (S) Pte., Ltd., (Singapore). The poly(amide amine) is pre-reacted with a portion of epoxy resin. This gives the product several advantages; improved low temperature curing, fast cure rate and improved sensitivity to moisture.

Table 3.3 Typical properties of poly(amide amine)

Properties	Typical Value
Color (Gardner)	11 Max
Viscosity (at 25 °C, cps)	5,000 – 12,000
Amine value, mg KOH/g	210 – 250
Specific gravity at 25 °C	0.98
Equivalent weight per [H]	137
Flash Point (°C)	33.5

The chemical structure of Poly(amide amine) is shown below.

$$H_2N\text{-}(CH_2\text{-}CH_2\text{-}NH)_m\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\left[\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}(CH_2\text{-}CH_2\text{-}NH)_m\text{-}CH_2\text{-}CH_2\text{-}NH\right]_n\text{-}H$$

(4) Cycloaliphatic amine used in this experiment was supplied by Capital Chemical Co., Ltd., (U.S.A.). This product is used as a room temperature curing agent for liquid epoxy resin. It is particularly suitable for free solvent, high solid floor, wall coating and self-levelling flooring. The chemical structure of cycloaliphatic amine is shown below.

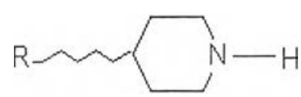

Table 3.4 Typical properties of cycloaliphatic amine

Properties	Typical Value
Color (Gardner)	1-2
Viscosity (at 25 °C, cps)	80
Amine value, mg KOH/g	360
Specific gravity at 25 °C	1.04
Equivalent weight per [H]	83
Flash Point (°C)	230

(5) Aminoethylaminopropyltrimethoxysilane (AEAPS) was supplied by Unique Fine Products Co.Ltd., (Germany). Silane is a reactive chemical containing an diamino-functional organic group and trimethoxysilyl inorganic groups. Possessing both organic and inorganic reactivity, silane can react with organic resins and

elastomers as well as with the surface of inorganic materials.The chemical structure of silane is shown below.

$$H_2N\ CH_2CH_2NH\ CH_2CH_2\ CH_2Si(OCH_3)_3$$

Table 3.5 Typical properties of aminoethylaminopropyltrimethoxysilane (AEAPS)

Properties	Typical Value
Appearance	Colorless
Specific gravity at 25°C	1.01-1.03
Refractive Index at 25°C	1.444
Flash point (closed cup) °C	>100

(6) Methyl isobutyl ketone (MIBK), xylene were used as the solvent without further purification.

(7) Steel panel (cold mild steel) was used as a substrate. The steel panel has the size of 70 x 150 x 0.8 mm.

3.2 Equipments

(1) Air-spray gun (DEVILBESS GFG JGX – 502, England) is used for preparing film. Air spray gun with compressed air is used to atomize the paint. The paint is forced through a spray gun orifice onto a surface in a diffused, directed fog, which is suitable for most liquid spray finishing and surface coating application.

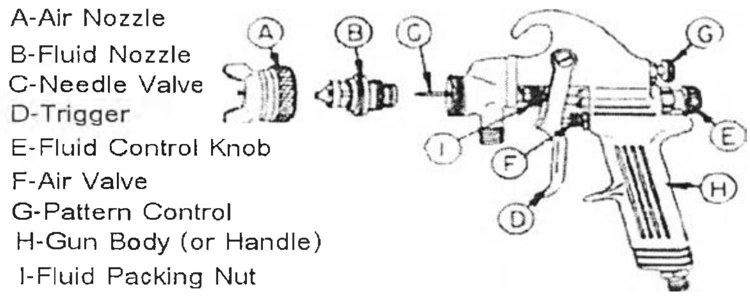

Figure 3.1 Air-spray gun

(2) Elecometer 345 (Elecometer Instruments Ltd., England) measures the thickness of non-magnetic coating on steel or iron, measuring the distance from the film surface to the substrate.

Figure 3.2 Elecometer 345

3.3 Methodology

3.3.1 Preparation of Steel

3.3.1.1 Steel cleaning

Oil or grease may be presented at the steel surface either as a temporary protection against rust or as a contaminant. The low-energy surface only will prevent proper wetting by the coating and subsequently act as a weak boundary layer between the metal and the coatings. Aromatic cleaning solvent is mainly used to remove fats, oils, wax and other organic materials from the steel surface. The process was repeated twice to remove them through cleaning of the steel. Finally, the steel was dried at room temperature and sanded by a sand paper No. 1000 .

