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(54) **LOW VOC CONSTRUCTION PRIMER**

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(57) **ABSTRACT**

The present disclosure relates to a primer composition. The primer composition comprises: a tert butyl acetate solvent; an organometallic reagent selected from organotitanates, organozirconates, aluminum organometallic compounds, and any combination thereof; an organotin compound; a silane with at least 3 hydrolyzable groups; and a polyorganosiloxane resin. Optionally, the primer composition further comprises a second solvent different from the tert butyl acetate solvent.

**20 Claims, 1 Drawing Sheet**







**LOW VOC CONSTRUCTION PRIMER****CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is the National Stage of International Patent Application No. PCT/US2013/064646, filed on Oct. 11, 2013, which claims priority to and all advantages of U.S. Patent Application No. 61/712,916, filed on Oct. 12, 2012, the content of which is hereby incorporated by reference.

**TECHNICAL FIELD**

The present disclosure relates to primer solutions and, more specifically, to primer solutions that contain low volatile organic content solvents for use in construction applications. The primer solutions can be used to prime painted metal substrates to improve adhesion to and cohesive failure mode of silicone-based sealants.

**BACKGROUND**

Silicone sealants are important products for structural glazing and weather sealing applications for the construction industry. The durability of silicone sealants is due in part to their elastomeric character that allows for warranty coverage of 20 years or more. However, the durable sealant matrix must also maintain adhesion to the various building materials that are used in constructing buildings. In some cases there is a need to prepare or treat the surface with a priming agent in order to provide a reactive surface to which the adhesion promoting components of the sealant can react. Functionalized silanes, organosilicon resins and titanates are commonly employed as priming agents for enhancing adhesion of silicone sealants.

Metal substrates are commonly used in construction, and they are often painted in order to prevent oxidation and to achieve an aesthetically pleasing appearance. Some paints are specifically formulated with fluorinated polymers to provide an inert surface that does not fade in color or attract dirt when used in outside applications, where exposure to UV and particulate can otherwise negatively impact the appearance. These inert surfaces that reduce dirt pick up and oxidation can also make sealant adhesion challenging. Thus, these inert surfaces often require a priming step to enable the durability warranty. Duranar® and Duracron® (both available from PPG Industries, Inc., Cleveland, Ohio) are common brands of paints used on metal substrates for construction.

There are numerous primers that are available for use in construction applications. Typically, these primers consist of reactive silanes, resins and/or other adhesion promoting molecules that are dissolved in solvents to improve the uniform coating of the surface to maximize adhesion development. These solvents release volatile organic compounds (VOCs) into the atmosphere. Because many commonly used solvents are known to contribute to lowering air quality, there are regulatory pressures to reduce their use in almost every country throughout the world. Government Agencies like the United States Environmental Protection Agency (EPA) and states like California have placed limits on the VOC content of primers used in their jurisdictions. Various other government agencies and states have placed similar restrictions on the use of VOCs.

Therefore, there is currently a need for a more ecologically friendly primer to reduce air pollution and meet the VOC restrictions set by government agencies. Additional

requirements for robust, durable adhesion to facilitate offering the desired warranty for building owners also need to be addressed. The embodiments disclosed herein address that need.

5 The present disclosure allows for use of solvents that are considered VOC exempt per certain government agencies, including the United States EPA and the state of California, while also improving adhesion durability.

**BRIEF SUMMARY**

An aspect of the present disclosure is directed to a primer including (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent.

Another aspect of the present disclosure is directed to a primer composition including (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent.

Another aspect of the present disclosure is directed to a method of improving adhesion of silicone-based sealants, the method including priming a substrate with a primer including (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent.

Another aspect of the present disclosure is directed to a method of providing an improved cohesive failure mode of silicone-based sealants within the sealant matrix, the method including priming the substrate with a primer including (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent.

Another aspect of the present disclosure is directed to a method of priming a painted substrate surface, including the steps of: optionally, cleaning the substrate surface to remove contaminants and drying the substrate surface and applying a primer composition as hereinbefore described to the painted substrate surface. The primer composition includes (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent. The method also includes the steps of allowing the primer composition to dry and applying a silicone-based sealant to the painted substrate.

