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(54) Title: AQUEOUS COATING COMPOSITION

(57) Abstract: An aqueous coating composition having a pH of 6.0-10.0 and having a VOC of less than 0.24 kg/l (2.0 pounds/gallon) comprises 30% to 70% by weight of film-forming binder and correspondingly 70% to 30% by weight of an aqueous liquid carrier for the binder; wherein the binder comprises (a) 20% to 95% by weight, based on the weight of the binder, of a carbamate reaction product formed by the reaction of (1) an aliphatic polyisocyanate, (2) a monohydric alcohol, (3) a hydroxy functional aliphatic carboxylic acid and (4) a polyalkylene ether glycol having a number average molecular weight of 100 to 2,000; said reaction product being further reacted with an amine to provide a water-dispersible product; (b) 5% to 80% by weight, based on the weight of the binder, of a water-compatible alkylated melamine formaldehyde crosslinking agent.



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## TITLE

### AQUEOUS COATING COMPOSITION

#### 5                    BACKGROUND OF THE INVENTION

##### 1. Field of the Invention

This invention is directed to coating compositions, in particular, to aqueous coating compositions having a low VOC (volatile organic content), good gloss and distinctness of image, and excellent hardness  
10                    and mar resistance.

##### 2. Description of the Prior Art

The finishing system of choice presently being used on the exterior of automobiles and trucks comprises a clear coating applied over pigmented base coating that is applied over a primer coating. The clear  
15                    coating provides protection to the pigmented base coating and improves the appearance of the overall finish, such as, gloss and distinctness of image. Many conventional coatings have a higher VOC content than desired and many clear coats have marginal acid etch resistance and mar resistance. Acid etching occurs when the clear coating is exposed to acid  
20                    rain and other air pollutants. Also, clear coatings and pigmented base coatings tend to yellow over time with exposure to UV light.

To reduce VOC in coatings, powder slurry coating compositions have been developed as shown in EP 0 990 685 A1. However, while the resulting coating composition has low VOC, the  
25                    composition is formed from polymeric components that contain organic solvents that must be removed or "stripped off", which requires the use of additional energy that increases the cost of the process for forming the coating composition, and then those organic solvents must be disposed of in some manner.

30                    Wilmes et al., US Patent 5,981,653 shows a process for the production of aqueous dispersions in which polyols and blocked polyisocyanates are emulsified through the use of solvents and a mechanical emulsification procedure. Any solvents are later removed from the dispersion.

35                    A technical paper "Cure of Secondary Carbamate Groups by MF Resins – Water Born Systems", Higginbottom et al., presented at ACS Meeting, Boston, MA (Aug. 25, 1998) shows the reaction of MF (melamine

formaldehyde) resins with urethane groups (i.e. secondary carbamate groups) and aqueous dispersions of such compositions. However, these aqueous dispersions do not have the long-term stability required for automotive coating compositions.

5 It would be desirable to form a stable low-VOC coating composition without the use of solvents or minimal use of solvents that can be used as an automotive coating, for example, as a primer coating, a clear top coating, a pigmented base coating or a pigmented mono coating.

## 10 SUMMARY OF THE INVENTION

An aqueous coating composition having a pH of 6.0-10.0 and having a VOC of less than 0.24 kg/l (2.0 pounds/gallon) comprises 30% to 70% by weight of film-forming binder and correspondingly 70% to 30% by weight of an aqueous liquid carrier for the binder; wherein the binder comprises

a. 20% to 95% by weight, based on the weight of the binder, of a carbamate reaction product formed by the reaction of (1) an aliphatic polyisocyanate, (2) a monohydric alcohol, (3) a hydroxy functional aliphatic carboxylic acid and (4) a polyalkylene ether glycol having a number average molecular weight of 100 to 2,000; said reaction product being further reacted with an amine to provide a water-dispersible product;

b. 5% to 80% by weight, based on the weight of the binder, of a water-compatible alkylated melamine formaldehyde crosslinking agent.