3.3.2. Preparation and Application of Epoxy Resin

3.3.2.1 Epoxy resin coating on steel substrate

A typical coating formulation was prepared by ingredients in Table 3.6.

Table 3.6 Epoxy-coating composition

Item	Ingredient	Weight, g, of samples				
		Control	1	2	3	4
1	Epoxy resin (E.E.W. = 475)	45.0	45.0	45.0	45.0	45.0
2	MIBK	27.5	27.5	27.5	27.5	27.5
3	Xylene	27.5	27.5	27.5	27.5	27.5
4	Silane (AEAPS)	-	1.0	3.0	5.0	7.0
5	Poly(amide amine)	13.0	13.0	13.0	13.0	-

The curing agent was calculated based on a stochiometric ratio of epoxy resin to amine hardener (as described in Appendix B).

<u>Procedure</u>

(1) Items 1-3 were added and mixed together until homogeneity for 20 minutes.

(2) Item 4 was mixed for 30 minutes. Silane (AEAPS) could be hydrolyzed and copolymerized further to produce inorganic crosslinked networks.

(3) Item 5 was then added and mixed for 10 minutes. Epoxy resin,a crosslinking

agent, could undergo a crosslinking reaction with poly(amide amine) to form an organic crosslinked networks.

The coating mixture was stirred in a small beaker. The homogenous solution was applied onto the cleaned steel substrate using the air-spray gun. Various film thickness of 25, 50, 75 and 100 μm were prepared. The coated samples were then cured at room temperature for 24 hours.

3.3.2.2 Epoxy resin flooring

A typical flooring formulation was prepared by ingredients in Table 3.7.

Table 3.7 Epoxy-flooring composition

Item	Ingredient	Weight, g, of samples			
		Control	1	2	3
1	Epoxy resin (E.E.W. = 190)	40.0	40.0	40.0	40.0
2	Polycarboxylic (wetting)	1.0	1.0	1.0	1.0
3	Polyether (defoamer)	0.8	0.8	0.8	0.8
4	Bentone (anti-setting)	0.2	0.2	0.2	0.2
5	Titanium dioxide	3.0	3.0	3.0	3.0
6	Barium sulfate	20.0	20.0	20.0	20.0
7	Silica	25.0	25.0	25.0	25.0
8	Benzyl alcohol	10.0	10.0	10.0	10.0
9	Silane (AEAPS)	-	3.0	5.0	15.5
10	Cycloaliphatic amine	17.5	17.5	17.5	-

The curing agent was calculated based on a stochiometric ratio of epoxy resin to amine hardener (as described in Appendix B).

Procedure

(1) Material items 1-8 were mixed and stirrered until homogeneity for 1 hour.

(2) Item 9 was then mixed for 30 minutes. Silane (AEAPS) could be hydrolyzed and copolymerized to produce inorganic crosslinked networks.

(3) Item 10 was mixed for 10 minutes. Epoxy resin, a crosslinking agent, could undergo a crosslinking reaction with cycloaliphatic amine to form an organic crosslinked networks.

The flooring mixture was stirred in a small beaker. The mixture was applied on a cement substrate. The specimens with many film thickness was applied to testing their mechanical properties, hardness (ASTM D 2240/Shore D), and compressive strength (ASTM C 579).

3.4 Characterization and Testing

3.4.1 Epoxy resin-based coating

3.4.1.1 Heat Resistance

All paint films with various thickness of 25, 50, 75 and 100 μm were cured at different temperatures of 200, 250 and 300°C for 20 minutes. The paint film was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to observe functional groups such as, silane. A colorimeter was used to measure color of the film. The thermal stability of the coating was determined using thermal gravimetric analysis (TGA). Each characterization on heat resistance was as follows:

a) Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained by Nicolet Fourier Transform IR Spectrometer (Model 400 Impact, U.S.A.). Transmission mode was used with 32 scans and resolution 8 cm^{-1}. Potassium bromide (KBr) pellets was used for investigating the functional groups by IR technique.

b) Colorimetry

Chroma Meter (Model CR-300, Japan), a general purpose compact tristimulus colorimeter for measuring the reflected color of sample surface was used. The built-in light source and double-beam feedback system ensure uniform illumination of the object for all measurements, and the data can be calculated according to CIE Standard Illuminant D_{65}. The CIE standardized D_{65} based on natural daylight at a color temperature of 6500 K is now the most widely used standard; its energy distribution is from 320 to 780 nm.

c) Thermal Gravimetric Analysis (TGA)

TGA data were obtained by Netzsch (Model TG 209, Germany). When the coating decomposed on heating, it loses volatile materials, which escape from the sample causing a decrease in sample weight. Each coating was heated at a rate of $20^{\circ}C$/min under a nitrogen flow, at temperatures from $100^{\circ}C$ to $600^{\circ}C$.

