



(43) International Publication Date
2 April 2015 (02.04.2015)

(10) International Publication Number
WO 2015/048033 A1

(51) International Patent Classification:
E01F 9/04 (2006.01)

(21) International Application Number:
PCT/US2014/057014

(22) International Filing Date:
23 September 2014 (23.09.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/884,179 30 September 2013 (30.09.2013) US

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: **CARLSON, Eugene, H.**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **KIM, Jong-Min**; 19th Floor, 82, Uisadang-daero, Yeongdeungpo-gu, Yeongdeungpo-ku, Seoul, Seoul 150-705 (KR).

(74) Agents: **ADAMSON, Trisha, D.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: CRACK-RESISTANT THERMOPLASTIC ROAD MARKING

(57) Abstract: The present application generally relates to a thermoplastic road marker having improved crack-resistance, to compositions of such road markers, and to methods of making and applying these road markers. Some embodiments of the present disclosure relate to a thermoplastic road marking composition, comprising: ethylene vinyl acetate ("EVA") and/or ethylene acrylic acid ("EAA") copolymers in an amount of between about 1.5 wt% to about 6.0 wt%; and core-shell particles in an amount of between about 0.5 wt% and about 3.0 wt%. In at least some embodiments, the EVA and/or EAA have a melt flow index equal to or less than 45 g/ 10 min at 190°C.



WO 2015/048033 A1

CRACK-RESISTANT THERMOPLASTIC ROAD MARKING

5

Technical Field

[0001] The present application generally relates to a thermoplastic road marking having improved crack-resistance, to compositions of such road markings, and to methods of making and applying these road markings.

10

Background

[0002] Pavement or road markings (*e.g.*, paints, tapes, and individually mounted articles) guide and direct motorists and pedestrians traveling along roadways and paths. Pavement or road markings can be used on, for example, roads, highways, parking lots, and recreational trails, to form stripes, bars, and markings for the delineation of lanes, crosswalks, parking spaces, symbols, legends, and the like. Paint was a preferred pavement marking for many years. However, modern pavement marking materials offer significant advantages over paint, such as increased visibility, retroreflectance, improved durability, and temporary and/or removable marking options. Further, currently available road marking materials can be, for example, sheets, films, tapes, sprayable compositions, and raised pavement markers.

15

20

[0003] Pavement or road markings are subject to continuous wear and exposure to the elements as well as road chemicals. Consequently, there is a need for pavement or road marking compositions and materials that provide durability and retained reflectivity once applied to a surface and dried and/or hardened. Thermoplastic polymers are often included in road markings because they are highly durable. Additionally, the use of thermoplastic polymers in road markings results in shorter track-free time. "Track-free time," as used herein, is the time between application and the point where material will no longer transfer to vehicle tires. Shorter track-free times increase marking efficiency by reducing or eliminating the need for traffic disruption through such measures as closing lanes or placing traffic control devices to protect such markings.

25

30

[0004] Examples of thermoplastic road marking materials include, for example, ethylene acrylic acid ("EAA") polymers (see, for example, U.S. Patent No. 6,217,252 (Tolliver)) or ethylene vinyl acetate ("EVA") polymers (see, for example, U.S. Patent No. 5,536,569 (Lasch et al.)).

Summary

35

[0005] The inventors of the present disclosure recognized that thermoplastic polymers are relatively brittle and crack during cold temperatures. Because pavement or road markings are outside year-round, they are exposed to very low temperatures and can experience cracking. The inventors of the present disclosure discovered ways to increase the crack-resistance of these thermoplastic pavement or road

markings. More specifically, the inventors of the present disclosure recognized that by including core-shell particles in thermoplastic road markings including ethylene vinyl acetate and/or ethylene acrylic acid, the cold weather crack-resistance of the road markings can be improved. The inventors of the present disclosure also determined the most desirable and beneficial weight percentages of the core-shell particles and of the ethylene vinyl acetate and/or ethylene acrylic acid copolymers.

[0006] Some embodiments of the present disclosure relate to a thermoplastic road marking composition, comprising: ethylene vinyl acetate and/or ethylene acrylic acid copolymers in an amount of between about 1.5 wt% to about 6.0 wt%; and core-shell particles in an amount of between about 0.5 wt% and about 3.0 wt%. In some embodiments, the core-shell particles are selected from a group consisting essentially of acrylics, MBS, and/or MABS copolymers. In some embodiments, the ethylene vinyl acetate and/or ethylene acrylic acid copolymers have a melt flow index of between 2 g/10 min and 400 g/10 min.

