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(54) Title: KETAL-PROTECTED POLYOLS FOR LOW VOC COATINGS

(57) Abstract: The invention relates to a coating composition wherein ketal groups block the hydroxyl groups of the poly(meth)acrylate and the ketal groups can be removed through hydrolysis in order to facilitate cross-linking through reaction with polyisocyanate compounds. The invention also relates to a process for curing the aforementioned coating composition. The invention also relates to a process for coating substrates wherein a clear coat comprising the aforementioned coating composition is coated over a base coat. The invention also relates to a process for blocking the hydroxyl groups of a poly(meth)acrylate compound through reaction with a ketal compound.



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TITLE

KETAL-PROTECTED POLYOLS FOR LOW VOC COATINGS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority under 35 U.S.C. §119 from U.S.

- 5 Provisional Application Serial No. 60/555,161 (filed March 22, 2004),
which is incorporated by reference herein as if fully set forth.

FIELD OF THE INVENTION

- This invention relates to the protection of hydroxyl groups in
poly(meth)acrylates useful in the production of low volatile organic
10 compound content coatings using polyisocyanates for cross-linking.

BACKGROUND OF THE INVENTION

- A key to refinish coatings is the ability to deliver a refinished vehicle
to the customer as quickly as possible with a maximum level of
appearance. The consumer wants to have a good-looking, repaired
15 vehicle as quickly as possible to minimize the inconvenience of being
without a vehicle. The repair shop wants to maximize the utilization of his
capital investment and minimize the overall labor and cost in repairing a
vehicle. Thus, productivity in the overall repair process and good
appearance are critical.

- 20 Additionally, pressures exist worldwide to develop low volatile
organic compounds ("VOC"), that is, environmentally friendly coating
systems. One key to resolving these issues is through the dramatic
reduction or elimination of solvents used in coatings. These new, low
VOC coatings need to meet key customer attributes including productivity,
25 appearance, and film properties while being robust, user-friendly systems.

- Currently, the automotive refinish market is comprised mostly of
two-component coatings capable of curing at ambient conditions into
cross-linked, three-dimensional, thin films. These coatings are
predominantly solvent based and use hydroxyl/isocyanate curing. One
30 component of the system contains the hydroxyl functional species; the
other component contains the isocyanate. These components are mixed
just prior to spraying on the vehicle. These two-part coatings need to
remain at a low enough viscosity to allow for spraying over an extended
timeframe and then, after spraying, require rapid curing to a three-

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dimensional network on the vehicle to maximize productivity and physical properties.

In repairing damage such as dents to auto bodies, the original coating in and around the damaged area is typically sanded or ground out by mechanical means. Sometimes the original coating is stripped off from a portion or off the entire auto body to expose the bare metal underneath. After repairing the damage, the repaired surface is coated, preferably with low VOC coating compositions, typically in portable or permanent low cost painting enclosures vented to atmosphere to remove the organic solvents from the freshly applied paint coatings in a safe manner from the standpoint of operator health and explosion hazard. Typically, the drying and curing of the freshly applied paint takes place within these enclosures. Furthermore, the foregoing drying and curing steps take place within the enclosure to prevent the wet paint from collecting dirt in the air or other contaminants.

As these paint enclosures take up significant floor space of typical small auto body paint repair shops, these shops prefer to dry and cure these paints as fast as possible. More expensive enclosures are frequently provided with heat sources such as conventional heat lamps located inside the enclosure to cure the freshly applied paint at accelerated rates. Therefore, to provide more cost effective utilization of shop floor space and to minimize fire hazards resulting from wet coatings from solvent based coating compositions, there exists a continuing need for fast curing coating formulations that cure under ambient conditions while still providing outstanding performance characteristics, particularly chip resistance, mar-resistance, durability, and appearance.

A key aspect of the productivity in refinish coatings is the ability for physical dry. High productivity coatings need to be able to dry to the touch very rapidly to allow for application of subsequent coats. Clears that are used for repairing smaller spots on a damaged vehicle (spot repair clears) need to have as low an overspray as possible to minimize the amount of taping needed to protect the undamaged painted area. High glass transition temperature (T_g), higher weight average molecular weight

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(M_w) acrylics perform very well in these types of products because of their ability to physically dry.

To develop a lower VOC productive system, therefore, it is critical to produce high T_g, relatively high M_w acrylics that can be used as
5 components of productive systems for physical dry without adversely effecting pot life.

WO 02/10298 discloses blocking polyols with hydrolyzable silyl groups. JP 2001-163922 describes reacting an oligomer comprising a polyorthoester, either an alpha- or beta-glycol, and an ethylenic
10 unsaturated group with a resin having at least two hydroxyl groups. WO 02/057339 describes protecting hydroxyl groups through the use of spiroorthocarbonate groups. U.S. Patent No. 6,297,329 issued to van den Berg et al. on October 2, 2001, discloses a coating composition comprising a first compound comprising at least one bicyclo- or spiro-
15 orthoester group and a second compound comprising at least two hydroxyl-reactive groups. U.S. Patent No. 6,045,870 issued to Noura et al. on April 4, 2000, discloses the protection of carboxyl groups through silylation.

It is desirable to improve physical dry and long pot life through the
20 use of novel polymers with protected hydroxyls. The coatings disclosed herein are stable under anhydrous conditions but become active, or de-block, after application via the absorption of atmospheric moisture, which will release the initial hydroxyl groups. Once the hydroxyl group is released, it will quickly react with the isocyanate cross-linker to develop a
25 three-dimensional network, and very rapid film formation will occur.