Additional aspects of the invention will be apparent to those of ordinary skill in the art in view of the detailed description of various embodiments, a brief description of which is provided below.

**BRIEF DESCRIPTION OF THE FIGURE**

A more complete appreciation of the present disclosure and the many embodiments thereof will be readily obtained



as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying FIGURE which demonstrates a significant difference between ethyl acetate and tert butyl acetate with regards to paint compatibility. Ethyl acetate disrupts the surface of a polyester powder coat paint, as evidenced by surface blisters and paint run-off, whereas the same surface in contact with tert-butyl acetate is essentially unchanged.

#### DETAILED DESCRIPTION

Features and advantages of the present disclosure will now be described with occasional reference to specific embodiments. However, the invention may be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the disclosure to those skilled in the art.

Unless otherwise indicated or defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. The terminology used herein is for describing particular embodiments only and is not intended to be limiting.

The term "ambient conditions" as used throughout the specification refers to surrounding conditions under about one atmosphere of pressure, at about 50 percent relative humidity, and at about 25° C., unless otherwise specified.

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent by weight, reaction conditions, and so forth as used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless otherwise indicated, the numerical properties set forth in the specification and claims are approximations that may vary depending on the desired properties sought to be obtained in embodiments of the present disclosure. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain errors necessarily resulting from error found in their respective measurements.

All percentages, parts, and ratios are based upon the total weight of the primer composition, unless otherwise specified and the total weight of any primer composition in accordance with the above is 100 weight %.

The present disclosure relates to a primer composition for use in various construction applications. The primer composition may be used to treat painted substrates, such as metal substrates, prior to application of a silicone-based sealant. The primer composition may include (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent. The primer composition may include between about 20 and about 99.5 percent by weight of ingredient (i), or, alternatively, between about 50 and about 95 percent by weight of ingredient (i) or, alternatively, between about 70 and about 95 percent by weight of ingredient (i). The primer composition may include between about 0.05 and about 5 percent by weight of ingredient (ii) or, alternatively, between about 0.5 and about 4 percent by weight of ingredient (ii). The

primer composition may include between about 0.05 and about 10 percent of ingredient (iii) or, alternatively, between about 2 and about 10 percent by weight of ingredient (iii). The primer composition may include between about 0.05 and about 10 percent by weight of ingredient (iv) or, alternatively, between about 0.5 and about 4 percent by weight of ingredient (iv). The primer composition may include between about 0.1 and about 5 percent by weight of ingredient (v) or, alternatively, between about 0.5 and about 4 percent by weight of ingredient (v). The primer composition may include between about 0 and about 80 percent by weight of ingredient (vi). Typically however, when ingredient (vi) is present, it is present in a ratio of ingredient (i):ingredient (vi) of from 70:30 to 95:5. The total weight of any primer composition herein is 100 weight %

The primer composition according to the present disclosure may be a transparent liquid. The primer composition may be stable at both very low and very high temperatures. The primer composition according to the present disclosure may be configured to have VOC content of below about 250 g/l. Alternatively, the primer composition according to the present disclosure may be configured to have VOC content of below about 100 g/l.

The present disclosure also relates to a method of improving adhesion of silicone-based sealants, the method including priming a substrate with a primer including (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent. Application of the primer according to the present disclosure results in greater adhesion than application of primers generally available in the art that do not include adhesion enhancers.

Applying a primer according to the present disclosure to a substrate improves cohesive failure mode of silicone-based sealants within the sealant matrix. The cohesive failure mode may be increased to above about 70% by applying a primer according to the present disclosure to a substrate.

Another aspect of the present disclosure is directed to a method of priming a painted substrate surface, including the steps of: optionally, cleaning the substrate surface to remove contaminants and drying the substrate surface and applying a primer composition to the painted substrate surface. The primer composition includes (i) a tert butyl acetate solvent; (ii) an organometallic reagent selected from organotitanate, organozirconate, organo aluminum, and any combination thereof; (iii) an organotin compound; (iv) a silane with at least three hydrolyzable groups; (v) a polyorganosiloxane resin and (vi) optionally, a second solvent. The method also includes the steps of allowing the primer composition to dry and applying a silicone-based sealant to the painted substrate.