25 DETAILED DESCRIPTION OF THE INVENTION

A typical auto or truck body is produced from a steel sheet or a plastic or a composite substrate. If steel is used, it is first treated with an inorganic rust-proofing compound, such as, zinc or iron phosphate and then a primer coating is applied generally by electrodeposition. Typically, these electrodeposition primers are epoxy-modified resins crosslinked with a polyisocyanate and are applied by a cathodic electrodeposition process. Optionally, a primer can be applied over the electrodeposited primer, usually by spraying, to provide better appearance and/or improved adhesion of a base coating or a mono coating to the primer. A mono coating of a pigmented coating composition then can be applied but preferably, a pigmented base coating with a clear top coating then is applied to form a finish on the truck or automobile body or auto or truck

part. Usually, after application, each of the coatings is cured by baking at elevated temperatures. It is generally known that a clear top coating can be applied over the base coating and both coatings cured together at an elevated temperature.

5           A "clear coating composition" for automotive use is a composition that forms a transparent coating upon curing and has a DOI (distinctness of image) of more than 80 and a 20° gloss of more than 80.

          A particular advantage of the novel coating composition of this invention is that it has a low VOC, i.e., a VOC less than 0.24 kg/l (2 pound  
10 per gallon) and meets current governmental air pollution regulations. The novel coating composition can readily be formulated to have a VOC of less than 0.12kg/l (1 pound per gallon). The low VOC of the composition is accomplished by forming the carbamate reaction product of the  
15 composition without the use of solvents and by using a water-soluble or water-dispersible melamine crosslinking agent. Prior art compositions achieve low VOC by stripping or removing solvent from the composition and the solvent is recovered or is disposed of in some manner. Since the novel composition can be formed without solvents being present, no removal or disposal of organic solvents is required. Under some  
20 circumstances only a small amount of solvent is used and such small amount of solvent need not be removed since the resulting composition will have a VOC within the above range.

          The VOC of the coating composition is determined in accordance with the procedure of EPA Method 24.

25           The novel composition has typically has a solids content of film forming binder of 30 to 70% by weight. Since the aqueous liquid carrier does not contribute to the VOC of the composition, sufficient amounts of the liquid may be added, for example, to reduce the composition to a spray viscosity or may be a portion of an additive solution, such as, a  
30 rheology control additive, without increasing the VOC of the composition.

          The novel coating composition has a pH of 6.0 to 10.0 and preferably, 7.5 to 8.5. The pH may be adjusted by the addition of various amines, such as those discussed hereinafter. One particularly preferred amine is AMP (2-amino-2-methyl-1-propanol).

35           The carbamate reaction product of the novel composition is formed by reacting an aliphatic polyisocyanate, a monohydric alcohol, a hydroxy functional aliphatic carboxylic acid and a polyalkylene ether glycol until all of the isocyanate groups have been reacted and then further

reacting the resulting product with an amine to form a water-dispersible composition. A water-compatible (water-soluble or water-dispersible) melamine crosslinking agent that acts as a reactive diluent is added along with a sufficient amount of an aqueous carrier liquid to provide a  
5 composition that can be applied by conventional techniques, such as, spraying or electrostatic spraying. Additional amine may be added to bring the pH of the composition within the desired range. Additional melamine that is the same as or compatible with the above melamine may be added to the novel composition to enhance crosslinking on curing after  
10 application of the composition.

One process used to form the carbamate reaction product is to react an aliphatic polyisocyanate in the presence of a catalyst, such as, dibutyl tin dilaurate with a monohydric alcohol at a temperature of 50 to 120 °C for about 2-90 minutes. Then a hydroxy functional acid, such as,  
15 hydroxy acetic acid is added while maintaining the reaction temperature within the above range and then the polyalkylene ether glycol is added and the reaction is continued until there is no isocyanate present in the reaction mixture that occurs in about 2-4 hours. An amine is then added. The melamine crosslinking agent usually is added before the water and  
20 the reaction mixture is stirred for 0.5 to 3.0 hours at ambient temperature. Water is then added to form an aqueous carbamate composition.

The melamine crosslinking agent does not react with the carbamate that has been formed but is a dispersion aid and can be considered a reactive diluent. The melamine crosslinking agent reacts  
25 after the coating composition has been applied during baking at an elevated temperature of the coating. Instead of a melamine crosslinking agent, it may be desirable add a water-soluble or water-dispersible polyester polyol or an acrylic polyol to the carbamate reaction product in amounts up to 40% by weight, based on the weight of the composition.