[0007] Some embodiments are road or pavement markers. Some embodiments are a road marker having a crack-resistance that passes the cold impact test provided in 4.2.1.4 (using the process described in Annex H) of the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000 (copyright 2000). Some embodiments are road markers that, when ten road markers are tested, six of the tested road markers do not crack when a 110,0 g (+/- 0.3 g and approximately a 30.0 mm diameter) steel ball is dropped on the road marker from a height of 2,00 m in conditions of a temperature of -10°C (+/- 3°C) using the method of testing described in the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000 (copyright 2000) Section 4.2.1.4 (using the testing method described in Annex H). Some embodiments are road makers having an indentation time of greater than 20 minutes when tested according to the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000 (copyright 2000) Section 4.2.3.3 (using the testing method described in Annex J). Some embodiments are road markers having a percent residue flow of between about 3.0% and about 15%.

Detailed Description

[0008] Some embodiments of the present disclosure relate to a thermoplastic road marking composition, comprising: ethylene vinyl acetate ("EVA") and/or ethylene acrylic acid ("EAA") copolymers in an amount of between about 1.5 wt% and about 6.0 wt%; and core-shell particles in an amount of between about 0.5 wt% and about 3.0 wt%.

[0009] Some exemplary commercially available EVA copolymers include, for example, Elvax™ 150, Elvax 250, Elvax 260, Elvax 350, Elvax 410, Elvax 450, Elvax 550, Ateva™ 1241, Ateva 1615, Ateva 1641, Ateva 9020, Ateva 9030, Evatane™ 20-20, Evatane 28-25, Evatane 28-40, Evatane 33-25, Evatane 33-45, Evatane 40-55, Escorene Ultra™ FL 01418, Escorene Ultra UL 02518CC, and Escorene Ultra UL 05540EH2. Some EVA copolymers capable of use in the retroreflective articles described and claimed herein have a melt flow index of between 2 g/10 min and 400 g/10 min.

[0010] Some exemplary commercially available EAA copolymers include, for example, Primacor 1430, Primacor 3004, Primacor 3440, Primacor 3460, Primacor 3330, Primacor 3340, Escor 5000 ExCo, Escor 5020 ExCo, Escor 5050 ExCo, Escor 5070, Escor 5200, Nucrel 699, Nucrel 960, Nucrel 3990, Nucrel 30907, and Nucrel 925. Some EAA copolymers capable of use in the retroreflective articles described and claimed herein have a melt flow index of between 2 g/10 min and 400 g/10 min.

[0011] Some exemplary commercially available core-shell particles include, for example, Durastrength™ 200, D300S, D320, Clearstrength™ W300, Paraloid™ EXL-2300, Paraloid EXL-2600, Paraloid EXL-3300, Paraloid EXL-3600, Paraloid EXL-5136, Paraloid EXL-6600, Paraloid BTA707, Paraloid BTA712, Paraloid BTA717, Paraloid BTA730, Paraloid BTA731, Paraloid BTA733ER, Metablen™ C-223A, Metablen C-323A, Metablen C-820J, Metablen C-830J, Metablen C-140A, Metablen C-130, Metablen W-300A, and Metablen W-450A.

[0012] In some embodiments, retroreflective or reflective articles, transparent microspheres, and/or skid-resisting particles are included in the composition or are placed on top of or adjacent to the composition. In some embodiments, these increase visibility or signaling performance of the road marker. Methods of applying the retroreflective or reflective articles, transparent microspheres, and/or skid-resisting particles are disclosed in, for example, U.S. Patent No. 3,451,537, incorporated in its entirety herein.

[0013] In some embodiments, the road marking composition includes a pigment for enhancing its visual appearance. Exemplary pigments include titanium dioxide and yellow pigment 83. Some embodiments include a stabilizing agent that assists in providing UV or heat resistance. Exemplary stabilizing agents include, for example, hindered amine light stabilizers (HALS), phosphonate heat stabilizers, benzophenones, and zinc compounds. Stabilizing agents may be present at levels up to about 5%. Some embodiments include a rheology control agent that assists in providing settling resistance. Exemplary rheology control agents include, for example, bentone and fumed silica.

