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(71) Applicant: **THAI MARINE PROTECTION CO., LTD.** [TH/TH]; 555/8 Moo.12, Bang Phasi, Bang Len, Nakhon Pathom 73130 (TH).

(72) Inventor: **MUNGSANTISUK, Pinai**; 75/28 Phetlada Village, Buddhamonthon Sai 2 Soi 19, Taweewattana, Bangkok 10170 (TH).

(74) Agent: **ORNTHANALAI, Veravej**; Intellectual Design Group Co., Ltd., 194, 196 Nonthaburi Road, Bangkrasor, Muang Nonthaburi, Nonthaburi 11000 (TH).

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(54) Title: ONE PART MOISTURE CURING POLYURETHANE COMPOSITION FOR HIGH PERFORMANCE PROTECTIVE COATING

(57) Abstract: The composition of one-part moisture curing polyurethane for high performance protective coating is disclosed. The steel plates coated with the one-part moisture curing polyurethane were alternate immersed in neutral 3.5 % sodium chloride solution as stated in ASTM G 44 - 99 for 6,500 hours. Only small rust was found at the edge of the steel plates but there was no paint blister or rust detected on the plates. The one-part moisture curing polyurethane in this invention can be served as the protective coating in severe environment like tidal zone or splash zone in seawater.

ONE PART MOISTURE CURING POLYURETHANE COMPOSITION FOR HIGH PERFORMANCE PROTECTIVE COATING

Technical Field

This invention is related to one-part moisture curing polyurethane composition for high performance protective coating.

Background Art

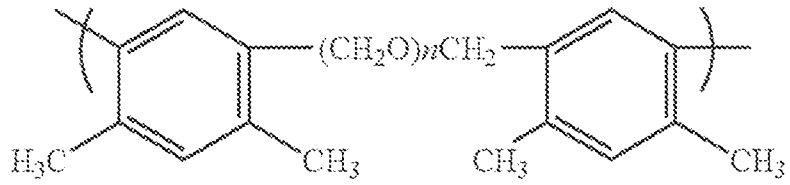
Protective coatings have been used to protect significant works or structures, such as seagoing ships, power plants, offshore platforms, petrochemical plants, many marine and industrial structures. The old traditional coating systems are based upon sandblasting for surface preparation, multiple coats, short lifetime endurance and required continual repair. Thus, the better performance and easy to use coatings are of great interest. Polyurethane coatings are widely used as protective coating and topcoat for both new and old structures because they possess recoat ability, chemical resistance, UV resistance, abrasion resistance, low curing temperature, etc.

One-part moisture curing polyurethane coatings (MCP) are easy to use and help to eliminate the mixing mistakes of two-part coating i.e. incorrect proportion, induction period delay and non-amalgamation. Therefore, the single component MCP is very attractive because of its high performance and advantages.

In US Patent 6,362,300 B1 by Araki et al., the moisture curable polyurethane composition comprises a urethane prepolymer, and a morpholine catalyst comprising a dimorpholinodiethylether (i) and a N,N-dimethylaminoethylmorpholine (ii). In the polyurethane composition, content of the dimorpholinodiethylether (i) in the polyurethane composition is preferably less than 0.15% by weight, and content of the N,N-dimethylaminoethylmorpholine (ii) in the polyurethane composition is preferably in the range of 0.04 to 2% by weight.

In EP 1 447 428 B1 by Inoue et al., one-part moisture curable urethane composition comprises an isocyanate-terminated urethane prepolymer as a main component. The additional components comprise of (A), an aliphatic hydrocarbon compound having a

solubility parameter value of 7.0 to 8.0 cal/cm^3 and (B), a compound having in the molecule at least one basic structure represented by the following formula:



Wherein n is 0 to 3.

The content of the compound (A) is 0.5 to 2.0% by weight in the whole composition. The content of the compound (B) is 0.5 to 2.0% by weight in the whole composition.

In US Patent 8,476,362 B2 by Wamprecht et al., the moisture curing polyisocyanate mixtures for coating comprise of a solvent-containing polyisocyanate mixture having a solvent content of less than 50 weight %, an NCO content of from 7 to 15 weight %, a content of monomeric TDI of less than 0.2 weight %, and a content of monomeric aliphatic and/or cycloaliphatic isocyanate of less than 0.2 weight %. A TDI component contains TDI isocyanurate poly isocyanates.

Disclosure of Invention

The present invention relates to one-part moisture curing polyurethane composition for high performance protective coating. The composition of high performance protective coating comprises aromatic polyisocyanate prepolymer based on diphenylmethane diisocyanate (MDI) (i), resin coated non-leafing aluminium flakes (ii), unsaturated polycarboxylic acid polymer (iii), polysiloxane copolymer (iv) and mono-oxazolidine (v)

For the one-part moisture curing system, the polyisocyanates cure through the reaction of free isocyanates, active NCO group, with atmospheric moisture or residual moisture in the surface rust. The primary amino group and carbon dioxide are produced from this reaction. Then, the amino groups react with isocyanate to form urea as shown below

$$R-N=C=O+H_2O \rightarrow R-NH_2+CO_2$$

$$R-NH_2+R-N=C=O+H_2O \rightarrow R-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{||}}{C}-\underset{\underset{H}{|}}{N}-R$$

One-component coating based on aromatic isocyanates (MDI) generally requires shorter drying time than that based on aliphatic isocyanates. However, Coatings based on MDI have a tendency to yellow in the light and show loss of gloss on weathering.