30 Examples of suitable aliphatic polyisocyanates that can be used to form the carbamate include aliphatic or cycloaliphatic di-, tri- or tetra-isocyanates, such as, 1,2-propylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate,  
35 dodecamethylene diisocyanate, omega-dipropyl ether diisocyanate, 1,3-cyclopentane diisocyanate, 1,2 cyclohexane diisocyanate, 1,4 cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanatocyclohexane, trans-vinylidene diisocyanate,

dicyclohexylmethane-4,4'-diisocyanate, 3,3'-dimethyl-dicyclohexylmethane 4,4'-diisocyanate, polyisocyanates having isocyanurate structural units, such as, the isocyanurate of hexamethylene diisocyanate and the isocyanurate of isophorone diisocyanate, the adduct of 2 molecules of a diisocyanate, such as, hexamethylene diisocyanate, uretidiones of hexamethylene diisocyanate, uretidiones of isophorone diisocyanate and a diol, such as, ethylene glycol, the adduct of 3 molecules of hexamethylene diisocyanate and 1 molecule of water, allophanates, trimers and biurets of hexamethylene diisocyanate, allophanates, trimers and biurets of isophorone diisocyanate. One preferred polyisocyanate is the trimer of hexamethylene diisocyanate sold under the trademark Desmodur® 3300 by Bayer Corporation, Pittsburgh, Pennsylvania.

Isocyanate functional adducts can be used, such as, an adduct of an aliphatic polyisocyanate and a polyol. Any of the aforementioned polyisocyanates can be used with a polyol to form an adduct. Polyols, such as, trimethylol alkanes, particularly, trimethylol propane or ethane can be used.

Aromatic diisocyanates generally are not suitable for use in clear coating compositions since they are light sensitive and tend to yellow and crack with exposure to sunlight.

Typical monohydric alcohols that can be used to form the carbamate are monohydric alcohols having 1-5 carbon atoms, such as, methanol, ethanol, propanol, isopropanol, butanol, isobutanol, and pentanol. Alicyclic alcohols can be used, such as, cyclohexanol.

Sufficient hydroxy functional acids are used to form a carbamate having an acid number in the range of 12 to 60, preferably in the range of 14 to 45. Typical hydroxy functional acids that can be used are hydroxy acetic acid, dimethylol propionic acid, lactic acid, epsilon caproic acid, and 12-hydroxy stearic acid.

Polyalkylene ether glycols are used in the formation of the carbamate to provide nonionic stabilization in the aqueous medium and can be used in amounts of 2 to 23% by weight, based on the weight of the carbamate. Typical polyalkylene ether glycols that can be used have a number average molecular weight of 100 to 2,000 and are, for example, polypropylene glycol, for example "Polyglycol" 725, polyethylene glycol, for example, "PEG" 600 and "PEG" 900, tripropylene glycol monomethyl ether, diethylene glycol monobutyl ether, and polybutylene glycol. Polypropylene glycols are preferred since these glycols reduce water

sensitivity of the resulting cured coating in comparison to polyethylene ether glycols. Preferably, 4.5 to 5.5% by weight, based on the weight of the carbamate, of polypropylene glycol having a molecular weight of approximately 725 is used.

5 All molecular weights disclosed herein are determined by gel permeation chromatography (GPC).

Sufficient amine is added to the carbamate to form a water-soluble or water-dispersible product. The amine reacts with any pending carboxyl groups of the carbamate to form a salt. Typical amines that can  
10 be used include AMP (2-amino-2-methyl-1-propanol), amino ethyl propanol, dimethyl ethanol amine, N-methyl diethanol amine, diethanol amine, diglycolamine, triethylamine, hydroxy functional amines, such as, tris(hydroxymethyl) aminomethane, 2-amino-2-ethylpropanediol, and triisopropanolamine. AMP is a preferred amine. The pH of the coating  
15 composition can be adjusted with these amines. Hydroxy functional amines (disclosed above) can be used to reduce yellowing of a finish of the composition when exposed to outdoor weathering.

The coating composition contains about 5-80% by weight, based on the weight of the binder, of a water-compatible alkylated  
20 melamine crosslinking agent, preferably 20-60% by weight of an alkylated melamine crosslinking agent. Typical alkylated melamines that can be used are water-soluble or water-dispersible melamines that are monomeric or polymeric and have a relatively low molecular weight. Alkoxy monomeric melamines that can be used are low molecular weight  
25 melamines that contain on an average three or more methylol groups reacted with a monohydric alcohol having 1 to 5 carbon atoms, such as, methanol, propanol, n-butanol and isobutanol and has an average degree of condensation of less than 2 and preferably, in the range of about 1.1 to 1.8.