SUMMARY OF THE INVENTION

The invention relates to a coating composition wherein ketal groups block the hydroxyl groups of the poly(meth)acrylate. The ketal groups can be removed through hydrolysis in order to facilitate cross-linking through
30 reaction with polyisocyanate compounds. The invention also relates to a process for curing the aforementioned coating composition. The invention also relates to a process for coating substrates wherein a clear coat comprising the aforementioned coating composition is coated over a base coat. The invention also relates to a process for blocking the hydroxyl

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groups of a poly(meth)acrylate compound through reaction with a ketal compound.

DETAILED DESCRIPTION OF THE INVENTION

Applicants specifically incorporate the entire content of all cited references in this disclosure. Applicants also incorporate by reference the co-owned and concurrently filed application Serial No. _____ entitled "Orthoester-Protected Polyols for Low VOC Coatings."

Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

In the context of this disclosure, a number of terms shall be utilized.

The term "(meth)acrylate" denotes both acrylate and methacrylate.

The term "polydispersity" of a polymer is a ratio of M_w to number average molecular weight (" M_n ").

The term "low VOC coating composition" means a coating composition that includes the range of from 0.1 kilograms (1.0 pounds per gallon) to 0.72 kilograms (6.0 pounds per gallon), preferably 0.3 kilograms (2.6 pounds per gallon) to 0.6 kilograms (5.0 pounds per gallon), and more preferably 0.34 kilograms (2.8 pounds per gallon) to 0.53 kilograms (4.4 pounds per gallon) of the solvent per liter of the coating composition. All VOCs are determined under the procedure provided in ASTM D3960.

In one embodiment, the present invention concerns a coating composition comprising a poly(meth)acrylate containing at least two hydroxyl groups blocked by hydrolyzable ketal groups and at least one polyisocyanate compound.

In another embodiment, the invention concerns a process for blocking the hydroxyl groups of poly(meth)acrylates comprising thermally reacting a poly(meth)acrylate containing at least two hydroxyl groups with at least one vinyl ether compound.

By "blocked" is meant forming a hydrolyzable ester through reaction between at least two hydroxyl groups of a poly(meth)acrylate and at least one vinyl ether compound to form hydrolyzable ketal groups. In one

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embodiment, from about 30% to 100% of hydroxyl groups are blocked by a vinyl ether compound. In a preferred embodiment, a vinyl ether compound blocks substantially all of the hydroxyl groups. By “substantially all of the hydroxyl groups” is meant vinyl ether compounds have blocked at least 70% of the hydroxyl groups.

In a preferred embodiment, coating compositions are formulated by first taking a poly(meth)acrylate compound containing at least two hydroxyl groups and protecting the hydroxyl groups through an acid catalysis reaction with at least one vinyl ether compound. The etherification reaction results in a poly(meth)acrylate compound wherein at least two hydroxyl groups have been blocked by ketal groups. When needed for use in a coating composition, the blocked poly(meth)acrylate compound is unblocked by hydrolyzing the ketal groups with water, optionally in the presence of an acid catalyst, either prior to or simultaneously with the addition of a polyisocyanate compound. The unblocked hydroxyl groups of the poly(meth)acrylate compound can freely react with the polyisocyanate compound to produce coating compositions by any method known to one of ordinary skill in the art.

Non-limiting examples of poly(meth)acrylates used in the coating composition are polymerized monomers of acrylic and methacrylic acid esters of straight-chain or branched monoalcohols of 1 to 20 carbon atoms. Preferred esters are alkyl acrylates and methacrylates having 1 to 12 carbons in the alkyl group such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, pentyl acrylate, hexyl acrylate, 2-ethyl hexyl acrylate, nonyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, pentyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, nonyl methacrylate, lauryl methacrylate, and the like. Isobornyl methacrylate and isobornyl acrylate monomers can be used. Cycloaliphatic (meth)acrylates can be used such as trimethylcyclohexyl acrylate, t-butyl cyclohexyl acrylate, cyclohexyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate, and the like. Aryl acrylates and methacrylates such as benzyl acrylate and benzyl methacrylate also can be used.

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Ethylenically unsaturated monomers containing hydroxy functionality including hydroxy alkyl acrylates and hydroxy alkyl methacrylates, wherein the alkyl group has 1 to 4 carbon atoms, can be used. Suitable monomers include hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyisopropyl acrylate, 2,3-dihydroxypropyl acrylate, hydroxybutyl acrylate, dihydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxyisopropyl methacrylate, hydroxybutyl methacrylate, dihydroxypropyl methacrylate, dihydroxybutyl methacrylate and the like, and mixtures thereof. Hydroxy functionality may also be obtained from monomer precursors, for example, the epoxy group of a glycidyl methacrylate unit in a polymer. Such an epoxy group may be converted, in a post polymerization reaction with water or a small amount of acid, to a hydroxy group.

Suitable other olefinically unsaturated comonomers that can be used include acrylamide and methacrylamide and derivatives such as alkoxy methyl (meth) acrylamide monomers, such as methacrylamide, N-isobutoxymethyl methacrylamide, and N-methylol methacrylamide; maleic, itaconic, and fumaric anhydride and its half and diesters; vinyl aromatics such as styrene, alpha methyl styrene, and vinyl toluene; and polyethylene glycol monoacrylates and monomethacrylates.

