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(54) **Title**: ADHESIVE COMPOSITION WITH ENHANCED CURE THROUGH VOLUME

(57) **Abstract**: Curing through large bond gaps, of approximately 0.5 - 1.0 mm, has proven particularly challenging in the field of adhesives technology. Most noteworthy is the difficulty associated with providing one-part adhesive formulations capable of curing through large bond gaps. Disclosed herein are radically curable compositions comprising a radically curable component, and an initiator component capable of initiating cure of the radically curable component. The initiator comprises at least one metal salt and a free radical generating component. The metal salt of the composition is chosen so that it is reduced at the surface to which it is applied. The compositions further comprise an additive, as disclosed herein, for improving the ability of the composition to cure through large bond gaps.

Title

Adhesive Composition with Enhanced Cure Through Volume

Field of the Invention

[0001] The present invention relates to stable one-part radically curable compositions for curing on a surface. These formulations are effective for bonding applications where there is a bond gap of greater than 0.1 mm.

Discussion of Background Art

[0002] When bonding two surfaces together it is desirable to have a zero gap therebetween, *i.e.* there is direct surface-to-surface contact. However, in reality, even when mating carefully finished surfaces a zero bond gap is rarely observed. Gaps of up to 50 µm are often observed due to uneven topographies of the surfaces.

[0003] Notably, anaerobic adhesives are considered to reliably cure through gaps of up to 0.125 mm but generally do not cure satisfactorily through larger gaps. This is attributable to the diffusion of oxygen in those exposed portions of the anaerobic adhesive residing in the gaps. Thus, cure of the anaerobic adhesive in the gaps is impeded or prevented by the presence of oxygen, the adhesive remains in a liquid, uncured state and the strength of the bond between the surfaces is reduced.

[0004] In particular, curing through a larger bond gap, of approximately 0.5 – 1.0 mm has proven particularly challenging in the field of adhesives technology. Most noteworthy is the difficulty associated with providing one-part adhesive formulations capable of curing through large bond gaps, whilst maintaining good room temperature stability.

[0005] Prior art adhesives exhibiting improved gap cure are typically two part systems, which activate on mixing. Such adhesives are similar to generic anaerobic formulations. In some cases, part A of the adhesive would contain an acrylic monomer and initiating peroxide and part B would consist of a metal salt, and an accelerator in the same or a different acrylic monomer.

[0006] European Patent No. 0659859 discloses a two-part, mixable, structural acrylic adhesive characterized by the ability to fill large gaps comprising a polymerizable acrylic monomer and peroxy polymerization initiator in one part and a mixture of a transition metal compound and o-benzosulfimide in acrylic monomer in the second part.

[0007] Another example of a two-part adhesive formulation with improved gap curing characteristics is disclosed in U.S. Patent No. 3970505. The composition comprises a polymerizable acrylate ester monomer, a cure-through-gap agent and at least 0.1% of a hydroperoxide polymerization initiator. The cure-through-gap agent consists of a combination of a substituted thiourea and an acid having a pK_A of less than about 6.

[0008] In U.S. Patent Application No. 2009/0288771 Farrell *et al.* describe surface promoted activation of one-part radically curable compositions that contain a transition metal salt.

[0009] Notwithstanding the prior art there remains a need for stable one-part compositions capable of achieving good cure-through-volume through large bond gaps.

Summary of the Invention

[0010] The present invention provides for curable compositions capable of reliably curing through bondline gaps of approximately 0.5 – 2.0 mm. In particular, the present invention provides for anaerobic adhesive compositions capable of reliably curing through bondline gaps of approximately 0.5 – 2.0 mm. Depending on the metal substrate/surface being bonded or sealed and the length of time over which the adhesive is allowed to set satisfactory cure through bondline gaps of 5 mm to 10 mm is observable utilising compositions according to the present invention.

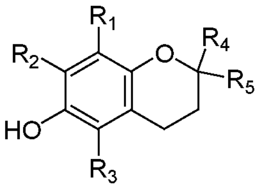
[0011] In one aspect the present invention provides for a one-part curable composition for curing on a surface comprising:

i) a radically curable component;

ii) a free radical generating component;

iii) at least one metal salt, the standard reduction potential of the at least one metal salt being greater than the standard reduction potential of the surface; and

iv) a reducing additive comprising a moiety selected from the group consisting of:



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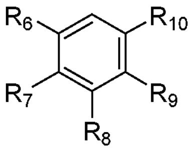

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benzoin or an ester thereof, ascorbic acid or an ester thereof, hydrazines, toluidines, and Tin(II) salts;

R_1, R_2 and R_4 are the same or different and can be C_1 to C_5 alkyl;

R_3 may be C_1 to C_5 alkyl or H;

R_5 may be C_1 to C_{20} alkyl;

R_6 to R_9 are the same or different and can be OH or H, such that at least two of R_6 to R_9 are always OH;

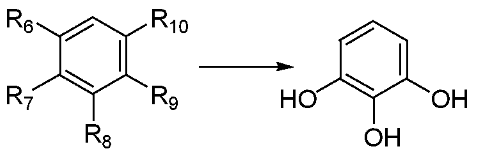
R_{10} may be $C(O)OR_{11}$ or H; and

R_{11} may be H or C_1 to C_{20} alkyl.

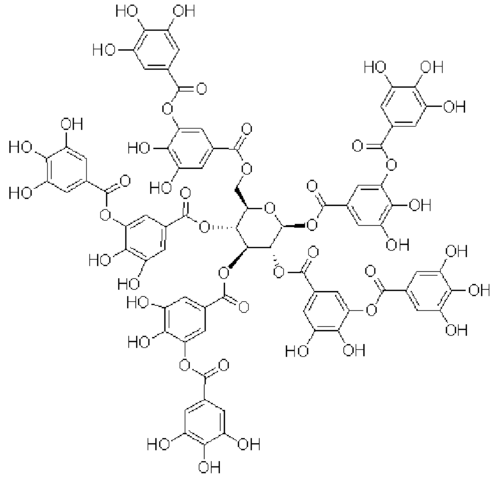
[0012] References to standard reduction potentials in this specification indicate the tendency of a species to acquire electrons and thereby be reduced. Standard reduction potentials are measured under standard conditions: 25 °C, 1 M concentration, a pressure of 1 atm and elements in their pure state.