There is a wide variety of painted substrates to which the primer composition according to the present disclosure may be applied. The primer may be applied to painted metal substrates. The metals may include aluminum, aluminum alloys, cast iron, steel alloys, stainless steel, copper, zinc, magnesium, galvanized steel, and many others.

There is a wide variety of types of paints that may be applied to such substrates to produce a painted substrate. Specific examples of paint include latex paint, rubber base paint, textured paint, alkyd resin paint, acrylic, polyvinylidene fluoride (PVF2), polyester powder and others.

The surface of the painted substrates should typically be cleaned and allowed to dry before applying the primer. The



surface may be cleaned using a variety of different methods. One method may include first brushing away any loose material on the surface of the substrate and then wiping with an appropriate solvent on a coarse-free cloth. The surface should be wiped dry immediately after cleaning.

Then, the primer according to the present disclosure should be applied to the substrate. The primer may be applied in a variety of different ways. One method includes applying the primer with a lint-free cloth to maximize primer coverage rate and to obtain a consistent film thickness. It is also possible to use a brush or any other acceptable tool known to those of ordinary skill in the art to apply the primer according to the present disclosure. Following application, the primer should be allowed to dry. Typically, the primer can dry in about 5 to about 60 minutes or less at ambient conditions. However, the drying time may be varied depending on the amount of tert butyl acetate and the optional second solvent or mixture of solvents added. An appropriate second solvent may be selected to adjust the drying time depending on the desired application, as will be discussed in further detail below.

The primer according to the present invention causes minimal or negligible run-off of the paint as can be seen in the FIG. Thus, the application of the primer according to the present disclosure to a painted substrate allows the paint to remain intact and does not cause surface marring or run-off of the paint.

#### Organometallic Reagent (Ingredient (ii))

Organometallic reagents that may be used in the primer composition according to the present disclosure include organotitanate, organozirconate, aluminum organometallic compounds, and any combination thereof. Organotitanate may include, but is not limited to, tetrabutyl titanate, tetrapropoxy titanate, tetraethoxy titanate, tetraamyl titanate, titanium di-isopropoxy bis ethylacetoacetate, di-isopropoxy bis acetylacetonate, and any combination thereof. Organozirconate may include, but is not limited to, zirconium acetylacetonate. Aluminum organometallic compounds may include, but is not limited to, aluminum acetylacetonate.

#### Organotin Compound (Ingredient (iii))

The organotin compound used in the primer according to the present disclosure may include, but is not limited to, alkyltin ester compounds such as Dibutyltin dioctoate, Dibutyltin dimaleate, butyltin 2-ethylhexoate dimethyl tin dineodecyl ester, or dibutyltin dilaurate, dibutyl tin laurate, dibutyl tin acetate and dibutyl tin 2-ethyl hexanoate, and any combination thereof.

#### Silane (Ingredient (iv))

Silanes used in the primer composition according to the present disclosure include silanes with at least three hydrolyzable groups per molecule which are reactive when the silane has three silicon-bonded hydrolysable groups per molecule; the fourth group is suitably a non-hydrolysable silicon-bonded organic group. These silicon-bonded organic groups are suitably hydrocarbyl groups which are optionally substituted by halogen such as fluorine and chlorine. Examples of such fourth groups include alkyl groups (for example methyl, ethyl, propyl, and butyl); cycloalkyl groups (for example cyclopentyl and cyclohexyl); alkenyl groups (for example vinyl and allyl); aryl groups (for example phenyl, and tolyl); aralkyl groups (for example 2-phenylethyl) and groups obtained by replacing all or part of the hydrogen in the preceding organic groups with halogen. Preferably however, the fourth silicon-bonded organic group is methyl.