Other functional monomers such as itaconic or maleic anhydride, the half ester thereof, acrylonitrile, allyl methacrylate, aceto acetoxyethyl methacrylate, methylacryl amidoglycolate methyl ether, ethylene urea ethyl methacrylate, 2- acrylamide-2 methyl propane sulfonic acid, trialkoxy silyl ethyl methacrylate, reaction products of mono epoxy esters or mono epoxy ethers with alpha-beta unsaturated acids, and reaction products of glycidyl (meth)acrylate with mono functional acids up to 22 carbon atoms can be used.

Preferably, the M_n of the poly(meth)acrylate is in the range of from about 200 to about 50,000. More preferably, the M_n of the poly(meth)acrylate is in the range of from about 300 to about 20,000. Even more preferably, the M_n of the poly(meth)acrylate is in the range of from about 500 to about 6,000. All molecular weights referred to herein

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are determined by gel permeation chromatography ("GPC") using a polystyrene standard.

The poly(meth)acrylate preferably includes in the range from 2 to 200, more preferably in the range from 2 to 50, and most preferably in the range from 2 to 20 hydroxyl groups per poly(meth)acrylate compound.

In a preferred embodiment, the poly(meth)acrylate has a polydispersity in the range of from about 1.5 to about 10.0. In a more preferred embodiment, the poly(meth)acrylate has a polydispersity in the range of from about 1.5 to about 5.0. In an even more preferred embodiment, the poly(meth)acrylate has a polydispersity in the range of from about 1.5 to about 3.0.

The polyisocyanate compound of the coating composition includes one or more cross-linking agents having at least two isocyanate groups. Any of the conventional aromatic, aliphatic, cycloaliphatic, isocyanates, trifunctional isocyanates, and isocyanate functional adducts of a polyol and a diisocyanate can be used. Typically useful diisocyanates are 1,6-hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-biphenylene diisocyanate, toluene diisocyanate, bis cyclohexyl diisocyanate, tetramethylene xylene diisocyanate, ethyl ethylene diisocyanate, 2,3-dimethyl ethylene diisocyanate, 1-methyltrimethylene diisocyanate, 1,3-cyclopentylene diisocyanate, 1,4-cyclohexylene diisocyanate, 1,3-phenylene diisocyanate, 1,5-naphthalene diisocyanate, bis-(4-isocyanatocyclohexyl)-methane, and 4,4'-diisocyanatodiphenyl ether.

Typical trifunctional isocyanates include triphenylmethane triisocyanate, 1,3,5-benzene triisocyanate, and 2,4,6-toluene triisocyanate. Trimers of diisocyanates also can be used, such as the trimer of hexamethylene diisocyanate, which is supplied by Bayer Corp., Pittsburgh, Pa., under the trademark Desmodur® N 3300A. Other suitable polyisocyanates from Bayer Corp. include Desmodur® N 3390A BA/SN and Z 4470BA polyisocyanates.

The relative amount of cross-linking agent used in the coating composition is adjusted to provide a molar equivalent ratio of NCO/(OH+NH) in the range of from about 0.5 to about 5, preferably in the

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range of from about 0.7 to about 3, and more preferably in the range of from about 0.85 to about 2.

The coating composition is suitable for use as a clear or pigmented composition. The coating composition can be used as a monocoat, as a
5 basecoat, or as a primer.

The coating composition can include additional components such as solvents, catalysts, pigments, fillers, and conventional additives.

Some of the suitable solvents include aromatic hydrocarbons, such as petroleum naphtha or xylenes; esters, such as, butyl acetate, t-butyl
10 acetate, isobutyl acetate or hexyl acetate; and glycol ether esters, such as propylene glycol monomethyl ether acetate. The amount of organic solvent added depends upon the desired solids level as well as the desired amount of VOC of the composition. If desired, the organic solvent may be added to both the components of the coating composition.

15 The coating composition preferably includes a catalytic amount of a catalyst for accelerating the curing process. Generally, in the range of about 0.001% to about 5%, preferably in the range of from about 0.002% to about 3%, more preferably in the range of from about 0.005% to about 1.5% of the catalyst is utilized, all in weight percent based on the total
20 weight of cross-linkable and cross-linking component solids. A wide variety of catalysts can be used, such as tin compounds, including dibutyl tin dilaurate and dibutyl tin diacetate and tertiary amines such as triethylenediamine. These catalysts can be used alone or in conjunction with carboxylic acids, such as acetic acid. One of the commercially
25 available catalysts, sold under the trademark Fastcat[®] 4202 dibutyl tin dilaurate (Elf-Atochem North America, Inc., Philadelphia, Pa.), is particularly suitable.

Hydrolyzing the protective group leads to the recovery of the original poly(meth)acrylate with hydroxyl groups available for cross-linking.
30 Hydrolysis can occur in water, optionally in the presence of an acid catalyst. Suitable acids, for example, include acetic acids and the like, phosphorous and phosphoric acids and their esters, hydrochloric acid, perchloric acid, hydrobromic acid, sulfuric acid and its half-esters, sulfonic

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acids like dodecylbenzenesulfonic acid, and compounds that generate acids upon hydrolysis such as, for example, POCl_3 , SOCl_2 , and PCl_5 .

The hydrolysis reaction can occur before or concurrently with the addition of cross-linker. Preferably, the blocked poly(meth)acrylates are unblocked, and the hydroxyl groups thus recovered, concurrently with the addition of cross-linker. It is to be understood that as the water contacts the ketal groups present in the composition, the ketal groups will start to hydrolyze, eventually leading to cross-linking of the composition. The water may be introduced in a variety of ways. For example, especially in the case of a coating, the water may be introduced into the uncross-linked or cross-linking (while the cross-linking is taking place) coating by absorption from the air. Absorption is very convenient for making an uncross-linked coating composition that is stable until exposed to (moist) air. Alternatively, water may be mixed in a mixing head or spray-mixing head (for a coating) just before cross-linking is to take place.