[0013] As used herein, the term "C_x-C_y alkyl" embraces C_x-C_y unbranched alkyl, C_x-C_y branched alkyl and combinations thereof.

[0014] As used herein, the expression "a reducing additive comprising a moiety selected from the group consisting of *...*" represents a molecule exactly equivalent to or comprising a substructure substantially equivalent to those indicated. The substructure should contain the carbon skeleton of the moiety in addition to all non-hydrogen functional groups. Hydrogens may be replaced with covalent bonds or other non-hydrogen functional groups. For example, pyrogallol is covered by the generic formula shown below, and pyrogallol would be considered a substructure of Tannic acid within this specification:



Pyrogallol



Tannic acid

[0015] Advantageously, compositions of the present invention show excellent cure through gap characteristics. Standard anaerobic formulations reported in the prior art can cure through gaps up to about 0.125 mm. Compositions according to the present invention are suitable for curing through bondline gaps of between about 0.2 to about 10 mm, such as bondline gaps between about 0.5 to about 5 mm, for example bondline gaps between about 0.5 to about 2 mm, suitably bondline gaps between about 0.5 to about 0.1 mm.

[0016] The one-part radically curable compositions discussed herein do not require any additional reducing agent to initiate cure of the composition. They are stable until contacted with a metallic substrate (or other surface) that is capable of participating in a RedOx reaction (*i.e.* transfer of electrons from the [metal] surface to the metal salt); thus the surface fulfils the role of a conventional reducing agent component.

[0017] The radically curable compositions of the invention are storage stable as a one-part compositions when stored in air permeable containers. The stability of large volumes of the radically curable coating compositions of the present invention may be improved by continuous agitation and/or bubbling air through the composition.

[0018] The inventive compositions may be encapsulated, where it is desirable to do so. Suitable encapsulation techniques comprise, but are not limited to, coacervation, softgel and co-extrusion.

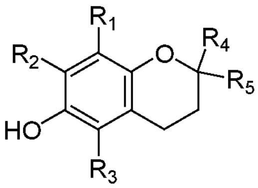
[0019] Accordingly, the present invention may further provide for a one-part curable composition for curing on a surface comprising:

i) a radically curable component;

ii) a free radical generating component;

iii) at least one metal salt, the standard reduction potential of the at least one metal salt being greater than the standard reduction potential of the surface; and

iv) a reducing additive comprising a moiety selected from the group consisting of:



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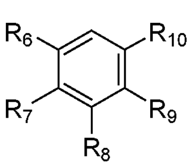

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benzoin or an ester thereof, ascorbic acid or an ester thereof, hydrazines, toluidines, and Tin(II) salts;

R_1, R_2 and R_4 are the same or different and can be C_1 to C_5 alkyl;

R_3 may be C_1 to C_5 alkyl or H;

R_5 may be C_1 to C_{20} alkyl;

R_6 to R_9 are the same or different and can be OH or H, such that at least two of R_6 to R_9 are always OH;

R_{10} may be $C(O)OR_{11}$ or H; and

R_{11} may be H or C_1 to C_{20} alkyl,

and the composition can cure through bondline gaps of between about 0.2 to about 10 mm, such as bondline gaps between about 0.5 to about 5 mm, for example bondline gaps between about 0.5 to about 2 mm, suitably bondline gaps between about 0.5 to about 0.1 mm.

[0020] The at least one metal salt of the composition of the present invention may comprise a transition metal cation. The transition metal cation may be selected from copper, iron, zinc and combinations thereof. In one embodiment, the transition metal cation may be zinc. The metal salt may be substituted with an organic ligand. This may improve the solubility of the metal salt in the composition of the present invention.

[0001] The metal salt of the composition of the present invention may include a counterion chosen from the group consisting of naphthenate, ethylhexanoate, benzoate, nitrate, chloride, acetylacetonate, ClO_4^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $(C_6F_5)_4B$, $(C_6F_5)_4Ga$, Carborane, triflimide, bis-triflimide, and combinations thereof. The metal salt counterion may be chosen from ClO_4^-, BF_4^-,

PF_6^-, SbF_6^- and combinations thereof. In one embodiment the metal salt counterion may be BF_4^-.

[0021] The solubility of the metal salt may be modified by changing the counterion, the addition and/or substitution of ligands to the metal of the metal salt and combinations thereof. This will allow for efficient electron transfer between the surface and the metal salt to be observed as appropriate solubility is achieved.

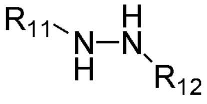
[0022] The radical generating component of the composition of the present invention may be selected from peroxides, hydroperoxides, hydroperoxide precursors, persulfates and combinations thereof. For example, the radical generating component may be selected from Cumene Hydroperoxide, *tert*-Butyl hydroperoxide, Hydrogen peroxide, 2-Butanone peroxide, Di-*tert*-Butyl peroxide, Dicumyl peroxide, Lauroyl peroxide, 2,4-Pentanedione peroxide, pentamethyl-trioxepane [such as that sold under the band name Trigonox® 311], Benzoyl Peroxide and combinations thereof.

[0023] The radically curable component of the composition of the present invention may have at least one functional group selected from acrylates, methacrylates, thiolene, siloxanes, vinyls and combinations thereof. In one embodiment, the radically curable component may have at least one functional group selected from acrylates, methacrylates, and combinations thereof.

[0024] Desirably, the surfaces to which the compositions of the present invention are applied may comprise a metal, metal oxide or metal alloy. Moreover, the surface may comprise a metal or metal oxide. Preferably, the surface may comprise a metal.