[0014] In at least some embodiments, the road marker composition is sprayed onto the road as a liquid composition.

[0015] Typical roadway surfaces are rough (rather than smooth). As such, good adhesion of the road marking composition to the roadway surface is preferred. The road marking compositions of the present disclosure adapt to and accommodate road surface irregularities.

[0016] Some embodiments are a road marker having a crack-resistance that passes the cold impact test provided in 4.2.1.4 (using the process described in Annex H) of the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000 (copyright 2000). Some embodiments are road markers that, when ten road markers are tested, six of the tested road markers do not crack when a 110,0 g (+/- 0.3 g and approximately a 30.0 mm diameter) steel ball is dropped on the road marker from a height of 2,00 m in conditions of a temperature of -10°C (+/- 3°C) using the method of testing described in the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000 (copyright 2000) Section 4.2.1.4 (using the testing method described in Annex H).

[0017] Some embodiments are road makers having an indentation time of greater than 20 minutes when tested according to the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000 (copyright 2000) Section 4.2.3.3 (using the testing method described in Annex J).

[0018] The following examples describe some exemplary constructions of various embodiments of the pavement or road markings and/or road or pavement marking compositions described in the present application. The following examples are intended to be illustrative, but are not intended to limit the scope of the present application.

Examples

[0019] MATERIALS

[0020] The following materials were used in preparation of Comparative Examples A – U and Examples 1 – 2, below.

<u>Trade Designation</u>	<u>Material</u>	<u>Supplier</u>
R-1100S	Hydrocarbon resin	Kolon Industries
CS-42F	Polyethylene wax	Coschem
1500K	Aliphatic oil	Michang Oil Industries
CLASS 1 BEAD	Glass bead	Langfang
SD80	Dolomite	Seongshin
SHF-T	Calcium carbonate	Seongchin Minefield
SONGSTAB SC-130	Calcium stearate	Songwon
CR-828	Titanium dioxide	Tronox
VASTOPLAST 708	Amorphous polyolefin	Evonik Industries
VASTOPLAST 702	Amorphous polyolefin	Evonik Industries
EASTOFLEX 1010PL	Amorphous polyolefin	Eastman Chemical
AFFINITY GA1900	Amorphous Polyolefin	Dow Chemical
EXL-2314	Core-shell particle	Dow Chemical
VC590	EVA having a melt flow index at 190°C of 4.0 g/10 min	Lotte Chemical
VA800	EVA having a melt flow index at 190°C of 20 g/10 min	Lotte Chemical
VA810	EVA having a melt flow index at 190°C of 45.0 g/10 min	Lotte Chemical
VA910	EVA having a melt flow index at 190°C of 400.0 g/10 min	Lotte Chemical
VA920	EVA having a melt flow index at 190°C of 150.0 g/10 min	Lotte Chemical

[0021] TEST METHODS:

[0022] Cold Impact Resistance: cold impact resistance was measured generally following the procedure described in the European standard EN 1871 (2000) "Road Marking Materials; Physical Properties". Steel balls weighing 66.8 g and 110 g were dropped onto the material to be tested at low temperatures and using a brine solution. Results are expressed in class of material (e.g., CI0, CI1, CI2, and CI3), according to Table 7 of the standard, wherein CI3 indicates highest cold impact resistance.

[0023] Indentation: samples of road marking material were tested generally following the procedure described in EN 1871 (2000). The time it took for a probe to sink 10 mm into the road marking material using a 53.5 kg steel block weight was measured. Results are expressed in class of material (e.g., IN0, IN1, IN2, IN3, IN4, and IN5), wherein IN5 indicates that the indentation time was longer than 20 minutes.

[0024] COMPARATIVE EXAMPLES A – J

[0025] Comparative thermoplastic road marking compositions comprising polyolefin resins were prepared by mixing the ingredients listed in Table 1, below, at 200 degrees C for at least 1 hour using a planetary mixer. Additionally, comparative Examples E-F, and G-J comprised core-shell particles.

[0026] Table 1. Composition of Comparative Examples A-J.