The coating composition can contain one or more coloring or special effect producing pigments. Examples of inorganic or organic coloring pigments include titanium dioxide, micronized titanium dioxide, iron oxide pigments, carbon black, azo pigments, phthalocyanine pigments, quinacridone pigments, and pyrrolopyrrol pigments. Examples of special effect producing pigments include aluminum flake, copper bronze flake, and other metal flakes; interference pigments such as, for example, metal oxide coated metal pigments, for example, titanium dioxide coated or mixed oxide coated aluminum, coated mica such as, for example, titanium dioxide coated mica and graphite special effect pigments.

Examples of fillers include silicon dioxide, aluminium silicate, barium sulfate, and talcum.

The coating composition may also include conventional additives such as wetting agents; leveling and flow control agents, for example, BYK[®] 320 and 325 (high molecular weight polyacrylates; BYK-Chemie USA Inc., Wallingford, Conn.), BYK[®] 347 (polyether-modified siloxane), and BYK[®] 306 (polyether-modified dimethylpolysiloxane); rheology control

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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. Such additional additives will, of course, depend on the intended use of the coating composition. Any additives that would adversely affect the clarity of the cured coating will not be included when the composition is used as a clear coating. The foregoing additives may be added to either component or both depending upon the intended use of the coating composition.

To improve weatherability of the coating, from about 0.1 to about 5 weight percent, preferably from about 0.5 to about 2.5 weight percent, and more preferably from about 1 to about 2 weight percent of ultraviolet light stabilizers screeners, quenchers, and antioxidants can be added to the composition, the percentages being based on the total weight of the binder and cross-linking components solids. Typical ultraviolet light screeners and stabilizers include the following:

Benzophenones such as hydroxy dodecycloxy benzophenone, 2,4-dihydroxy benzophenone, and hydroxy benzophenones containing sulfonic acid groups.

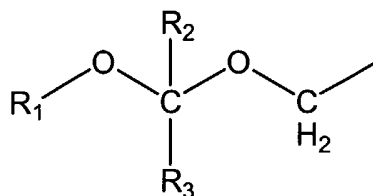
Benzoates such as dibenzoate of diphenylol propane and tertiary butyl benzoate of diphenylol propane.

Triazines such as 3,5-dialkyl-4-hydroxyphenyl derivatives of triazine and sulfur containing derivatives of dialkyl-4-hydroxy phenyl triazine and hydroxy phenyl-1,3,5-triazine.

Triazoles such as 2-phenyl-4-(2,2'-dihydroxy benzoyl)-triazole and substituted benzotriazoles such as hydroxy-phenyltriazole.

Hindered amines such as bis(1,2,2,6,6-entamethyl-4-piperidinyl sebacate) and di[4(2,2,6,6-tetramethyl piperidinyl)]sebacate; and any mixtures of any of the above.

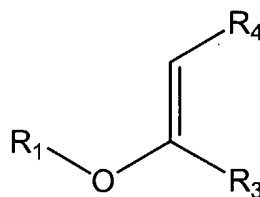
Preferably, the hydrolyzable ketal group has the following chemical structure:



wherein R_1 is an alkyl substituent of 1 to 6 carbon atoms; and R_2 and R_3 are, independently, alkyl substituents of 1 to 6 carbon atoms or cyclic substituents of 4 to 7 carbon atoms.

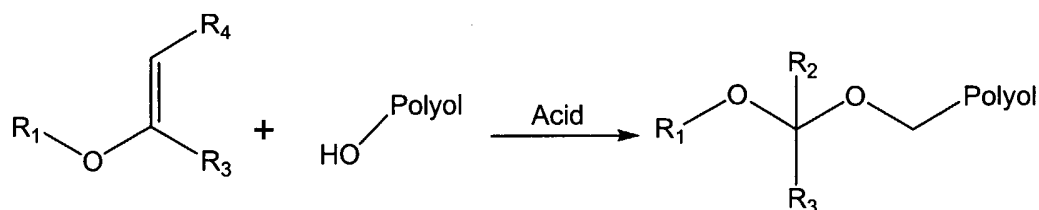
- 5 In another embodiment, the invention concerns a process for curing coating composition comprising thermally reacting a poly(meth)acrylate containing at least two hydroxyl groups with at least one vinyl ether compound, hydrolyzing the product of the thermal reaction step to unblock the poly(meth)acrylate containing at least two hydroxyl groups, and
- 10 reacting the unblocked poly(meth)acrylate containing at least two hydroxyl groups with at least one polyisocyanate compound.

Preferably, the at least one vinyl ether compound has the following chemical structure:



- 15 wherein R_1 is an alkyl substituent of 1 to 6 carbon atoms; R_3 is an alkyl substituent of 1 to 6 carbon atoms or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond; and R_4 is hydrogen, an alkyl substituent of 1 to 6 carbon atoms, or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond. In a preferred
- 20 embodiment, the at least one vinyl ether compound is 2-methoxypropene.

- The blocking reaction occurs through acid catalysis. To block the hydroxyl groups of a poly(meth)acrylate compound, the poly(meth)acrylate is reacted with an excess of a vinyl ether compound in presence of an acid catalyst. Suitable acid catalysts include any of those listed above. The
- 25 hydroxyl groups are blocked, for example, by the following reaction:

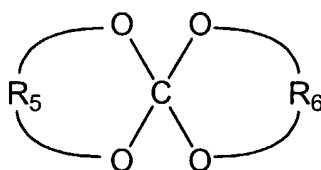


wherein R_1 is an alkyl substituent of 1 to 6 carbon atoms; R_2 is an alkyl substituent of 1 to 6 carbon atoms or a cyclic substituent of 4 to 7 carbon atoms; R_3 is an alkyl substituent of 1 to 6 carbon atoms or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond; and R_4 is hydrogen, an alkyl substituent of 1 to 6 carbon atoms, or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond. "Polyol" represents the poly(meth)acrylate backbone.