[0025] Suitable surfaces can be selected from iron, steel, aluminium, aluminium oxide, copper, zinc, zinc oxide, and zinc bichromate. References to steel include a steel selected from mild steel, gritblasted mild steel, e-coated steel (e-coat is an organic paint which is electrodeposited, with an electrical current, to a metallic surface, such as steel) and stainless steel. References to aluminium and aluminium oxide include alclad aluminium (low copper content), and oxide removed alclad aluminium (low copper content) respectively.

[0026] As used herein the term "hydrazines" refers to compounds having a "–HN-NH-" moiety in the molecule. For example, the hydrazine may be of the formula:



R_{11} can be C_1-C_{20} aliphatic, C_3-C_{20} cycloaliphatic, C_2-C_{20} acyl, C_5-C_{20} aryl, C_3-C_{20} heteroaryl and combinations thereof; and

R_{12} can be H, C_1-C_{20} aliphatic, C_3-C_{20} cycloaliphatic, C_2-C_{20} acyl, C_5-C_{20} aryl, C_3-C_{20} heteroaryl and combinations thereof.

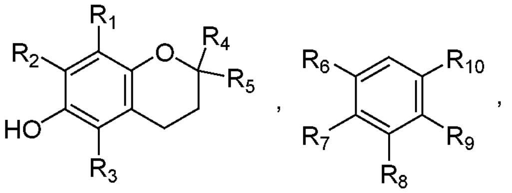
[0027] Desirably, R_{11} is selected from C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} acyl, C_5-C_{20} aryl, C_3-C_{20} heteroaryl and combinations thereof and R_{12} is selected from H, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} acyl, C_5-C_{20} aryl, C_3-C_{20} heteroaryl and combinations thereof.

[0028] Suitable hydrazines may include those described in U.S. Patent Application Publication No. 2009/0281335 of Messana *et al.* For example, suitable hydrazines may be selected from the group consisting of ethylcarbazate, acetylphenylhydrazine, *para*-nitrophenylhydrazine and *para*-tolylsulfonylhydrazide.

[0029] As used herein, the term "toluidines" refers to the isomers *o*-toluidine, *m*-toluidine, and *p*-toluidine and substituted derivatives thereof. For example, the *N* atom of the toluidines may be mono- or di- substituted (in the case of di- substitution the substituents may be the same or different) with one of C_1-C_{20} aliphatic, C_3-C_{20} cycloaliphatic, C_2-C_{20} acyl, C_5-C_{20} aryl, C_3-C_{20} heteroaryl, and combinations thereof. The *N* atom of the toluidines may be mono- or di-substituted with one of C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} acyl, C_5-C_{20} aryl, C_3-C_{20} heteroaryl, and combinations thereof. Desirably, the *N* atom of the toluidine is di- substituted with a C_1-C_{20} alkyl chain (each substituent may be the same or different C_1-C_{20} alkyl chain). Suitable toluidines may include *N,N*-diethyl-*p*-toluidine and *N,N*-dimethyl-*o*-toluidine.

[0030] The present invention also provides for a reducing additive comprising a combination of a toluidine and saccharin.

[0031] The reducing additive may be selected from the group consisting of:



benzoin or an ester thereof, ascorbic acid or an ester thereof, and acetylphenylhydrazine;

R_1, R_2 and R_4 may be the same or different and can be C_1 to C_5 alkyl;

R_3 may be C_1 to C_5 alkyl or H;

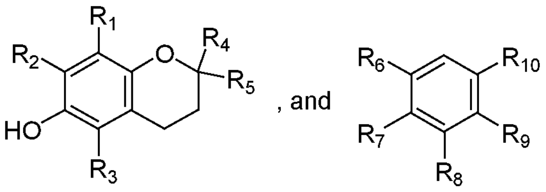
R_5 may be C_1 to C_{20} alkyl;

R_6 to R_9 are the same or different and can be OH or H, such that at least two of R_6 to R_9 are always OH;

R_{10} may be C(O)OR_{11} or H; and

R_{11} may be H or C_1 to C_{20} alkyl.

[0032] The reducing additive may be selected from the group consisting of:



wherein R_1, R_2 and R_4 are the same or different and can be Me;

R_3 may be Me or H;

R_5 may be C_1 to C_{20} alkyl;

R_6 to R_9 are the same or different and can be OH or H, such that at least two of R_6 to R_9 are always OH; and

R_{10} may be C(O)OH or H.

[0033] When the reducing additive comprises an ascorbic acid moiety, desirably the ascorbic acid moiety is an ester of ascorbic acid. Ascorbic acid esters are preferred as solubility is much better compared with ascorbic acid. In particular, ascorbic acid 6-palmitate ester is desirable.

[0034] The reducing additive may be selected from acetyl phenyl hydrazine, benzoin, ascorbic acid, ascorbic acid 6-palmitate, α-tocopherol, γ-tocopherol, 2,2,5,7,8-pentamethylchromanol, gallic acid [3,4,5-trihydroxybenzoic acid], tannic acid, pyrogallol [benzene-1,2,3-triol], hydroquinone and combinations thereof.

[0035] The reducing additive may be present in the composition in an amount of 0.05 to 10% by weight of the composition. The reducing additive may be present in the composition in an amount of 0.05 to 3% by weight of the composition. The reducing additive may be present in the composition in an amount of 0.1 to 0.5% by weight of the composition.

[0036] The radical generating component may be present in the composition in an amount of 0.1 to 10% by weight of the composition. The radical generating component may be present in the composition in an amount of 0.1 to 3% by weight of the composition. The radical generating component may be present in the composition in an amount of 0.5 to 1.5% by weight of the composition.

[0037] The metal salt may be present in the composition in an amount of 0.1 to 10% by weight of the composition. The metal salt may be present in the composition in an amount of 0.1 to 3% by weight of the composition. The metal salt may be present in the composition in an amount of 0.5 to 1.5% by weight of the composition.