30 Suitable monomeric melamines include highly alkylated melamines, such as, methylated melamines, methylated and butylated melamines, butylated melamines, isobutylated melamines and mixtures thereof. More particularly, hexamethoxymethylol melamine, butylated melamines and mixed methylated and butylated melamines are preferred.  
35 Particularly preferred alkylated melamines for clear coating compositions include hexamethoxymethylol melamines, such as, Cymel® 303 and Resimene® 747, Cymel® 1156 which is reported to be a 100% butylated melamine having a degree of polymerization of 2.9. A particularly

preferred mixture of melamines is Cymel® 1156 and Resimene® CE-4514 which is reported to be a 50/50 methylated/butylated melamine.

These melamines are supplied commercially; for example, by Cytec Industries Inc. West Patterson, New Jersey and by Solutia Inc., St. Louis, Missouri.

Curing catalysts, are generally used in the coating composition in amounts of 0.1% to 5.0% by weight, based on the weight of the binder, for catalyzing the crosslinking of the carbamate reaction product with the alkylated melamine crosslinking agent. Preferred are blocked sulfonic acid catalysts. Typical blocked acid catalysts include blocked paratoluene sulfonic acid, blocked dodecyl benzene sulfonic acid, blocked dinonyl naphthalene disulfonic acid in which the blocking agent is a hydroxy functional alkyl amine, such as, AMP, or dimethyl oxazolidine. In the event the composition contains an excess of amine, the acid catalyst need not be blocked and the acid form of the catalyst can be used.

An alkyl or aryl acid phosphate catalyst, such as, butyl acid phosphate or phenyl acid phosphate can be used in addition to the above acid catalysts.

The coating composition of this invention can be used as a clear coat that is applied over a pigmented base coat that may a pigmented version of the composition of this invention or another type of pigmented base coat. The clear coating can be in solution or in dispersion form.

Typically, a clear coating is then applied over the base coating before the base coating is fully cured, a so called "wet-on-wet process", and the base coating and clear coating are then fully cured usually by baking at 100°C to 150°C for 15 to 45 minutes. The base coating and clear coating preferably have a dry coating thickness ranging from 2.5 to 75 microns and 25 to 100 microns, respectively.

To improve the weatherability of a clear coating, an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers can be added to the clear coat composition in the amount of 0.1% to 10% by weight, based on the weight of the binder. Such stabilizers include ultraviolet light absorbers, screeners, quenchers, and specified hindered amine light stabilizers. Also, an antioxidant can be added, in the amount 0.1% to 5% by weight, based on the weight of the binder.

Typical ultraviolet light stabilizers that are useful include benzophenones, triazoles, triazines, benzoates, hindered amines and



mixtures thereof. Specific examples of ultraviolet stabilizers are disclosed in U.S. Patent 4,591,533, the entire disclosure of which is incorporated herein by reference. For good durability, a blend of Tinuvin® 1130, 384 and 123 (hindered amine light stabilizers), all commercially available from  
5 Ciba Specialty Chemicals, Tarrytown, New York is preferred.

The clear coating composition may also include other conventional formulation additives, such as, wetting agents, leveling and flow control agents, for example, Resiflow®S (polybutylacrylate), BYK®  
10 320 and 325 (high molecular weight polyacrylates), BYK® 347 (polyether-modified siloxane), rheology control agents, such as, fumed silica, defoamers, surfactants and emulsifiers to help stabilize the composition. Other additives that tend to improve mar resistance can be added, such as, silsesquioxanes and other silicate-based micro-particles.

The novel coating composition may be used as a base coat or  
15 as a pigmented monocoat topcoat. Both of these compositions require the presence of pigments. Typically, a pigment-to-binder ratio of 0.1/100 to 200/100 is used depending on the color and type of pigment used. The pigments are formulated into mill bases by conventional procedures, such as, grinding, sand milling, and high speed mixing. Generally, the mill base  
20 comprises pigment and a dispersant in an aqueous medium. The mill base is added in an appropriate amount to the coating composition with mixing to form a pigmented coating composition.