Ingredients	Comp. Ex. A	Comp. Ex. B	Comp. Ex. C	Comp. Ex. D	Comp. Ex. E	Comp. Ex. F	Comp. Ex. G	Comp. Ex. H	Comp. Ex. I	Comp. Ex. J
R-1100S	18	18	18	18	18	18	18	18	18	18
CS-42F	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
1500K	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CLASS 1 BEAD	20	20	20	20	20	20	20	20	20	20
SD80	20	20	20	20	20	20	20	20	20	20
SHF-T	29.8	29.8	29.8	29.8	30.8	29.8	29.8	27.8	27.8	27.8
SONGSTAB SC-130	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
CR-828	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
VASTOPLAST 708	5.0	0	0	0	3.0	3.0	2.5	2.5	0	0
VASTOPLAST 702	0	5.0	0	0	0	0	2.5	2.5	5.0	0

EASTOFLEX 1010PL	0	0	5.0	0	0	0	0	0	0	5.0
EXL-2314	0	0	0	0	1.0	2.0	0	2.0	2.0	2.0
AFFINITY GA1900	0	0	0	5.0	0	0	0	0	0	0

[0027] Cold impact resistance and indentation were measured as described above. Results are reported in Table 2, below.

5 [0028] Table 2. Cold Impact Resistance and Indentation

Examples	Cold impact resistance	Indentation
Comp. Ex. A	CI 1	IN2
Comp. Ex.B	CI 1	IN2
Comp. Ex.C	CI 1	IN5
Comp. Ex.D	CI 2	IN5
Comp. Ex.E	CI 1	IN3
Comp. Ex.F	CI 1	IN4
Comp. Ex. G	CI 1	IN3
Comp. Ex.H	CI 1	IN3
Comp. Ex.I	CI 1	IN3
Comp. Ex.J	CI 1	IN5

[0029] COMPARATIVE EXAMPLES K – U

[0030] Road marking compositions were prepared as described in Comparative Examples A – J, above, except that EVA resins were used. In Comparative Examples S – U both EVA and polyolefin resins were used. Ingredients are listed in Table 3, below.

10 [0031] Table 3. Composition of Comparative Examples K-U

Ingredients	C. Ex. K	C. Ex. L	C. Ex. M	C. Ex. N	C. Ex. O	C. Ex. P	C. Ex. Q	C. Ex. R	C. Ex. S	C. Ex. T	C. Ex. U
R-1100S	18	18	18	18	18	18	18	18	18	18	18
CS-42F	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
1500K	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CLASS 1 BEAD	20	20	20	20	20	20	20	20	20	20	20
SD80	20	20	20	20	20	20	20	20	20	20	20

SHF-T	32.3	30.8	30.8	32.3	31.8	31.3	29.3	29.3	30.8	30.8	30.8
SONGSTAB SC-130	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
CR-828	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3
VASTOPLAST 7082	0	0	0	0	0	0	0	0	2	0	0
AFFINITY GA1900	0	0	0	0	0	0	0	0	0	2	2
VC590	2.5	4.0	0	1.5	2.0	0	0	0	2	0	1
VA800	0	0	4.0	0	0	0	0	0	0	0	0
VA910	0	0	0	0	0	2.5	4	0	0	2	1
VA920	0	0	0	0	0	0	0	4	0	0	0
VA810	0	0	0	0	0	0	0	0	0	0	0
EXL-2314	0	0	0	1.0	1.0	0	0	0	0	0	0

[0032] Cold impact resistance and indentation are listed in Table 4, below.

[0033] Table 4. Cold Impact Resistance and Indentation

Examples	Cold impact resistance	Indentation
Comparative Example K	CI1	IN5
Comparative Example L	CI2	IN5
Comparative Example M	CI1	IN5
Comparative Example N	CI1	IN5
Comparative Example O	CI2	IN5
Comparative Example P	CI2	IN4
Comparative Example Q	CI2	IN4
Comparative Example R	CI2	IN5
Comparative Example S	CI1	IN3
Comparative Example T	CI2	IN3
Comparative Example U	CI2	IN3

[0034] EXAMPLES 1 – 2

5 [0035] Road marking compositions were prepared as described in Comparative Examples A – J, above, except that core-shell particles and EVA resins having a melt flow index equal to or less than 45 g/ 10 min at 190°C were used. Ingredients are listed in Table 5, below.

[0036] Table 5. Composition of Examples 1 and 2

Ingredients	Example 1	Example 2
R-1100S	18	18
CS-42F	1.6	1.6
1500K	1.0	1
CLASS 1 BEAD	20	20
SD80	20	20
SHF-T	31.3	29.3
SONGSTAB SC-130	0.3	0.3
CR-828	4.3	4.3
VC590	2.5	0
VA810	0	4
EXL-2314	1.0	1.5

[0037] Cold impact resistance and indentation were measured. Results are shown in Table 6, below.