[0038] In general, the inventive compositions disclosed herein can cure on oxidised metal surfaces without the need for additional etchant or oxide remover. However, the compositions of the invention may optionally include an oxide remover. For example, including an etchant or oxide remover, such as those comprising chloride ions and/or a zinc (II) salt, in formulations of the invention may allow etching of any oxide layer. This will in turn expose the (zero-oxidation state) metal below, which is then sufficiently active to allow reduction of the (transition) metal salt of the radically curable composition of the present invention.

[0039] The composition of the present invention may further comprise a suitable filler such as a silica filler material. Advantageously, the filler material may increase the viscosity of the adhesive formulation thereby helping to retain the formulation in the bondline, thus facilitating good cure-through-gap properties.

[0040] In yet a further aspect, the present invention provides for a method of sealing or bonding comprising:

a. applying a composition according to the present invention to a first surface;
b. mating the first surface and a second substrate so as to form a bond or seal with the composition,

and the standard reduction potential of the at least one metal salt of the composition of the present invention is greater than the standard reduction potential of at least one of the first surface and the second substrate.

[0041] The method of the present invention may be used to cure through a bondline gap of greater than about 0.2 mm. The method of the present invention may be used to cure through bondline gaps of between about 0.2 to about 10 mm, such as bondline gaps between about 0.5 to about 5 mm, for example bondline gaps between about 0.5 to about 2 mm, suitably bondline gaps between about 0.5 to about 0.1 mm.

[0042] In yet a further aspect the present invention provides for use of a composition according to the present invention for sealing or bonding through a bondline gap of greater than about 0.2 mm. The composition of the present invention may be used to cure through bondline gaps of between about 0.2 to about 10 mm, such as bondline gaps between about 0.5 to about 5 mm, for example bondline gaps between about 0.5 to about 2 mm, suitably bondline gaps between about 0.5 to about 0.1 mm.

[0043] In a further aspect, the invention relates to a pack comprising:

a) a closeable container; and
b) a composition according to the present invention held within the container,

the container being air permeable.

[0044] It will be appreciated by a person skilled in the art that curable compositions of the present invention may additionally comprises conventional additives such as fillers, pigments, stabilisers, moisture scavengers, *etc.*, subject to the additives not interfering with effective curing of the compositions.

[0045] As will be appreciated by a person skilled in the art, the metal salt in the compositions of the present invention will be chosen such that the anion of the metal salt will not result in quenching of the polymerization/cure process.

[0046] Where suitable, it will be appreciated that all optional and/or preferred features of one embodiment of the invention may be combined with optional and/or preferred features of another/other embodiment(s) of the invention.

Detailed Description of the Invention

[0047] It should be readily apparent to one of ordinary skill in the art that the examples disclosed herein below represent generalised examples only, and that other arrangements and methods capable of reproducing the invention are possible and are embraced by the present invention.

Results

[0048] Tensile strengths are quoted at 72h where full strength was not yet achieved at 24h. Fixture time is defined as the time required for two mild steel lap shears bonded together with a 0.5 inch overlap to hold a 3 Kg weight without failure of the bond for 30 s.

[0049] Samples used to cure across a gap were filled with 6-10% of Evonik Aerosil R8200 [a hydrophobic, surface modified fumed silica], unless otherwise noted. Silica was added to formulations to increase the viscosity thereof. Increasing the viscosity of the adhesive formulation helps to retain it in the bondline, thereby facilitating good cure-through-gap properties. Formulations absent a silica filler are very low viscosity and run out of the bondline at the gap. When this silica is used in these formulations, the fixture time remains the same compared with the unfilled sample.

[0050] A gap was induced between the mild steel lapshears using a non-metallic spacer material such as Teflon wire of 250, 500 or 1000 microns in diameter.

General Procedure for Testing Tensile Strengths:

[0051] A standard test method was followed for testing all adhesive formulations based on ASTM E177 and ASTM E6.

Apparatus

[0052] Tension testing machine [Instron], equipped with a suitable load cell.

Test Specimens

[0053] Lap-shear specimens, as specified in the quality specification, product or test program.

Assembly procedure

1. Five test specimens were used for each test.
2. Specimen surface was prepared where necessary.
3. Test specimens were cleaned by wiping with acetone or isopropanol before assembly.
4. Bond area on each lap-shear was 25.4 mm^2 (0.5 in^2). This is marked before applying the adhesive sample.
5. A sufficient quantity of adhesive was applied to the prepared surface of one lap-shear.

6. A second lap-shear was placed onto the adhesive and the assembly was clamped on each side of the bond area.

Test Procedure

[0054] After allowing for cure as specified in test program the shear strength was determined as follows:

1. The test specimen was placed in the grips of the testing machine so that the outer 25.4 mm (1 in.) of each end were grasped by the jaws. The long axis of the test specimen coincided with the direction of applied tensile force through the centre line of the grip assembly.
2. The assembly was tested at a crosshead speed of 2.0 mm/min or 0.05 in./min, unless otherwise specified.
3. The load at failure was recorded.

[0055] The following information was recorded:

1. Identification of the adhesive including name or number, and lot number.
2. Identification of the test specimens used including substrate and dimensions.
3. Surface preparation used to prepare the test specimens.
4. Cure conditions (Typically ambient room temperature only, 20 – 25 °C).
5. Test Conditions (Standard Temperature and Pressure, i.e. Room temperature).
6. Environmental conditioning, if any (None, all substrates to be bonded are freshly prepared before use).
7. Number of specimens tested, if other than 5 (Typically an average of 5 results for each quoted result).
8. Results for each specimen.
9. Average shear strength for all replicates.
10. Failure mode for each specimen when required by the quality specification, product profile, or test program.
11. Any deviation from this method.

Simple Formulations with Zinc tetrafluoroborate

Component g (mmol)	**#1**	**#2**	**#3**
$Zn(BF_4)_2.xH_20$	0.05 (0.2)	0.05 (0.2)	0.05 (0.2)
TBPB	0.05 (0.25)	0.1 (0.5)	0.15 (0.75)
HPMA	10	10	10

HPMA – Hydroxypropylmethacrylate; TBPB – Tertbutylperoxybenzoate.