Blocking the hydroxyl groups of the poly(meth)acrylate compound can reduce the viscosity of the coating composition, thus allowing for the preparation of higher solids, lower VOC coating compositions. If necessary, the viscosity of the blocked poly(meth)acrylate can be adjusted using, for example, ethyl acetate.

In an alternative embodiment, coatings of the invention can comprise at least one of a spiroorthocarbonate compound and an amide acetal compound. Spiroorthocarbonate compounds are described in co-pending, co-owned application Serial No. 60/261,450, and amide acetal compounds are described in co-pending, co-owned application Serial No. 60/509,885.

Preferably the spiroorthocarbonate compound has the following chemical structure:



wherein R_5 and R_6 are, independently, hydrocarbylene or substituted hydrocarbylene bridging groups that have at least two bridging carbon atoms. It is preferred that there independently be 2 or 3 atoms in each bridge between oxygen atoms. By hydrocarbylene is meant a group containing only carbon and hydrogen that has two free valences to carbon atoms, and both free valences are not to the same carbon atom. By

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substituted hydrocarbylene is meant one or more hydrogen atoms are substituted for by a functional group that does not interfere with the desired reactions of, or the formation of, the compound involved. Suitable functional groups include halo, ether including alkoxy, hydroxyl, etc.

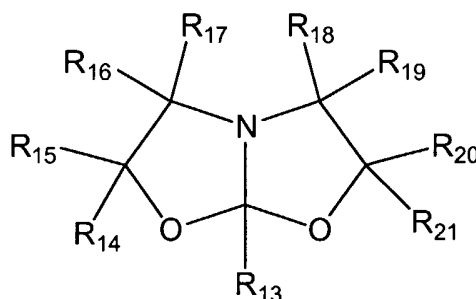
- 5 Preferred groups for R_5 and R_6 each independently have the formula $-CR_7R_8-CR_9R_{10}-(CR_{11}R_{12})_n-$, wherein n is 0 or 1, and each of R_7 - R_{12} independently is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that any two of R_7 - R_{12} vicinal or geminal to each other taken together may form a ring. In one preferred form R_5 and R_6 are the same.
- 10 Independently preferred groups for R_7 - R_{12} are hydrogen; alkyl, especially alkyl containing 1 to 10 carbon atoms, more preferably methyl or ethyl; and hydroxyalkyl, especially hydroxymethyl. Substitution patterns for specific preferred compounds are given in Table 1.

15

Table 1

Compound	R_5							R_6						
	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	n	R_7	R_8	R_9	R_{10}	R_{11}	R_{12}	n
A	CH ₃	H	H	H	H	H	1	CH ₃	H	H	H	H	H	1
B	H	H	CH ₂ OH	C ₂ H ₅	H	H	1	H	H	CH ₂ OH	C ₂ H ₅	H	H	1
C	H	H	H	H	-	-	0	H	H	CH ₂ OH	C ₂ H ₅	H	H	1
D	H	H	H	H	H	H	1	H	H	CH ₂ OH	C ₂ H ₅	H	H	1
E	H	H	H	H	H	H	1	H	H	H	H	H	H	1
F	CH ₃	H	H	H	-	-	0	CH ₃	H	H	H	-	-	0
G	H	H	H	H	-	-	0	H	H	H	H	-	-	0
H	H	H	n-C ₄ H ₉	C ₂ H ₅	H	H	0	H	H	n-C ₄ H ₉	C ₂ H ₅	H	H	0
I	H	H	n-C ₈ H ₁₇	H	-	-	0	H	H	n-C ₈ H ₁₇	H	-	-	0

Preferably, the amide acetal compound has the following chemical structure:



- 20 wherein R_{13} - R_{21} are, independently, hydrogen, C_1 to C_{22} alkyl, C_1 to C_{20} alkenyl, C_1 to C_{20} alkynyl, C_1 to C_{20} aryl, C_1 to C_{20} alkyl ester, or C_1 to C_{20}

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aralkyl group; said alkyl, alkenyl, alkynyl, aryl, or aralkyl each optionally having at least one substituent selected from the group consisting of halo, alkoxy, nitro, amino, alkylamino, dialkylamino, cyano, alkoxy silane and amide acetal (difunctional), and carbamoyl.

- 5 In a further alternative embodiment, coatings of this invention can comprise at least one of a conventional acrylic polymer, a polyester, a reactive oligomer, a dispersed acrylic polymer, an aldimine or ketimine, and a polyaspartic ester.

 The conventional acrylic polymer suitable for use in the present
10 invention can have a GPC M_w exceeding 5,000, preferably in the range of from 5,000 to 20,000, more preferably in the range of 6,000 to 20,000, and most preferably in the range of from 8,000 to 12,000. The T_g of the acrylic polymer varies in the range of from 0°C to 100°C, preferably in the range of from 30°C to 80°C.

- 15 The acrylic polymer suitable for use in the present invention can be conventionally polymerized from typical monomers, such as alkyl (meth)acrylates having alkyl carbon atoms in the range of from 1 to 18, preferably in the range of from 1 to 12, and styrene and functional monomers such as hydroxyethyl acrylate and hydroxyethyl methacrylate.