Specific examples of silanes used in the primer composition according to the present disclosure include but are not

limited to, alkyltrialkoxysilanes such as methyltrimethoxysilane (MTM) ethyltrimethoxysilane and methyltriethoxysilane, alkenyltrialkoxysilanes such as vinyltrimethoxysilane and vinyltriethoxysilane, isobutyltrimethoxysilane (iBTM). Other suitable silanes include, phenyltrimethoxysilane, alkoxytrioximosilane, alkenyltrioximosilane, 3,3,3-trifluoropropyltrimethoxysilane, methyltris(methylethylketoximo)silane, vinyl-tris-methylethylketoximo)silane, methyltris(methylethylketoximino)silane, methyltris(isopropenoxy)silane, vinyltris(isopropenoxy)silane, (ethylenediaminepropyl)trimethoxysilane, vinyl trimethoxysilane, tetraalkylorthosilicate having the general formula  $\text{SiOR}_4$ , tetraethoxysilane, mercapto functional-silanes, glycidylpropyl trimethoxysilane, and any combination thereof.

#### Polyoroanosiloxane Resin (Ingredient (v))

Polyorganosiloxane resins used in the primer composition according to the present disclosure generally may be depicted using the following general formula of the following groups  $(\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2})_a(\text{R}^4\text{R}^5\text{SiO}_{2/2})_b(\text{R}^6\text{SiO}_{3/2})_c(\text{SiO}_{4/2})_d$ . (often referred to as M, D, T, or Q units respectively) with,  $0 < a < 1$ ,  $b \geq 0$ ,  $c \geq 0$ ,  $0 < d < 1$ ,  $a + b + c + d = 1$ , and  $0.2 < a/d < 3.5$ , (when a, b, c and d are mole fractions) with the resin having a weight-average molecular weight between about 1,000 and about 100,000, on a standard polystyrene basis by gel permeation chromatography.

Each  $\text{R}^1$ - $\text{R}^6$  is independently selected from a monovalent hydrocarbon groups, a carbinol group, an alkoxy group (preferably methoxy or ethoxy) or an amino group. Suitable exemplary monovalent hydrocarbon groups include, but are not limited to, alkyl groups such as methyl, ethyl, propyl, pentyl, octyl, undecyl, and octadecyl; alkenyl groups, cycloalkyl groups such as cyclopentyl and cyclohexyl; and aryl groups such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl, and any combination thereof. In one embodiment, the organopolysiloxane is free of halogen atoms. In another embodiment, the organopolysiloxane includes one or more halogen atoms. Halogenated hydrocarbon groups include, but are not limited to, 3,3,3-trifluoropropyl, 3-chloropropyl, dichlorophenyl, and 6,6,6,5,5,4,4,3,3-nonafluorohexyl groups; and combinations thereof. The cyano-functional groups may include cyanoalkyl groups such as cyanoethyl and cyanopropyl groups, and combinations thereof.

Suitable alkenyl groups contain from 2 carbon atoms to about 6 carbon atoms and may be exemplified by, but not limited to, vinyl, allyl, and hexenyl. The alkenyl groups in this component may be located at terminal, pendant (non-terminal), or both terminal and pendant positions.  $\text{R}^1$ - $\text{R}^6$  do not include acrylate functional groups. One particularly preferred resin for the present invention is an MQ resin which comprises substantially only M units ( $\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2}$ ) and Q units ( $\text{SiO}_{4/2}$ ). But may contain minor amounts of D units ( $\text{R}^4\text{R}^5\text{SiO}_{2/2}$ ) and/or T units ( $\text{R}^6\text{SiO}_{3/2}$ ) The polyorganosiloxane resin may have a weight-average molecular weight between about 1,000 and about 100,000, on a standard polystyrene basis by gel permeation chromatography. The polyorganosiloxane resin may have less than about 0.7% of hydroxyl groups bonded to silicon atoms

#### Solvents (Ingredient (vi))

A variety of solvents may be used in the primer according to the present disclosure. Solvents that have gained VOC exempt status may be used. Solvents that may be used include, but are not limited to, methyl acetate, ethyl acetate, n-butyl acetate, methyl formate, ethyl formate, and any combination thereof. Typically however, when ingredient (vi) is present, it is present in a ratio of ingredient (i):



ingredient (vi) of from 70:30 to 95:5. In order to achieve faster drying times, a larger proportion of optional second solvent (vi) is used.