Performance on Mild Steel

Tensile Strength (N/mm2)	**#1**	**#2**	**#3**
24h	6.2	7.1	6.3
72h	7.7	8.4	8.3
Fixture Time (mins)	2	2	2

[0056] Noteably, formulations 1, 2 and 3 did not provide for effective bonding when used to cure through gaps of 250 µm or higher. Formulations 1, 2 and 3 also exhibit good stability, remaining active for greater than 8 hours at 100 °C.

Formulations with Acetyl Phenylhydrazine (APH) added

Component g (mmol)	**#4**	**#5**	**#6**
Zn(BF4)2.xH20	0.05 (0.2)	0.1 (0.4)	0.1 (0.4)
TBPB	0.05 (0.25)	0.1 (0.5)	0.15 (0.75)
APH	0.025 (0.16)	0.0125 (0.08)	0.0025 (0.016)
HPMA	10	10	10

	#4	**#5**	**#6**
Fixture Time on Mild Steel (mins)	2	2	3

Performance on mild steel – values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#4	15.5	14.5	8.6	5.6	6.6	5.2	6.4	4.3
#5	15.8	15.2	8.9	6.0	6.5	5.5	5.8	4.3
#6	14.3	11.8	8.7	6.2	7.3	6.1	4.8	3.4

[0057] At surfaces with a zero bond gap, compositions 4, 5 and 6 containing APH all exhibit good bond strengths. This drops to approximately half when the bond gap increases to 500 µm, and continues to drop with increasing bond gap size.

Formulations with Benzoin added

Component g (mmol)	**#7**	**#8**	**#9**
Zn(BF4)2.xH20	0.05 (0.2)	0.1 (0.4)	0.1 (0.4)
TBPB	0.05 (0.25)	0.1 (0.5)	0.15 (0.75)
Benzoin	0.025 (0.12)	0.0125 (0.06)	0.0025 (0.012)
HPMA	10	10	10

	#7	**#8**	**#9**
Fixture Time on Mild Steel (mins)	2	2	2

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#7	2.0	2.3	3.7	4.6	3.9	4.5	3.3	2.4
#8	12.2	11.3	7.3	5.8	6.0	4.5	3.7	3.7
#9	11.1	11.5	6.0	5.2	6.0	5.6	4.0	3.4

[0058] Composition 7 with benzoin exhibits weak bond strengths for a zero bond gap and bond gaps of 250 – 1000 µm. Compositions 8 and 9 with increasing zinc salt concentration and decreasing benzoin concentrations exhibit improved bond strengths at zero gap and bond gaps of 250 µm. However, little change is observed at bond gaps of 500 µm or 1000 µm.

Formulations with Ascorbic Acid 6-Palmitate (A6HEX)

Component g (mmol)	**#10**	**#11**	**#12**
Zn(BF4)2.xH20	0.05 (0.2)	0.1 (0.4)	0.1 (0.4)
TBPB	0.05 (0.25)	0.1 (0.5)	0.15 (0.75)
A6HEX	0.025 (0.06)	0.0125 (0.03)	0.0025 (0.006)
HPMA	10	10	10

	#10	**#11**	**#12**
Fixture Time on Mild Steel (mins)	2	1	2

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#10	9.1	9.6	6.1	5.5	5.2	4.4	3.6	4.1
#11	15.3	13.1	6.9	6.3	5.3	4.9	3.9	3.2
#12	8.1	9.2	-	2.3	-	1.2	-	-

[0059] Compositions 10 to 12 containing Ascorbic acid 6-palmitate all exhibit good bond strengths for zero gap bonding. A ten fold decrease in the Ascorbic acid 6-palmitate concentration between compositions 10 and 12 results in drastically reduced performance once the bond gap increases in size. The concentrations indicated in composition 11 appear to provide for the optimal performance.

[0060] In order to compare the efficacy of all three additives repeat experiments with Benzoin and A6HEX were performed utilising the same mmol concentrations as indicated for APH in formulations 4 to 6. The results of the comparative experiments are provided below.

BENZOIN:

Component g (mmol)	**#7B**	**#8B**	**#9B**
Zn(BF4)2.xH20	0.05 (0.2)	0.1 (0.4)	0.1 (0.4)
TBPB	0.05 (0.25)	0.1 (0.5)	0.15 (0.75)
Benzoin	0.035 (0.16)	0.017 (0.08)	0.0035 (0.016)
HPMA	10	10	10

	#7B	**#8B**	**#9B**
Fixture Time on Mild Steel (mins)	2	2	3

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	0		250		500		1000	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#7B	13.3	16.9	8.5	10.3	6	6.3	4.5	5.5
#8B	14.2	15.8	10.12	10.4	6.4	6.6	4.2	5.4
#9B	12.3	11.7	10.41	8.6	8.4	8.4	5.1	5.3

[0061] Whilst formulations 7B to 9B illustrate slightly diminished performance at a zero bond gap relative to formulations 4 to 6, improved performance is observable at bond gaps of 250 µm and 500 µm.

A6HEX:

Component g (mmol)	**#10B**	**#11B**	**#12B**
Zn(BF4)2.xH20	0.05 (0.2)	0.1 (0.4)	0.1 (0.4)
TBPB	0.05 (0.25)	0.1 (0.5)	0.15 (0.75)
A6HEX	0.07 (0.16)	0.035 (0.08)	0.007 (0.016)
HPMA	10	10	10

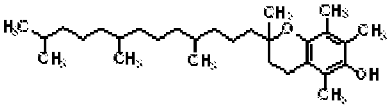
	#10B	**#11B**	**#12B**
Fixture Time on Mild Steel (mins)	2	2	3

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	0		250		500		1000	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#10B	13.1	10.6	6.6	6.5	5.2	4.5	4.4	4.1
#11B	12.4	9.3	7.0	5.8	4.5	4.2	4.3	3.9
#12B	14.7	14.6	8.5	8.3	5.4	7.5	5.5	3.6

[0062] Formulations 10B and 11B exhibit slightly inferior performance to formulations 4 and 5 containing APH. However, formulation 12B shows improved performance relative to formulation 6 at zero bond gaps and larger bond gaps up to 1 mm.