- 20 The polyester suitable for use in the present invention can have a GPC M_w exceeding 1,500, preferably in the range of from 1,500 to 100,000, more preferably in the range of 2,000 to 50,000, still more preferably in the range of 2,000 to 8,000, and most preferably in the range of from 2,000 to 5,000. The T_g of the polyester varies in the range of from
25 –50°C to 100°C, preferably in the range of from –20°C to 50°C.

- Suitable polyesters can be conventionally polymerized from suitable polyacids, including cycloaliphatic polycarboxylic acids, and suitable polyols, which include polyhydric alcohols. Examples of suitable cycloaliphatic polycarboxylic acids are tetrahydrophthalic acid,
30 hexahydrophthalic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 4-methylhexahydrophthalic acid, endomethylenetetrahydrophthalic acid, tricyclodecanedicarboxylic acid, endoethylenehexahydrophthalic acid, camphoric acid, cyclohexanetetracarboxylic acid, and

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cyclobutanetetracarboxylic acid. The cycloaliphatic polycarboxylic acids can be used not only in their *cis* but also in their *trans* form and as a mixture of both forms. Examples of suitable polycarboxylic acids, which, if desired, can be used together with the cycloaliphatic polycarboxylic acids, are aromatic and aliphatic polycarboxylic acids, such as, for example, phthalic acid, isophthalic acid, terephthalic acid, halogenophthalic acids, such as, tetrachloro- or tetrabromophthalic acid, adipic acid, glutaric acid, azelaic acid, sebacic acid, fumaric acid, maleic acid, trimellitic acid, and pyromellitic acid.

Suitable polyhydric alcohols include ethylene glycol, propanediols, butanediols, hexanediols, neopentylglycol, diethylene glycol, cyclohexanediol, cyclohexanedimethanol, trimethylpentanediol, ethylbutylpropanediol, ditrimethylolpropane, trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, dipentaerythritol, tris(hydroxyethyl) isocyanate, polyethylene glycol, and polypropylene glycol. If desired, monohydric alcohols, such as, for example, butanol, octanol, lauryl alcohol, ethoxylated, or propoxylated phenols may also be included along with polyhydric alcohols. The details of polyester suitable for use in the present invention are further provided in the U.S. Patent No. 5,326,820. One commercially available polyester, which is particularly preferred, is SCD[®]-1040 polyester, which is supplied by Etna Products Inc., Chagrin Falls, Ohio.

Useful reactive oligomers are covered in U.S. Patent No. 6,221,494. Non-alicyclic (linear or aromatic) oligomers can also be used, if desired. Such non-alicyclic-oligomers can be made by using non-alicyclic anhydrides, such as succinic or phthalic anhydrides, or mixtures thereof. Caprolactone oligomers described in U.S. Patent No. 5,286,782 can also be used.

Typical useful dispersed acrylic polymers are prepared by dispersion polymerizing at least one vinyl monomer in the presence of a polymer dispersion stabilizer and an organic solvent. The polymer dispersion stabilizer may be any of the known stabilizers used commonly in the field of dispersed acrylic polymers. These dispersed acrylic polymers are covered in U.S. Patent No. 5,763,528.

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Suitable aldimines may be prepared from aldehydes such as acetaldehyde, formaldehyde, propionaldehyde, isobutyraldehyde, n-butyraldehyde, heptaldehyde, and cyclohexyl aldehydes by reaction with amine. Representative amines that may be used to form the aldimine

5 include ethylene diamine, ethylene triamine, propylene diamine, tetramethylene diamine, 1,6-hexamethylene diamine, bis(6-aminoethyl)ether, tricyclodecane diamine, N,N'-dimethyldiethyltriamine, cyclohexyl-1,2,4-triamine, cyclohexyl-1,2,4,5-tetraamine, 3,4,5-

10 triaminopyran, 3,4-diaminofuran, and cycloaliphatic diamines.

Suitable polyaspartic esters are typically prepared by the reaction of diamines such as isophorone diamine with dialkyl maleates such as diethyl maleate.

The foregoing polyaspartic ester and selected aldimines are supplied commercially under the trademark Desmophen[®] amine co-

15 reactants by Bayer Corp.

Suitable ketimines are typically prepared by the reaction of ketones with amines. Representative ketones, which may be used to form the ketimine, include acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, benzyl methylketone, diisopropyl

20 ketone, cyclopentanone, and cyclohexanone. Representative amines which may be used to form the ketimine include ethylene diamine, ethylene triamine, propylene diamine, tetramethylene diamine, 1,6-hexamethylene diamine, bis(6-aminoethyl)ether, tricyclodecane diamine, N,N'-dimethyldiethyltriamine, cyclohexyl-1,2,4-triamine, cyclohexyl-1,2,4,5-

25 tetraamine, 3,4,5-triaminopyran, 3,4-diaminofuran, and cycloaliphatic diamines. Preparation and other suitable imines are shown in U.S. Patent No. 6,297,320.

In another embodiment, the invention concerns a process for coating a substrate comprising applying a base coat to the substrate,

30 applying a clear coat over the base coat wherein the clear coat comprises a poly(meth)acrylate containing at least two hydroxyl groups blocked by hydrolyzable ketal groups and at least one polyisocyanate compound, hydrolyzing the ketal groups of the poly(meth)acrylate containing at least two hydroxyl groups, and cross-linking the unblocked poly(meth)acrylates

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from the hydrolyzing step through reaction with at least one polyisocyanate compound.