Any of the conventionally-used organic and inorganic pigments, such as, white pigments, like, titanium dioxide, color pigments,  
25 metallic flakes, such as, aluminum flake, special effects pigments, such as, coated mica flakes, coated aluminum flakes and the like and extender pigments can be used. It may be desirable to add one of the aforementioned UV light stabilizers and flow control additives.

The novel coating composition may be used as a primer in  
30 which case typical pigments used in primers would be added, such as, carbon black, barytes, silica, iron oxide and other pigments that are commonly used in primers in a pigment-to-binder ratio of 5/100 to 100/100.

The coating composition can further contain from 1% to 20%  
35 by weight, based on the weight of binder solids, of a water-soluble or water-dispersible polyester resin that is the esterification product of a dicarboxylic acid or anhydride, a polyol having at least three reactive hydroxyl groups, a diol, and a cyclic alcohol and having a number

average molecular weight in the range of 500 to 4,000. One preferred polyester resin is the esterification product of adipic acid, trimethylol propane, hexanediol, hexahydrophthalic anhydride and cyclohexane dimethanol. Also, the coating composition can further contain from 1% to 20% by weight, based on the weight of binder solids, of a hydroxy functional acrylic resin that is water-soluble or water-dispersible. Also, the coating composition can further contain from 1% to 20% by weight, based on the weight of binder solids, of one of the aforementioned polyalkylene ether glycols which act as a reactive diluent that reacts with the alkylated melamine and becomes part of the film-forming constituent of the coating composition. Polypropylene ether glycols, such as, PPG 425 and PPG 1025 are preferred since these glycols reduce the water sensitivity of the resulting coating. The coating composition may contain 1-40% by weight of a polyurethane resin that is water-soluble or water-dispersible.

Other catalysts that can be used to improve the cure rate of the composition, include dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin dichloride, dibutyl tin dibromide, triphenyl boron, tetraisopropyl titanate, triethanolamine titanate chelate, dibutyl tin dioxide, dibutyl tin dioctoate, tin octoate, aluminum titanate, aluminum chelates, zirconium chelate, and other such catalysts or mixtures thereof known to those skilled in the art.

To improve, for example, application properties, such as, flow or leveling, it may be necessary to add small amounts of conventional organic solvents that are commonly used in coating compositions. Typically, such solvents should be in small amounts and only increase the VOC of the coating composition to about 0.025-0.010 kg/l.

The coating composition can be applied by conventional techniques, such as, spraying, electrostatic spraying, dipping, brushing, and flow coating.

### **Testing Procedures used in the Examples**

20° Gloss – test method ASTM D523 – a rating of at least 80 is an acceptable minimum.

DOI – distinctness of image – test method ASTM D5767 – a rating of at least 80 is an acceptable minimum.

Hardness – Tukon Hardness – test method ASTM D1474.

### **Dry Mar Resistance**

The clear coating of the panel was coated with a thin layer of Bon Ami abrasive supplied by Faultless Starch/Bon Ami Corporation,

Kansas City, Missouri. The panels were then tested for mar damage by applying 10 double rubs against a green felt wrapped fingertip of A.A.T.C.C. Crockmeter (Model CM-1, Atlas Electric Devices Corporation, Chicago, Illinois). The dry mar resistance was recorded as percentage of gloss retention by measuring the 20° gloss of the mar areas versus the non-marred areas of the coated panels.

#### Wet Mar Resistance

Similar procedure was used as above except that a wet alumina slurry was used instead of the Bon Ami abrasive. The alumina slurry consisted of 294 parts deionized water, 21 parts ASE-60 Thickener, 25 parts AMP 95% aqueous solution of amino methyl propanol and 7 parts of aluminum oxide (120# grit)

#### Acid Etch Resistance Test

10.16 x 30.48 cm (4 x 12 inches) primed steel panels coated with a black waterborne polyester-modified acrylic melamine base coating was sprayed with a clear coating composition prepared in the Example and cured for 30 minutes at 140°C. The resulting panel was tested on a Byk Gradient oven, programmed with a temperature gradient that is 40°C at the bottom of the gradient and 90°C at the top of the gradient. Drops of a synthetic rain are placed on the panel at 5°C intervals. The synthetic rain is a mixture of 100 parts by weight of an aqueous cationic solution of ammonium hydroxide, calcium hydroxide, sodium hydroxide and potassium hydroxide and 33 parts by weight of an aqueous anionic solution of sulfuric acid, nitric acid and hydrochloric acid and the resulting mixture has a pH of 1. The panels reside in the gradient oven for 30 minutes and then are rinsed with water. The degree of damage at each spot where the synthetic rain was dropped is evaluated vs. a control clear coating composition. The control clear coating composition is a one-component commercial acrylosilane coating composition (Gen® IVAW from DuPont). The performance of the clear coating under test is judged by the accumulated degree of damage that occurs over the entire gradient. The damage scale is 0-10 with 10 being the most damage. The commercial clear coating composition (control) has a degree of damage of 6 and any acceptable clear coating composition must have a degree of damage of 6 or less.