Non-leafing aluminium flakes in the coating are uniformly dispersed in the coating film which will provide great barrier effects for moisture corrosive substances. The aluminium flakes also reflect light and heat through the coating film which make the coating films UV and heat resistance with bright surface finish. The aluminium flakes can be coated with some resin such as acrylic resin. The resin coated aluminium flakes have excellent chemical resistance, adhesiveness and arc resistance.

Unsaturated polycarboxylic acid polymer and polysiloxane copolymer are additives having medium to high polarity which will act as bridges between the individual pigment particles, thereby creating three-dimensional networks. This mechanism helps to control flocculation of the pigments.

Mono-oxazolidine is an additive that acts as moisture scavenger in polyurethane coating. It is used to eliminate moisture from the raw materials, the atmosphere and substrate. It prevents bubbling and downglossing caused by high moisture levels.

The one-part moisture curing polyurethane for high performance protective coating can be prepared by mixing the following raw materials together:

i	Aromatic polyisocyanate prepolymer based on diphenylmethane diisocyanate (MDI) with active NCO about 15 – 35 weight %	50.0 – 75.0	weight %
ii	Aluminium pigment, resin coated non-leafing aluminium flakes with mean diameter smaller than 45 micron	20.0 – 40.0	weight %
iii	Solution of a low molecular weight, unsaturated polycarboxylic acid polymer and polysiloxane copolymer	0.1 – 3.0	weight %
iv	Mono-oxazolidine	1.0 – 5.0	weight %
v	Solvent, divided between isobutyl acetate and xylene	10.0 – 20.0	weight %

Performance Test

4 carbon steel plates with dimension 75x75x2 mm were sand blasted and painted by brush with the one-part moisture curing polyurethane composition above. The dry film

thickness was about 150 microns for 2 steel plates and about 300 microns for the rest. All steel plates were alternate immersed in neutral 3.5 % sodium chloride solution as stated in ASTM G 44 – 99. After 6,500 hours of alternate immersion, only small rust was detected at the edge of all steel plates but there was no paint blister or rust found on the plates. The result shows that the one-part moisture curing polyurethane in this invention can be used as the protective coating in severe environment like tidal zone or splash zone in seawater.

Claims

1. The composition of one-part moisture curing polyurethane for high performance protective coating, comprising:

i	Aromatic polyisocyanate prepolymer based on diphenylmethane diisocyanate (MDI) with active NCO about 15 – 35 weight %	50.0 – 75.0	weight %
ii	Aluminium pigment, resin coated non-leafing aluminium flakes with mean diameter smaller than 45 micron	20.0 – 40.0	weight %
iii	Solution of a low molecular weight, unsaturated polycarboxylic acid polymer and polysiloxane copolymer	0.1 – 3.0	weight %
iv	Mono-oxazolidine	1.0 – 5.0	weight %
v	Solvent, divided between isobutyl acetate and xylene	10.0 – 20.0	weight %

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C09D175/04, C09C1/64, C09C3/10, C09D5/10, C09D7/20, C09D7/62, C09D7/63, C09D175/02, C09D183/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2019
Registered utility model specifications of Japan 1996-2019
Published registered utility model applications of Japan 1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/0069482 A1 (MIZUTARI, Takeaki) 2009.03.12, Whole Document & WO 2008/010466 A1 & EP 2042575 A1 & KR 10-2009-0031513 A & CN 101426868 A	1
A	US 2016/0024318 A1 (SIKA TECHNOLOGY AG) 2016.01.28, Whole Document & WO 2014/114640 A1 & JP 2016-510354 A & CN 104903371 A & KR 10-2015-0108359 A	1
A	JP 2010-189541 A (AUTOCHEMICAL INDUSTRY CO.,LTD) 2010.09.02, Whole Document (Family: none)	1

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

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Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	TAZAWA, Toshiki 4Z 3836 Telephone No. +81-3-3581-1101 Ext. 3480

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International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5747627 A (THE YOKOHAMA RUBBER CO.,LTD.) 1998.05.05, Whole Document & WO 1996/020231 A1 & JP 09-169829 A	1
A	US 5473043 A (DAI-ICHI KOGYO SEIYAKU CO.,LTD.) 1995.12.05, Whole Document & JP 07-010949 A	1
A	JP 2003-128743 A (DIC CORPORATION) 2003.05.08, Whole Document (Family: none)	1

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C09D7/63(2018.01)i, C09D175/02(2006.01)i, C09D183/04(2006.01)i