The coating composition can be supplied in the form of a two-pack coating composition. Generally, the cross-linkable component and the cross-linking component are mixed, typically just prior to application to form a pot mix. The mixing can take place through a conventional mixing nozzle or separately in a container. A layer of the pot mix generally having a thickness in the range of 15 μm to 200 μm is applied over a substrate, such as an automotive body or an automotive body that has precoated layers, such as electrocoat primer. The foregoing application step can be conventionally accomplished by spraying, electrostatic spraying, roller coating, dipping, or brushing the pot mix over the substrate. The layer after application is typically dried to reduce the solvent content from the layer and then cured at a temperature ranging from ambient to about 204°C. Under typical automotive original equipment manufacturer ("OEM") applications, the dried layer of the composition can be typically cured at elevated temperatures ranging from about 60°C to about 160°C in about 10 to 60 minutes. Preferably, for automotive refinish applications, curing can take place at about ambient to about 60°C, and for heavy duty truck body applications, curing can take place at about 60°C to about 80°C. The cure under ambient conditions occurs in about 30 minutes to 24 hours, generally in about 30 minutes to 4 hours, to form a coating on the substrate having the desired coating properties. It is further understood that the actual curing time can depend upon the thickness of the applied layer, the cure temperature, humidity, and on any additional mechanical aids, such as fans, that assist in continuously flowing air over the coated substrate to accelerate the cure rate. It is understood that actual curing temperature would vary depending upon the catalyst and the amount thereof, thickness of the layer being cured, and the amount of the cross-linking component utilized.

The suitable substrates for applying the coating composition include automobile bodies; any and all items manufactured and painted by automobile sub-suppliers; frame rails; commercial trucks and truck bodies, including but not limited to beverage bodies, utility bodies, ready mix

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concrete delivery vehicle bodies, waste hauling vehicle bodies, and fire and emergency vehicle bodies, as well as any potential attachments or components to such truck bodies, buses, farm, and construction equipment; truck caps and covers; commercial trailers; consumer trailers; recreational vehicles, including but not limited to, motor homes, campers, conversion vans, vans, pleasure vehicles, pleasure craft snow mobiles, all terrain vehicles, personal watercraft, motorcycles, boats, and aircraft. The substrate further includes industrial and commercial new construction and maintenance thereof; cement and wood floors; walls of commercial and residential structures, such office buildings and homes; amusement park equipment; concrete surfaces, such as parking lots and drive ways; asphalt and concrete road surface; wood substrates; marine surfaces; outdoor structures, such as bridges; towers; coil coating; railroad cars; printed circuit boards; machinery; OEM tools; signage; fiberglass structures; sporting goods; and sporting equipment.

EXAMPLES

The present invention is further defined in the following Examples. It should be understood that these Examples, while indicating preferred embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the preferred features of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various uses and conditions.

The meaning of abbreviations is as follows: "hr." means hour(s), "min." means minute(s), "sec." means second(s), "d." means day(s), "ml" means milliliter(s), "cm" means centimeter(s), "mm" means millimeter(s), "g" means gram(s), "N" means newton(s), "HEMA" means 2-hydroxyethyl methacrylate, "IBOA" means isobornyl acrylate, "MMA" means methyl methacrylate, "M_n" means number average molecular weight, "M_w" means weight average molecular weight, "cps" means centipoise.

EXAMPLE 1

Ketal Composition A

1,500 ml of HEMA/IBOA copolymer (HEMA/IBOA = 37/63; M_n = 1,700; M_w = 2,450) 55% solution in aromatic hydrocarbon was placed into a 2 liter flask equipped with a magnetic stirrer, a thermocouple, and a downward condenser. The flask was flashed with nitrogen gas, and 250 g of 2-methoxypropene was added. After 10 min. of stirring, 0.1 ml of phosphorous oxychloride was added. After 45 min. of stirring, 8 g of basic alumina was added. After 15 min. of stirring, the flask's contents were filtered and evaporated under 15 Torr vacuum at 60 °C to remove all volatile components. After 1 hr., the flask was filled with nitrogen, and its contents were transferred into an airtight container. IR spectrum of the mixture showed no significant signal from hydroxyl groups in the 3,100-3,300 cm^{-1} region.

EXAMPLE 2

Ketal Composition B

200 ml of HEMA/IBOA copolymer (HEMA/IBOA = 37/63; M_n = 1,850; M_w = 2,830) 75% solution in aromatic hydrocarbon was placed into a 0.5 liter flask equipped with a magnetic stirrer, a thermocouple, and a downward condenser. The flask was flashed with nitrogen gas, and 75 ml of 2-methoxypropene was added. After 10 min. of stirring, 0.05 ml of phosphorous oxychloride was added. After 45 min. of stirring, 2 g of basic alumina was added. After 15 min. of stirring, the flask's contents were filtered and evaporated under 15 Torr vacuum at 60 °C to remove all volatile components. After 1 hr., the flask was filled with nitrogen, and its contents were transferred to an airtight container. IR Spectrum of the mixture showed no significant signal from hydroxyl groups in the 3,100-3,300 cm^{-1} region.

EXAMPLE 3

Ketal Composition C

0.6 liter of HEMA/IBOA copolymer (HEMA/IBOA = 37/63; M_n = 1,700; M_w = 2,450) 55% solution in aromatic hydrocarbon was placed into a 1 liter flask equipped with a magnetic stirrer, a thermocouple, and a downward condenser. The flask was flashed with nitrogen gas, and 180

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ml of 2-methoxypropene was added. After 10 min. of stirring, 0.05 ml of phosphorous oxychloride was added. After 15 min. of stirring, 0.5 ml of dry triethylamine was added. After 15 min. of stirring, the flask's contents were evaporated under 15 Torr vacuum at 40 °C to remove all volatile components. After 1 hr., the flask was filled with nitrogen, and its contents were transferred into an airtight container. IR spectrum of the mixture showed no significant signal from hydroxyl groups in the 3,100-3,300 cm⁻¹ region.