The following examples illustrate the invention. All parts and percentages are on a weight basis unless otherwise indicated. Molecular

weights are determined by GPC (Gel Permeation Chromatography) using polymethyl methacrylate as the standard.

### **EXAMPLE 1**

- 5                   An aqueous carbamate composition was prepared by charging the following constituents into reaction vessel equipped with a nitrogen inlet, dropping funnel and a heating source:

<u>Components</u>	<u>Parts by Weight</u>
<u>Portion 1</u>	
Desmodur® 3300 trimer of hexamethylene diisocyanate	582.0
Dibutyl tin dilaurate catalyst	0.1
<u>Portion 2</u>	
Cyclohexanol	271.0
<u>Portion 3</u>	
"GlyPure" glycolic acid (hydroxy acetic acid)	17.9
<u>Portion 4</u>	
"PolyGlycol" 725 (polypropylene glycol having a weight average molecular weight of 725)	45.3
<u>Portion 5</u>	
AMP - 2-amino-2-methyl-1-propanol	22.0
<u>Portion 6</u>	
Resimene® 747 (hexamethoxymethylol melamine)	233.72
<u>Portion 7</u>	
Deionized water	1167.25
Total	2339.27

- Portion 1 was charged into the reaction vessel and blanketed with nitrogen. Portion 2 was added over a 30 minute period while  
 10   adjusting the rate of addition to maintain the temperature below 80°C. The resulting reaction mixture was held at this temperature for 60 minutes. Portion 3 was added in two equal amounts about 5 minutes apart. There was a slight exothermic reaction. Exactly 15 minutes after all of Portion 3 was added, Portion 4 was added and the reaction mixture held at 80°C  
 15   until no isocyanate was present in the reaction mixture as determined by infra red analyzer or for a period of 3 hours which ever comes first. Portion 5 was added. The reaction mixture was held at the above temperature for 10 minutes and Portion 6 was mixed with the reaction

mixture and then Portion 7 was added and mixed and the reaction mixture was stirred for an additional 1-2 hours.

The resulting aqueous carbamate composition had a 49.5% solid content.

- 5 A clear coating composition was prepared by blending the following constituents together:

Components	Parts by Weight
<u>Portion 1</u>	
Acrylic flow modifier (59.0% solids)	101.4
Tinuvin® 1130 UV stabilizer	12.0
Tinuvin® 123 Hindered amine light stabilizer	6.0
<u>Portion 2</u>	
Resimene®CE 4514 (94.5% solids of a 50/50 methylated and butylated melamine having a degree of polymerization of 2.0)	222.0
Cymel®1156 (100% solids of a butylated melamine having a degree of polymerization of 2.9)	30.0
<u>Portion 3</u>	
Deionized water	150.0
Aqueous Carbamate Composition (prepared above)	606.0
Byk® 347 – wetting agent of a polyether modified siloxane	12.0
<u>Portion 4</u>	
Acid Catalyst Solution (dodecyl benzene sulfonic acid neutralized with AMP)	<u>21.8</u>
Total	1161.2

- Portion 1 was charged into a mixing vessel and mixed for 20 minutes. Portion 2 then was added with mixing and mixing was continued for 30 minutes. The constituents of Portion 3 were added in the order shown with mixing and then mixed an additional 15 minutes. Portion 4 was added with mixing and mixed for an additional 30 minutes. The pH of the resulting coating composition was adjusted to a pH of 8.1-8.2 with AMP and the composition was diluted with deionized water to a viscosity of 30 seconds measured with a #4 Ford Cup. The composition was filtered by passing it through a 10 micron filter. The resulting composition had a theoretical solids of 47.3% and a VOC (measured according to EPA Method 24) of 0.168 – 0.214 kg/l (1.1 – 1.4 pounds/gallon).