The optional second solvents used in the present disclosure may be fully miscible with the other ingredients used in the primer composition—namely, the organometallic reagent, the organotin compound, the silane, and the polyorganosiloxane resin.

#### Silicone-Based Sealant

A variety of different silicone-based sealants may be applied to the painted substrate after priming with the primer according to the present disclosure.

Typically the silicone based sealant will comprise a one or two part composition containing the following ingredients

- (A) A polymer selected from an organopolysiloxane polymer containing at least 2 hydrolysable groups per molecule and a telechelic polymer having silicon containing end groups containing at least 2 hydrolysable groups per molecule
- (B) A siloxane and/or silane cross-linker having at least three groups per molecule which are reactable with the hydrolysable groups in (A);
- (C) one or more reinforcing fillers and
- (D) a condensation catalyst

Other ingredients which may be included in the compositions include but are not restricted to non-reinforcing fillers, co-catalysts for accelerating the cure of the composition such as metal salts of carboxylic acids and amines; extenders and/or plasticisers, rheological modifiers; adhesion promoters, pigments, UV stabilizers, Chain extenders, Fungicides and/or biocides and the like (which may suitably be present in an amount of from 0 to 0.3% by weight), water scavengers, (typically the same compounds as those used as cross-linkers or silazanes). It will be appreciated that some of the additives are included in more than one list of additives. Such additives would then have the ability to function in all the different ways referred to.

Examples of each component of a silicone based sealant described above are detailed in US20080284106 which is hereby incorporated by reference.

#### EXAMPLES

These examples are intended to illustrate the invention to one of ordinary skill in the art and should not be interpreted as limiting the scope of the invention set forth in the claims.

All measurements and experiments were conducted at 25° C., unless indicated otherwise.

Features and advantages of the present disclosure will now be described with occasional reference to specific embodiments. However, the disclosure may be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the disclosure to those skilled in the art.

#### Examples 1-5

Table 1a below shows the compositions for Examples 1-5. Example 1 was included preparation of a primer composition with n-Hexane and Isopropyl Alcohol (IPA), which represents a solvent mixture commonly used in the prior art primer formulations. The resulting primer was applied on a painted aluminum substrate. The quality of the adhesion of the sealant to the painted aluminium surface pre-treated with the primer as hereinbefore described was then evaluated by in accordance with Standard tensile adhesion property test method JIS A 1439. Primers were aged for 30 minutes at 23° C., 50% relative humidity. Type H test specimens (12 mm×12 mm×50 mm) were aged for 7 days at 23° C., 50% relative humidity plus at 50° C. for 7 days for initial data.

Examples 2 and 3 were formulated with tert butyl acetate solvent. The resulting formulation was applied on a painted aluminum substrate. Adhesion spectrum was then evaluated as discussed above.

Example 4 was formulated with ethyl acetate solvent. The resulting formulation was applied on a painted aluminum substrate. Adhesion spectrum was then evaluated as discussed above.

Example 5 was formulated with n-butyl acetate. The resulting formulation was applied on a painted aluminum substrate. Adhesion spectrum was then evaluated as discussed above.

In the adhesion assessment, the results for which are in Table 1 b, the Type H test specimens was tested with a tensiometer and the mode of failure was rated as follows:  
 AF: adhesive failure—poor adhesion  
 BF: boundary or mixed mode (adhesive/cohesive) failure—acceptable adhesion  
 CF: cohesive failure—excellent adhesion

TABLE 1a

		Examples 1-5 In which				
		Examples				
Formulation		1 n-Hexane/ IPA	2 Tert-butyl acetate 1	3 Tert-butyl acetate 2	4 Ethyl acetate	5 n-butyl acetate
N-HEXANE	Solvent, Specific gravity (Sg) = 0.655 g/ml, boiling point (b.p.) = 69° C.	86				
Isopropyl Alcohol	Solvent, Sg = 0.781 g/ml, b.p. = 82.4° C.	2.5				
Tert-butyl acetate	Solvent, Sg = 0.866 g/ml, b.p. = 98° C.		88.5	90.8		
Ethyl acetate	Solvent, Sg = 0.897 g/ml, b.p. = 77.1° C.				91.1	
n-butyl acetate	Solvent, Sg = 0.880 g/ml, b.p. = 126° C.					90.81
MQ Polyorganosiloxane Resin Consisting		2.0	2.0	1.6	1.5	1.6