Formulations using α-Tocopherol



[0063] #13

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and α-Tocopherol (0.05, 0.12mmol) were dissolved in hydroxypropylmethacrylate (10g, 69mmol)

Fixture time on mild steel: 2 mins

[0064] #14

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and α-Tocopherol (0.025, 0.06mmol) were dissolved in hydroxypropylmethacrylate (10g, 69mmol)

Fixture time on mild steel: 2 mins

[0065] #15

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and α-Tocopherol (0.005, 0.012mmol) were dissolved in hydroxypropylmethacrylate (10g, 69mmol)

Fixture time on mild steel: 2 mins

Component g (mmol)	**#13**	**#14**	**#15**
Zn(BF4)2.xH20	0.05 (0.2)	0.05 (0.2)	0.05 (0.2)
TBPB	0.05 (0.26)	0.05 (0.26)	0.05 (0.26)
α-Tocopherol	0.05 (0.12)	0.025 (0.06)	0.005 (0.012)
HPMA	10	10	10

	#13	**#14**	**#15**
Fixture Time on Mild Steel (mins)	2	2	3

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (μm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#13	12	14.3	6.7	6.8	7.9	6.3	3.1	3.8
#14	9.5	8.4	6.7	5.1	7.7	4.6	4.4	3.3
#15	10.3	11.8	4.95	6.0	1.6	4.9	1.2	2.8

[0066] Formulation 15 excepting [due to the smaller quantities of α-Tocopherol in the formulation], formulations containing α-Tocopherol exhibited an almost 50% retention of bond strength at bond gaps of up to 500 μm.

[0067] In closed bondline tests, formulation 13 exhibited curing to a depth in excess of 10 mm within a 72hr period. Closed bondline testing comprises mating two mild steel substrates and covering/sealing the exposed bondline edges with sheets of steel, *i.e.* the bondline edges are essentially boxed in.

Alternative Formulations with α-Tocopherol

[0068] For formulations 16, 17, 18, 19, and 20 the following resin combination was used:

Resin Mixture 1

Hydroxypropylmethacrylate	75 %
Proprietary Polyurethane	20 %
Ricacryl 3850	5 %

Ricacryl 3850 is a Sartomer product, and is a tradename for the mono-2-methacryloylethylester of Maleic acid, sometimes referred to as HEMA-maleate. Its CAS number is 51978-15-5.

Proprietary Polyurethane - reaction product of Toluene-2,4-diisocyanatehydroxyethyl methacrylate and a polyether glycol.

[0069] #16

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and α-Tocopherol (0.025g, 0.06mmol) were dissolved in 10g of Resin mixture 1

Fixture time on mild steel: 2mins

[0070] #17

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and α-Tocopherol (0.005g, 0.01mmol) were dissolved in 10g of Resin mixture 1

Fixture time on mild steel: 2.5mins

Component g (mmol)	**#16**	**#17**
Zn(BF4)2.xH20	0.05 (0.2)	0.05 (0.2)
TBPB	0.05 (0.26)	0.05 (0.26)
α-Tocopherol	0.025 (0.06)	0.005 (0.012)
Resin Mixture 1	10	10

	#16	**#17**
Fixture Time on Mild Steel (mins)	2	2.5

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (μm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#16	14.6	23.4	10.5	13.6	8.6	11.2	4.2	6.4
#17	7.7	13.6	4.3	8.9	4.5	7.4	2.3	4.3

[0071] Compositions 16 and 17 comprising Resin mixture 1 exhibited much improved bond strengths at bond gaps of 250 μm, 500 μm and 1000 μm relative to related α-Tocopherol compositions 14 and 15.

[0072] #18 - Using $Zn(SbF_6)_2$ prepared *in situ*
A 10% premix of $Zn(SbF_6)_2$ was prepared *in situ* by speed mixing equimolar amounts of Zinc(II) methacrylate with hydrated hexafluoroantimonic acid in hydroxypropylmethacrylate.

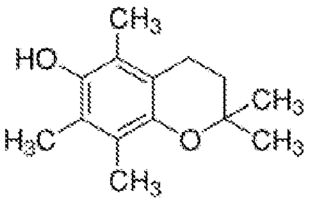
$Zn(SbF_6)_2$, (0.5g of 20% premix, 0.2mmol) Tertbutylperoxybenzoate (0.05g, 0.26mmol) and α-Tocopherol (0.025, 0.06mmol) were dissolved in 10g of Resin Mixture 1.
Fixture time on mild steel: 25 mins

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (μm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#18	14.6	19.3	10.1	14.4	7.2	8.8	3.3	6.4

[0073] Composition 18 comprising a $Zn(SbF_6)_2$ salt generated *in situ* exhibits a comparable performance to composition 16 when bonding across zero bond gaps and bond gaps of up to 1 mm.