The above prepared clear coating composition was applied by spraying as a clear coat onto a phosphatized steel panel coated with a cured cathodic epoxy resin based electrodeposition primer over which a black pigmented waterborne base coating composition of an acrylic polymer crosslinked with a melamine resin was applied to a wet film thickness of 12.7-20.32 microns (0.5-0.8 mils), flash dried for 5 minutes and baked for 10 minutes at 82°C (180°F). The above prepared clear coating was applied to a wet film thickness of 43.2-48.26 microns (1.7-1.9) mils and flash dried for 15 minutes and baked for 5 minutes at 82.2 °C (180°F), 5 minutes at 104 °C (220°F) and 30 minutes at 140°C (285°F) to provide a clear coat film on the panel (Panel A).

A control was prepared using the same phosphatized steel panel coated with a cured cathodic epoxy resin based electrodeposition primer over which a black pigmented waterborne base coating composition of an acrylic polymer crosslinked with a melamine resin was applied to the same wet film thickness and flash dried and baked as above and then a conventional commercially-available acryosilane clear coating composition (Gen® IVAW from DuPont) was applied and baked as above to provide a clear coat film on the panel (Panel B).

The following test were conducted on each of the panels and the results of these test are shown in the following Table 1:

Table 1

TEST	RESULTS	
	Panel A (invention)	Panel B (control)
20° Gloss	96	87
DOI	97	95
HARDNESS (Tukon Hardness knoops)	17.1	4.7
Dry Mar Resistance (% gloss retention)	90%	80%
Wet Mar Resistance (%gloss retention)	85%	67%
Acid Etch Resistance (Synthetic rain etch data)	5	6

The clear coating on Panel A, the invention, showed an improvement in 20° Gloss and DOI and a significant improvement in Hardness, Dry Mar Resistance and Wet Mar Resistance in comparison to the control of a conventional commercial acrylosilane containing clear

coating composition (Gen® IVAW from DuPont) that is used on automobiles and trucks. Acid etch data showed a small improvement of Panel A, the invention, in comparison to the control.

5

### **EXAMPLE 2**

A primer composition was prepared by blending the following constituents together:

<u>Components</u>	<u>Parts by Weight</u>
Aqueous carbamate composition (prepared in Ex. 1)	367.0
Monomeric fully methylated melamine formaldehyde crosslinking agent (Cymel® 301)	12.4
PPG 425 (Polypropylene ether glycol Mw 425)	41.3
Taupe color aqueous pigment dispersion (62.4% solids of a pigment dispersion of an acrylic polymer/titanium dioxide pigment/iron oxide/isoindolinone pigment/carbon black pigment in a weight ratio of 8.0/68.8/17.5/3.8/1.9)	139.2
Acid catalyst (25% paratoluene sulfonic acid blocked with 2-amino-2-methyl-1-propanol)	4.1
2-Amino-2-methyl-1-propanol	3.0
Deionized water	<u>12.0</u>
Total	580.0

The resulting primer composition had a pH of 8.2, a VOC (measured according to EPA Method 24) of 0.07 kg/l (0.59 pounds/gallon), and a measured solids content of 55%, a viscosity measured with a #4 Ford Cup of 38 seconds.

The above prepared primer was applied to a phosphatized steel panel coated with a cathodic epoxy electrocoating composition and baked at 150 –165°C for about 25 minutes to form a primer layer about 25-32 microns thick. A second primed panel identical to the above panel was prepared and was spray coated with a black pigmented waterborne base coating composition of an acrylic polymer crosslinked with a melamine resin to a wet film thickness of 12.7-20.32 microns (0.5-0.8 mils), flash dried for 5 minutes and baked for 10 minutes at 82°C (180°F). The above described acrylosilane clear coating was applied to the same wet film thickness, flash dried and baked as described in Example 1 to provide a clear coat/base coat film on the panel.

The primed panel had a film build of 32 microns and had a Tukon Hardness of 8-10 knoops and a 60 degree gloss of 83 and had no loss of adhesion when subjected to an adhesion test.

- 5 The primed panel coated with the base coat and clear coat was subjected to testing with a gravelometer and had a test result of 4 and showed no adhesion failure when subjected to a standard adhesion test. The test results indicated that the primer was acceptable for a commercial automotive coating use.