TABLE 1a-continued

Formulation	Examples 1-5				
	In which				
	Examples				
	1	2	3	4	5
	n-Hexane/ IPA	Tert-butyl acetate 1	Tert-butyl acetate 2	Ethyl acetate	n-butyl acetate
Essentially of (CH <sub>3</sub> ) <sub>3</sub> SiO <sub>1/2</sub> (M) Units and SiO <sub>4/2</sub> (Q) Units in a Molar Ratio of M Units to Q Units of 0.8:1 but with an Average of 2.1 Mass % Hydroxyl Groups					
Tetrabutyl Titanate	2.0	2.0	1.6	1.5	1.6
Phenyltrimethoxysilane	2.0	2.0	1.6	1.5	1.6
(Ethylenediaminepropyl) trimethoxysilane	3.0	3.0	2.4	2.3	2.4
Dimethyl Tin	2.5	2.5	2.0	1.9	2.0
Di-Neodecyl Ester					
Coating weight (g/m <sup>2</sup> )-70° C. @ 60 min	0.26	0.54	0.26	0.26	0.26

Note:

The values of specific gravity (Sg) and boiling point (b.p.) in Table 1a were obtained from standard reference materials and not measured.

TABLE 1b

Substrate		Examples 1-5				
		Adhesion to coated aluminums				
		Ex 1	Ex 2	Ex 3	Ex 4	Ex 5
Acryl Electrocoated Aluminum	Sankyo Tateyama	CF 100	CF 100	CF 100	AF 100	CF 100
	LIXIL	CF 100	CF 100	CF 100	CF 100	CF 100
PVFD(polyvinylidene fluoride) Coated Solid		AF 100	CF 100	CF 100	CF 50	CF 100
Duffner#100S(KYNAR)/DAI NIPPON					AF 50	
TORYO	Metallic color	AF 100	CF 90, AF 10	CF 100	CF 100	CF 100
FEVE Coated (1 part type)	Solid	CF 100	CF 100	CF 100	AF 100	CF 100
V-FLON #2000(LUMIFLON)/DAI	Metallic	AF 100	CF 100	CF 70, AF 30	AF 100	AF 100
NIPPON TORYO	color					
FEVE Coated (2 part type)	Solid	CF 100	CF 100	CF 100	CF 100	CF 100
V-FLON #200(LUMIFLON)/DAI	Metallic	CF 100	CF 100	CF 100	CF 100	CF 100
NIPPON TORYO	color					
Thermosetting acryl resin paint	Solid	CF 100	CF 100	CF 100	CF 100	CF 100
DURACRON CW/DAI NIPPON	Metallic	AF 100	CF 90, AF 10	CF 100	CF 100	CF 100
TORYO	color					
Acryl urethane resin type coating	Solid	CF 100	CF 100	CF 100	CF 100	CF 100
V-CROMA100CW/DAI NIPPON	Metallic	CF 100	CF 100	CF 100	AF 100	CF 50, AF 50
TORYO	color					
Polyester TGIC powder coating	Solid	CF 70, AF 30	CF 100	CF 100	CF 100	CF 100
Corro-Coat PE-F Series 1303/JOTUN	Metallic	CF 100	CF 100	CF 100	CF 100	CF 100
	color					
Super weather resistant polyester powder coating (TGIC-free)	Solid	CF 70 AF 30	CF 100	CF 100	CF 100	CF 100
Drylac Series 68/Tiger Drylac	Metallic	CF 100	CF 100	CF 100	CF 100	CF 90, AF 10
	color					

The primed painted aluminum surface was coated with a silicone sealant comprising:-Dimethyl hydroxyl terminated dimethyl siloxane polymer having a viscosity of 80,000 mPa·s at 25° C., calcium carbonate filler treated with C8-C18 mixture of unsaturated fatty acids, trimethylsiloxy terminated dimethyl siloxane plasticiser having a viscosity of 100 mPa·s at 25° C., a mixture of alkyl trimethoxysilane and aryl trimethoxysilane crosslinkers and Dimethyltindineodecyl ester catalyst. Viscosity measurements were car-

ried out using a Brookfield® HB DV-II+PRO with a cone plate spindle at a speed of 5 rpm.