5

[0038] Table 6. Cold Impact Resistance and Indentation

Examples	Cold impact resistance	Indentation
Example 1	CI3 met	IN5 met
Example 2	CI3 met	IN5 met

[0039] The terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

10

[0040] Moreover, the terms top, bottom, over, under and the like in the description and the claims are used for descriptive purposes and not necessarily for describing relative positions. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other orientations than described or illustrated herein.

15

[0041] The recitation of all numerical ranges by endpoint is meant to include all numbers subsumed within the range (*i.e.*, the range 1 to 10 includes, for example, 1, 1.5, 3.33, and 10).

[0042] Those having skill in the art will appreciate that many changes may be made to the details of the above-described embodiments and implementations without departing from the underlying principles thereof. Further, various modifications and alterations of the present invention will become apparent to those skilled in the art without departing from the spirit and scope of the invention. The scope of the present application should, therefore, be determined only by the following claims.

5

What is claimed is:

1. A thermoplastic road marking composition, comprising:
at least one of an ethylene vinyl acetate copolymer and/or an ethylene acrylic acid
5 copolymer having a melt flow index equal to or less than 45 g/ 10 min at 190° C in an amount of between
about 2.5 wt% to about 4.5 wt%; and
core-shell particles in an amount of between about 0.5 wt% and about 2.5 wt%.
2. The thermoplastic road marking composition of claim 1, wherein the ethylene vinyl
acetate copolymer and/or an ethylene acrylic acid copolymers have a melt flow index of between 2 g/10
10 min and 400 g/10 min.
3. A road marker including the thermoplastic road marking composition of claim 1.
4. The road marker of claim 3, having a crack-resistance that passes the cold impact test
provided in Section 4.2.1.4 of the National Standards Authority of Ireland Irish Standard No. I.S. EN
1871:2000.
- 15 5. The road marker of claim 3, having a crack resistance that when ten road markers are
tested, six of the ten tested road markers do not crack when a 110,0 g (+/- 0.3 g) steel ball (approximately
30,0 mm in diameter) is dropped on the road marker from a height of 2,00 m in conditions of a
temperature of -10°C (+/- 3°C) using the testing method described in the National Standards Authority of
Ireland Irish Standard No. I.S. EN 1871:2000 Section 4.2.1.4 and Annex H.
- 20 6. The road marker of claim 3, having an indentation time of greater than 20 minutes when
tested according to the National Standards Authority of Ireland Irish Standard No. I.S. EN 1871:2000
Section 4.2.3.3 (using the testing method described in Annex J).
7. The road marking composition of claim 1, having a percent residue flow of between
about 3.0% and about 15%.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/057014

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - E01F 9/04 (2014.01)

CPC - E01F 9/04 (2014.10)

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)

IPC(8) - C09D 5/00, 5/22; E01F 9/00, 9/04, 9/08 (2014.01)

CPC - C09D 5/00, 5/004, 5/22; E01F 9/00, 9/04, 9/041, 9/08 (2014.10) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 260/998.19; 404/9, 12; 427/136, 137; 523/1, 172 (keyword delimited)

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

Orbit, Google Patents, Google Scholar

Search terms used: road street pavement marker paint ethylene vinyl acetate EVA ethylene acrylic acid EAA EVAC EAAC core shell particles melt flow index indentation time cold impact crack resistance residue flow

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,935,158 A (WATANABE) 27 January 1976 (27.01.1976) entire document	1-7
Y	CA 2 825 450 A1 (HILF et al) 02 August 2012 (02.08.2012) entire document	1-7
Y	US 4,342,810 A (ADCOCK) 03 August 1982 (03.08.1982) entire document	4, 5
Y	Prismo Road Markings Ltd. Road Marking Products Technical Data Sheet. 2010. [retrieved on 07.11.2014]. Retrieved from the Internet. <URL: http://sak.com.sa/2013/images/pdf/9-TDS259SprayTrop131VY.15Jan10%20%28AASHTO%29.pdf >. entire document	6
Y	US 3,523,029 A (SEARIGHT et al) 04 August 1970 (04.08.1970) entire document	7

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

Date of the actual completion of the international search

07 November 2014

Date of mailing of the international search report

29 DEC 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774