[0074] #19, 20 & 21: Formulations using 2,2,5,7,8 Pentamethyl-6-chromanol



Component g (mmol)	**#19**	**#20**	**#21**
Zn(BF4)2.xH20	0.05 (0.2)	0.05 (0.2)	0.05 (0.2)
TBPB	0.05 (0.26)	0.05 (0.26)	0.05 (0.26)
α-2,2,5,7,8-pentamethylchromanol	0.025 (0.12)	0.0125 (0.06)	0.00625 (0.03)
HPMA	10	10	10

	#19	**#20**	**#21**
Fixture Time on Mild Steel (mins)	3	3	3

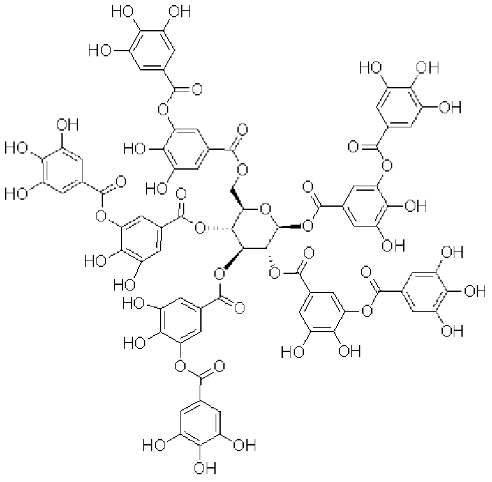
Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	**0**	**250**	**500**
	24h	**24h**	**24h**
#19	12.2	10.6	8.0
#20	14.4	9.3	8.2
#21	11.7	6.1	4.0

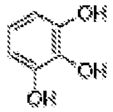
[0075] Compositions 19 and 20 containing 2,2,5,7,8 Pentamethyl-6-chromanol exhibit good bond strengths at bond gaps of 250 µm and 500 µm, with very little loss of bond strength observable for composition 19 and a retention of bond strength of approximately 57% observable for composition 20 at a bond gap of 500 µm.

Examples using Tannic Acid, Pyrogallol and Gallic Acid

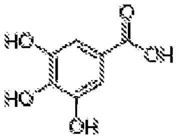
Tannic acid:



Pyrogallol



Gallic Acid



[0076] #22

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and Tannic Acid (0.025g, 0.015mmol) were dissolved in hydroxypropylmethacrylate (10g, 69mmol)

Fixture time on mild steel: 2.0 mins

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (µm)	**0**		**250**		**500**		**1000**	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#22	13	11.6	10.9	8.2	8.6	7.7	5.2	4.9

[0077] Compositions containing tannic acid illustrate good bond strengths at bond gaps of up to 1 mm. For example, a 40% retention of bond strength is observed at a bond gap of 1 mm.

[0078] #23

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and Pyrogallol (0.025g, 0.2mmol) were dissolved in hydroxypropylmethacrylate (10g, 69mmol)

Fixture time on mild steel: 2.5 mins

[0079] #24

Resin mixture is an 80:20 hydroxypropylmethacrylate: triethyleneglycoldimethacrylate mixture.

Fixture time on mild steel: 2.5 mins

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (μm)	0		250		500		1000	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#23	13.3	-	9.1	-	8.0	-	6.9	-
#24	10.6	12	9.0	10.6	9.5	8.4	7.2	4.4

[0080] Compositions containing pyrogallol illustrate good bond strengths at bond gaps of up to 1 mm. For example, bond strengths in excess of 50% of the zero gap bond strength were observed at a bond gap of 1 mm.

[0081] #25

$Zn(BF_4)_2$ (0.05g, 0.2mmol), Tertbutylperoxybenzoate (0.05g, 0.26mmol) and Gallic acid (0.0375g, 0.2mmol) were dissolved in hydroxypropylmethacrylate (10g, 69mmol)
Fixture time on mild steel: 2.5 mins

Performance on mild steel - values indicated are Tensile Strength (N/mm2)

Bond gap (μm)	0		250		500		1000	
	24h	**72h**	**24h**	**72h**	**24h**	**72h**	**24h**	**72h**
#25	8.5		5.2		4.4		6.1	

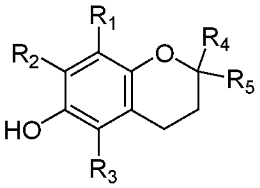
[0082] Similarly, compositions containing Gallic acid illustrate good bond strengths at bond gaps of up to 1 mm. For example, a 71% retention of bond strength relative to the zero gap control was observed at a bond gap of 1 mm.

[0083] The words “comprises/comprising” and the words “having/including” when used herein with reference to the present invention are used to specify the presence of stated features, integers, steps or components but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

[0084] It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

Claims

1. A one-part curable composition for curing on a surface comprising:
    - i) a radically curable component;
    - ii) a free radical generating component;
    - iii) at least one metal salt, wherein the standard reduction potential of the at least one metal salt is greater than the standard reduction potential of the surface; and
    - iv) a reducing additive comprising a moiety selected from the group consisting of:



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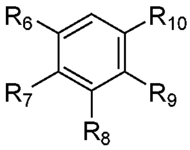

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benzoin or an ester thereof, ascorbic acid or an ester thereof, hydrazines, toluidines, and Tin(II) salts;

wherein R_1, R_2 and R_4 are the same or different and can be C_1 to C_5 alkyl;

R_3 is C_1 to C_5 alkyl or H;

R_5 is C_1 to C_{20} alkyl;

R_6 to R_9 are the same or different and can be OH or H, such that at least two of R_6 to R_9 are always OH;

R_{10} is $C(O)OR_{11}$ or H; and

R_{11} is H or C_1 to C_{20} alkyl.

2. A curable composition according to Claim 1, wherein the at least one metal salt comprises a transition metal cation.

3. A curable composition according to Claim 2, wherein the transition metal cation is selected from copper, iron, zinc and combinations thereof.

4. A curable composition according to Claim 3, wherein the transition metal cation is zinc.

5. A curable composition according to Claims 1 to 4, wherein the metal salt includes a counterion chosen from the group consisting of naphthenate, ethylhexanoate, benzoate, nitrate, chloride, acetylacetonate, ClO_4^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $(C_6F_5)_4B$, $(C_6F_5)_4Ga$, Carborane, triflimide, bis-triflimide, and combinations thereof.

6. A curable composition according to any preceding Claim, wherein the radical generating component is selected from the group consisting of peroxides, hydroperoxides, hydroperoxide precursors, persulfates and combinations thereof.

7. A curable composition according to any preceding Claim, wherein the radical generating component is selected from the group consisting of Cumene Hydroperoxide, *tert*-Butyl hydroperoxide, Hydrogen peroxide, 2-Butanone peroxide, Di-*tert*-Butyl peroxide, Dicumyl peroxide, Lauroyl peroxide, 2,4-Pentanedione peroxide, pentamethyl-trioxepane, Benzoyl Peroxide and combinations thereof.