In Table 2 below, five different metal substrates were wiped with five different solvents, to compare the amount and extent of damage to the painted surface. Each wipe was performed for 10 seconds at ambient conditions. Each solvent was then scored on a scale of “+++” to “---”, wherein “+++” is used to represent no damage or otherwise negative effect to the painted surface and “---” is used to



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represent the situation where the solvent completely removes the paint down to the metal.

TABLE 2

Chemical Name	Substrate Type				
	White Polyester Powder Coat Aluminum	Tnemec 1C Hi-Build Epoxoline Black	Aluminum w/PPG Dark Briar Sunstorm UC106694F	Aluminum w/PPG Bristol Beige Duranar LT149975XL	Aluminum w/Tiger Drylac Yellow Green Powder 544/50005
Ethyl Acetate	---	++	--	++	-
Methyl Acetate	---	++	--	+	-
Ted Butyl Acetate	+++	+++	+++	+++	+++
Methyl Formate	---	++	-	++	+
Acetone	--	+	--	0	+++

As seen from Table 2 above, tert butyl acetate had the best results when applied to all five types of paint, with no or minimal damage to the paint. All the other solvents did not demonstrate consistent results. Moreover, all the other solvents caused significant damage to white polyester paint, with three of the solvents—ethyl acetate, methyl acetate, and methyl formate—completely removing the paint. Further, all the other solvents also significantly damaged Aluminum w/PPG Dark Briar Sunstorm UC106694 paint.

While the present disclosure is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the examples and described in detail herein. It should be understood, however, that the present disclosure is not intended to be limited to the particular forms disclosed. Rather, the present disclosure is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the present disclosure as defined by the appended claims.

What is claimed is:

1. A primer composition for application to a substrate, the primer composition comprising:

- (i) a tert butyl acetate solvent;
- (ii) an organometallic reagent selected from organotitanates, organozirconates, aluminum organometallic compounds, and any combination thereof;
- (iii) an organotin compound;
- (iv) a silane with at least three hydrolyzable alkoxy groups; and
- (v) a polyorganosiloxane resin; and
- (vi) optionally, a second solvent;

wherein adhesion of a material applied to the substrate is improved via priming of the substrate with the primer composition; and

wherein ingredient (v) is an MQ resin having hydroxyl groups and comprised substantially of M units ( $R^1R^2R^3SiO_{1/2}$ ) and Q units ( $SiO_{4/2}$ ), with each  $R^1-R^3$  independently selected from monovalent hydrocarbon groups.

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2. The primer composition of claim 1, including: between about 20 percent by weight and about 99.5 percent by weight of ingredient (i); and between about 0 percent by weight and about 80 percent by weight of ingredient (vi).

3. The primer composition of claim 1, including: between about 0.05 percent by weight and about 5 percent by weight of ingredient (ii); and/or between about 0.05 percent by weight and about 10 percent by weight of ingredient (iii); and/or between about 0.05 percent by weight and about 10 percent by weight of ingredient (iv); and/or between about 0.1 percent by weight and about 5 percent by weight of ingredient (v).

4. The primer composition of claim 1, wherein ingredient (vi) is present and selected from VOC exempt solvents or any combination thereof.

5. The primer composition of claim 1, wherein ingredient (ii) is selected from tetrabutyl titanate, tetrapropoxy titanate, zirconium acetylacetonate, tetraethoxy titanate, tetraamyl titanate, titanium di-isopropoxy bis ethylacetoacetate, di-isopropoxy bis acetylacetonate, aluminum acetylacetonate, and any combination thereof.

6. The primer composition of claim 1, wherein ingredient (iii) is selected from dimethyl tin di-neodecyl ester, dibutyltin dilaurate, dibutyl tin laurate, dibutyl tin acetate, dibutyl tin 2-ethyl hexanoate, and any combination thereof.

7. The primer composition of claim 1, wherein ingredient (iv) includes a phenyltrimethoxysilane and an (ethylenediaminepropyl)trimethoxysilane.