**CLAIMS**

1. An aqueous coating composition having a pH of 6.0-10.0 and having a VOC of less than 0.24 kg/l and comprising 30% to 70%  
5 by weight of film-forming binder and correspondingly 70% to 30% by weight of an aqueous liquid carrier for the binder; wherein the binder comprises
  - a. 20% to 95% by weight, based on the weight of the binder, of a carbamate reaction product consisting of the reaction of (1) an  
10 aliphatic polyisocyanate, (2) a monohydric alcohol, (3) a hydroxy functional aliphatic carboxylic acid and (4) a polyalkylene ether glycol having a number average molecular weight of 100 to 2,000; said reaction product being further reacted with an amine to provide a water-dispersible product;
  - 15 b. 5% to 80% by weight, based on the weight of the binder, of a water-compatible alkylated melamine crosslinking agent.
2. The coating composition of claim 1 containing 0.1 to 5.0 % by weight, based on the weight of the binder, of a blocked acid  
20 catalyst.
3. The coating composition of claim 2 in which the blocked acid catalyst comprises an organic sulfonic acid blocked with an amine.  
25
4. The coating composition of claim 1 in which the crosslinking agent is selected from the group consisting of a monomeric hexamethoxymethylol melamine and a mixed methylated and butylated melamine.  
30
5. The coating composition of claim 1 in which the aliphatic polyisocyanate is the trimer of hexamethylene diisocyanate.
6. The coating composition of claim 1 in which the  
35 monohydric alcohol is cyclohexanol.
7. The coating composition of claim 1 in which the hydroxy functional aliphatic carboxylic acid is hydroxy acetic acid.

8. The coating composition of claim 1 in which the polyalkylene ether glycol is polypropylene ether glycol.

5 9. The coating composition of claim 1 in which the amine is amino methyl propanol.

10 10. The coating composition of claim 1 containing pigments dispersed therein a pigment to binder weight ratio of 0.1/100 to 200/100.

11. The coating composition of claim 1 which contains about 0.1% to 10% by weight, based on the weight of the binder, of ultraviolet light stabilizers.

15 12. The coating composition of claim 1 useful as a clear coating composition in which the carbamate reaction product consists essentially of the reaction product of the trimer of hexamethylene diisocyanate, cyclohexanol, hydroxy acetic acid, polypropylene ether glycol and amino methyl propanol and the composition contains 0.1 to 5 %  
20 by weight, based on the weight of the binder, of a blocked sulfonic acid catalyst wherein the blocking agent is amino methyl propanol and the alkylated melamine crosslinking agent comprises a mixed methylated and butylated melamine.

25 13. The coating composition of claim 1 useful as a primer composition containing pigment in a pigment to binder ratio of 5/100 to 100/100 in which the carbamate reaction product consists essentially of the reaction product of the trimer of hexamethylene diisocyanate,  
30 cyclohexanol, hydroxy acetic acid, polypropylene ether glycol and amino methyl propanol, and the composition contains 0.1 to 5 % by weight, based on the weight of the binder, of a blocked sulfonic acid catalyst wherein the blocking agent is amino methyl propanol and the alkylated melamine crosslinking agent comprises a monomeric  
35 hexamethoxymethylol melamine.

14. A substrate coated with the composition of claim 1.

15. A substrate having a base coating of a pigmented coating composition, which is top coated with a clear coating of the composition of claim 1.

5 16. A substrate having a multi-layer coating comprising a pigmented primer coating of the composition of claim 1, a base coating of a pigmented coating composition, and a top-coating of a clear coating of the composition of claim 1.

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## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 02/26874

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D175/04 C08G18/08 C08G18/66 C08G18/28

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 7 C09D C08G

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)

PAJ, 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	JP 01 193367 A (SANYO CHEM IND LTD) 3 August 1989 (1989-08-03)	1-6, 8-11, 14-16
Y	page 2, left-hand column, line 3 -page 4, right-hand column, line 9; claim; examples 5-8	7,12,13
Y	US 4 046 729 A (SCRIVEN ROGER L ET AL) 6 September 1977 (1977-09-06) column 3, line 19-36 column 11, line 17-24	7,12,13
A	EP 0 622 387 A (BASF CORP) 2 November 1994 (1994-11-02) page 5, line 2 -page 6, line 39; claims; examples	1-16
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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\*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.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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