8. A curable composition according to any preceding Claim, wherein the radically curable component has at least one functional group selected from the group consisting of acrylates, methacrylates, thiolene, siloxanes, vinyls and combinations thereof.

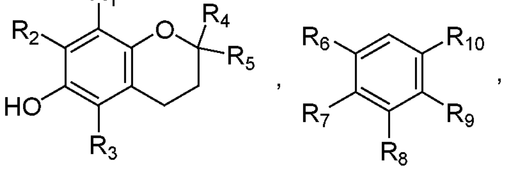
9. A curable composition according to Claim 8, wherein the radically curable component has at least one functional group selected from the group consisting of acrylates, methacrylates, and combinations thereof.

10. A curable composition according to any preceding Claim, wherein the surface comprises a metal, metal oxide or metal alloy.

11. A curable composition according to Claim 10, wherein the surface is selected from the group consisting of iron, steel, aluminium, aluminium oxide, copper, zinc, zinc oxide, and zinc bichromate.

12. A curable composition according to Claim 11, wherein the steel is selected from the group consisting of mild steel, gritblasted mild steel, and stainless steel.

13. A curable composition according to any preceding Claim, wherein the reducing additive is selected from the group consisting of:



benzoin or an ester thereof, ascorbic acid or an ester thereof, and acetylphenylhydrazine;

wherein R_1, R_2 and R_4 are the same or different and can be C_1 to C_5 alkyl;

R_3 is C_1 to C_5 alkyl or H;

R_5 is C_1 to C_{20} alkyl;

R_6 to R_9 are the same or different and can be OH or H, such that at least two of R_6 to R_9 are always OH;

R_{10} is $C(O)OR_{11}$ or H; and

R_{11} is H or C_1 to C_{20} alkyl.

14. A curable composition according to any preceding Claim, wherein the reducing additive is selected from the group consisting of acetyl phenyl hydrazine, benzoin, ascorbic acid 6-palmitate, α-tocopherol, γ-tocopherol, 2,2,5,7,8-pentamethylchromanol, gallic acid, tannic acid, pyrogallol, hydroquinone and combinations thereof.

15. A curable composition according to any preceding Claim, wherein the reducing additive is present in the composition in an amount of 0.05 to 10% by weight of the composition.

16. A curable composition according to Claim 15, wherein the reducing additive is present in the composition in an amount of 0.1 to 0.5% by weight of the composition.

17. A curable composition according to any preceding Claim, wherein the radical generating component is present in the composition in an amount of 0.1 to 10% by weight of the composition.

18. A curable composition according to Claim 17, wherein the radical generating component is present in the composition in an amount of 0.5 to 1.5% by weight of the composition.

19. A curable composition according to any preceding Claim, wherein the metal salt is present in the composition in an amount of 0.1 to 10% by weight of the composition.

20. A curable composition according to Claim 19, wherein the metal salt is present in the composition in an amount of 0.5 to 1.5% by weight of the composition.

21. A curable composition according to any preceding Claim further comprising a metal oxide removal agent.

22. A curable composition according to Claim 21, wherein the metal oxide removal agent is selected from the group consisting of chloride ions, zinc (II) salts and combinations thereof.

23. A curable composition according to any preceding claim further comprising a silica filler material.

24. A method of sealing or bonding comprising:
    a. applying a composition according to Claims 1 to 23 to a first surface;
    b. mating the first surface and a second substrate so as to form a bond or seal with the composition,

    wherein the standard reduction potential of the at least one metal salt of the composition of Claims 1 to 23 is greater than the standard reduction potential of at least one of the first surface and the second substrate.

25. A method according to Claim 24 for sealing or bonding through a bondline gap of greater than about 0.2 mm.

26. A method according to Claim 25 wherein the bondline gap is from about 0.2 mm to about 10 mm.

27. Use of a composition according to Claims 1 to 23 for sealing or bonding through a bondline gap of greater than about 0.2 mm.

28. Use according to Claim 27 wherein the bondline gap is from about 0.2 mm to about 10 mm.

29. A pack comprising:
    a) a closeable container; and
    b) a composition according to Claims 1 to 23 held within the container,

    wherein the container is air permeable.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/063491

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/08 C08K5/00 C08K5/14 C09J4/00 C09J4/06
C09J11/02
ADD.

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)
C08K C09J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/137444 A2 (HENKEL CORP [US]; MESSANA ANDREW [US]; JACOBINE ANTHONY F [US]; NAKOS) 12 November 2009 (2009-11-12) paragraph [0081] paragraph [00102] - paragraph [00103] paragraph [0108] paragraph [00112]	1-29
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/063491

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X	WO 2006/119469 A2 (ILLINOIS TOOL WORKS [US]; WANG XIAOBIN [US]; DOE DANIEL K [US]; SAVORY) 9 November 2006 (2006-11-09) paragraph [0024] paragraph [0032] paragraph [0038] paragraph [0046] paragraph [0049]; example 1; table 2 paragraph [0050] - paragraph [0052]; examples 2-5; tables 3-6 -----	1,6-12, 15-20, 24-29
A	WO 2005/087850 A1 (HENKEL CORP [US]; LOCTITE R & D LTD [IE]; EARLE JAMES J [US]; LAKES AI) 22 September 2005 (2005-09-22) page 6, line 4 - line 11 page 7, line 21 - line 23 page 9, line 9 - page 10, line 18 page 12, line 7 - page 13, line 10 page 16, line 6 - page 17, line 2; examples 1, Part A and B -----	1-29
A	US 6 096 842 A (FRIESE CARSTEN [DE] ET AL) 1 August 2000 (2000-08-01) column 1, line 26 - line 32 column 1, line 46 - line 49 column 6, line 34 - page 7, line 10 claims 1, 12, 15, 16 -----	1-29

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