3.4.1.2 Corrosion Resistance Testing

Various film thickness of epoxy coating and silane (AEAPS) were tested for the corrosion resistance by exposure to salt spray (fog) (Sheen Instrument Co., Ltd., (England)) for 500 and 1000 hours. A standard salt solution was prepared from the analytical quality reagents. The salt solution was composed of the following reagents:

Sodium chloride (NaCl)		26.50 g
Magnesium chloride ($MgCl_2$)		2.40 g
Magnesium sulphate ($MgSO_4$)		3.30 g
Potassium choride (KCl)		0.73 g
Sodium hydrogen carbonate ($NaHCO_3$)		0.20 g
Sodium bromide (NaBr)		0.28 g
Calcium chloride ($CaCl_2$)		1.10 g
Distilled water	to	1000 ml

The test condition in the salt spray chamber (ASTM B 117) is as follows. The exposure zone of the salt spray chamber was maintained at 35 ^{o}C. The compressed air was supplied to the nozzles for atomizing. The salt solution was free of oil and dirt and the spraying pressure was maintained between 69 and 172 kPa/m^2 (10 and 25 psi). In addition, the fog was collected in each collector from 1.0 to 2.0 ml. Finally, the panels were checked for the rate of blistering and rusting according to ASTM D 1654 (as described in Appendix A).

a) Evaluating the corrosion rate (ASTM G 1).

The evaluation of corrosion by mass loss during the test was determined. The average corrosion rate could then be obtained as follows:

$$\text{Corrosion Rate} = (K \times W)/(A \times T \times D) \tag{3.1}$$

Where:

K = a constant

T = exposure time in hours

A = area in cm^2

W = mass loss in grams

D = density in g/cm^3

3.4.1.3 Adhesion Tape Test

The adhesion tape test is the most commonly used qualitative adhesion test method. These test methods cover procedures for assessing the adhesion of coating film. The selected area, free of blemished and minor surface imperfections, was cut parallel as follows: The lattice pattern was cut by 2 millimeters apart and six cuts were made by a cutter knife. A pressure sensitive adhesion, cellophane tape, on it was adhered. It was rub by a eraser to adhere completely the tape on the paint film. The adhesive tape was then removed, the superiority or inferiority property of the substrate of paint film was carefully examined. The evaluation of the paint number is shown in Appendix A, and the evaluation of point numbers specified in the standard, and sample, (as described in ASTM D 3359) was compared.

3.4.2 Epoxy resin-based flooring

3.4.2.1 Hardness Test

Durometer D from PTC Instruments (Model 475, U.S.A) was used for determining the indentation hardness of a paint film. The thickness of a the specimen was at least 3 mm (0.12 in), 76.2 mm (3 in) in length. The surface of specimen was flat. The specimen was placed on a hard plate, the durometer was held in a vertical position with the point of the indentor at least 12 mm height. The indentor was then pressed into the specimen. Making sure that it was parallel to the surface, the presser foot was applied to the specimen as rapidly as possible without shock. The scale reading was taken within one second of a firm contact with the specimen. (described in ASTM D 2240/Shore D).

3.4.2.2 Compression Test

The compression machine (Shimadzu, (Model UHM 200A, Japan)) was used. Specimens are in form a cylinder shape $1 \pm 1/32$ in (25 ± 0.8 mm) in diameter and $1 \pm 1/32$ in (25 ± 1.6 mm) high was used as a testing specimen. The rate of loading was applied continuously without shock to the sample. The test rate is 6000 psi/min (41 MPa/min). Compressive strength is tested for a degree of cure, load bearing capability, and maximum stress at the moment of cracking or breaking. (described in ASTM C 579)

Compressive strength can be calculated as follows:

$$S = (4W)/(\pi \times D^2) \qquad (3.2)$$

S = compressive strength, psi (MPa)

W = maximum load, lb (N)

D = diameter measured (mm)

3.4.2.3 Chemical Resistance

The epoxy flooring systems were evaluated for chemical resistance using an immersion test method. The epoxy flooring curing condition is conditioned for 7 days at room temperature before testing. Specimens are in the form of bars, 76.2 mm (3 in) in length, 25.4 mm (1 in) in width and 3.18 mm (0.13 in) thick. Shore D hardness was measured on cured floors prior to chemicals immersion and the surface of film was observed against time. After 7 days of immersion, the reagents were removed by washing, and the surface was wipe dried with cloth. Shore D hardness of each sample was re-measured and percent hardness retention was calculated.