8. The primer composition of claim 1, wherein ingredient (iv) is selected from phenyltrimethoxysilane, (ethylenediaminepropyl)trimethoxysilane, vinyl trimethoxysilane, tetraalkylorthosilicate having the general formula  $SiOR_4$ , tetraethoxysilane, mercapto functional-silanes, glycidylxypropyl trimethoxysilane, and any combination thereof.

9. The primer composition of claim 1, wherein  $R^1-R^3$  do not include acrylate functional groups.

10. The primer composition of claim 1, wherein ingredient (v) has a molar ration of M units to Q units of 8:1 and/or an average of 2.1 mass % hydroxyl groups.

11. The primer composition of claim 1, being configured to have a VOC content of below about 250 g/l, optionally below about 100 g/l.

12. The primer composition of claim 1, wherein application of the primer to a painted substrate is configured to allow the paint to remain intact and does not cause surface marring or run-off of the paint.

13. The primer composition of claim 1, wherein ingredients (i) and (vi) are fully miscible with ingredients (ii), (iii), (iv), and (v), either alone or in combination.

14. A method for improving adhesion of silicone-based sealants to painted substrates, comprising priming a painted substrate with the primer composition as defined in claim 1.

15. A method of providing an improved cohesive failure mode of silicone-based sealants within the sealant matrix, comprising priming a substrate with the primer composition as defined in claim 1.

16. The method of providing an improved cohesive failure mode of silicone-based sealants within the sealant matrix as set forth in claim 15, wherein cohesive failure mode of silicone-based sealants within the sealant matrix is increased to above about 70%.



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17. A method of priming a painted substrate surface, comprising the steps of:

optionally, cleaning the painted substrate surface to remove contaminants and drying the painted substrate surface;

applying a primer composition to the painted substrate surface, the primer composition comprising:

- (i) a tert butyl acetate solvent;
- (ii) an organometallic reagent selected from organotitanates, organozirconates, aluminum organometallic compounds, and any combination thereof;
- (iii) an organotin compound;
- (iv) a silane with at least three hydrolyzable alkoxy groups; and
- (v) a polyorganosiloxane resin; and
- (vi) optionally, a second solvent selected from VOC exempt solvents or any combination thereof;

allowing the primer composition to dry; and

applying a silicone-based sealant to the painted substrate; wherein adhesion of the silicone-based sealant to the painted substrate is improved via application of the primer composition to the painted substrate; and

wherein ingredient (v) is an MQ resin having hydroxyl groups and comprised substantially of M units ( $R^1R^2R^3SiO_{1/2}$ ) and Q units ( $SiO_{4/2}$ ), with each  $R^1$ - $R^3$  independently selected from monovalent hydrocarbon groups.

18. A primer composition for application to a substrate, the primer composition comprising:

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(i) a tert butyl acetate solvent;

(ii) an organometallic reagent selected from organotitanate, organozirconate, aluminum organometallic compounds, and any combination thereof;

(iii) an organotin compound;

(iv) an alkoxy-functional silane; and

(v) a polyorganosiloxane resin; and

(vi) optionally, a second solvent selected from VOC exempt solvents or any combination thereof;

optionally, wherein ingredient (iv) has at least one amine group;

wherein ingredient (v) is an MQ resin having hydroxyl groups and comprised substantially of M units ( $R^1R^2R^3SiO_{1/2}$ ) and Q units ( $SiO_{4/2}$ ), with each  $R^1$ - $R^3$  independently selected from monovalent hydrocarbon groups, the MQ resin having weight-average molecular weight between about 1,000 and about 100,000 on a standard polystyrene basis by gel permeation chromatography; and

wherein adhesion of a material applied to the substrate is improved via priming of the substrate with the primer composition.

19. The primer composition of claim 18, wherein ingredient (v) has a Molar Ratio of M Units to Q units of 8:1 and/or an average of 2.1 mass % hydroxyl groups.

20. The primer composition of claim 18, wherein ingredient (iv) includes a phenyltrimethoxysilane and an (ethyl-enediaminepropyl)trimethoxysilane.

\* \* \* \* \*