EXAMPLE 4

10 Coatings using Ketal Composition A

In a glass container, 26.76 g of Ketal Composition A was combined with 7.15 g of propylene glycol monomethylether acetate, 2.16 g of a 2% dibutyl tin dilaurate solution in ethyl acetate, and 1.1 g of a 10% BYK[®] 306 solution (polyether-modified dimethylpolysiloxane; Byk-Chemie) in xylene. To this mixture was added 17.38 g of Desmodur[®] N 3300A (hexamethylene diisocyanate trimer; Bayer Corp.) and 4.35 g of propylene glycol monomethylether acetate. This mixture was stirred, and 0.43 g of Nacure[®] XP-221 (a 70% solution of dodecylbenzene sulfonic acid in isopropanol; King Industries, Norwalk, Conn.) was added. The mixture was stirred and then drawn down to give coatings of about 2 mils (approximately 50 microns) in thickness. These coatings were baked at 60 °C for 30 min. After 24 hr., the coating demonstrated microhardness of 87 N/mm² and a swell ratio of 1.66. This solution was 73% solids with an initial Gardner-Holt viscosity of C that rose to J at 1 hr.

25 EXAMPLE 5

Coatings using unprotected HEMA/IBOA

In a glass container, 35.67 g of HEMA/IBOA (37/63) was combined with 3.32 g of propylene glycol monomethylether acetate, 1.97 g of a 2% dibutyl tin dilaurate solution in ethyl acetate, 1.0 g of a 10% BYK[®] 306 solution in xylene, and 0.39 g of a 10% acetic acid solution in butyl acetate. To this mixture was added 14.12 g of Desmodur[®] N 3300A and 3.53 g of propylene glycol monomethylether acetate. This mixture was stirred and then drawn down to give coatings of about 2 mils (approximately 50 microns) in thickness. These coatings were baked at

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60°C for 30 min. After 24 hr., the coating demonstrated a microhardness of 48 N/mm² and a swell ratio of 1.61. This solution was 66% solids with an initial Gardner-Holt viscosity of D and was gelled at 1 hr.

EXAMPLE 6

5 Three coating compositions were created. The first, Coating A, contained neither unprotected nor ketal-protected HEMA/IBOA. The second, Coating B, contained unprotected HEMA/IBOA. The third, Coating C, contained ketal-protected HEMA/IBOA (in the form of Ketal Composition B). To create the coating compositions, the components in

10 Table 2 were mixed. All three coatings contained a spiroorthocarbonate component (3,9-dibutyl-3,9-diethyl-1,5,7,11-tetraoxaspiro[5,5]undecane) as described in Experiment 2 of co-pending, co-owned application Serial No. 60/261,450, wherein 2-ethyl-1,3-hexanediol replaces 2-butyl-2-ethyl-1,3-propanediol.

15

Table 2

DESCRIPTION	Coating A	Coating B	Coating C
HEMA/IBOA (37/63)	0	4.93	0
Spiroorthocarbonate Compound (from Experiment 2 of Serial No. 60/261,450)	16.1	13.9	13.6
Ketal Composition B (from Example 2)	0	0	4.17
Propylene Glycol Monomethylether Acetate	1.63	0.49	1.08
2% Dibutyl Tin Dilaurate in Ethyl Acetate	5.69	5.69	5.69
10% BYK® 306 in Xylene	1.16	1.16	1.16
TOTAL	24.6	26.2	25.7

The components in Table 3 were mixed.

Table 3

DESCRIPTION	Coating A	Coating B	Coating C
Desmodur [®] Z 4470 BA ¹	4.20	4.01	4.06
Desmodur [®] N 3300A ²	26.4	25.2	25.5
Propylene Glycol Monomethylether Acetate	4.75	4.54	4.59
TOTAL	35.3	33.8	34.2

¹Isocyanate trimer of isophorone diisocyanate supplied by Bayer Corp.²Isocyanate trimer of hexamethylene diisocyanate supplied by Bayer Corp.

- 5 The resultant mixture for each coating of Table 3 was added to the resultant mixture for each coating of Table 2 and stirred. To these mixtures was added Nacure[®] XP-221. The final volumes of the three coating compositions are listed in Table 4.

10 Table 4

PART	Coating A	Coating B	Coating C
Table 1 Mixture	24.6	26.2	25.7
Table 2 Mixture	35.3	33.8	34.2
Nacure [®] XP-221	0.65	0.65	0.65
TOTAL	60.6	60.7	60.6

The three coating compositions were tested for viscosity, cotton tack free time, BK3 time, and water spot rating.

Gardner-Holt viscosity was measured under ASTM test D1545.

- 15 In order to determine cotton tack free time, a coated panel is allowed to dry for a set period of time (for example, 30 min.). A cotton ball is dropped from a height of 2.5 cm onto the surface of the panel, and the cotton ball is left on the surface for a set time interval (for example, intervals of 30 min.). The panel is then inverted. These steps are
- 20 repeated until the cotton ball drops off the panel on inversion (that is, the cotton tack free time).

The dry time of a coated layer of the composition was measured as BK3 surface dry time under ASTM test D5895.

- 25 Water spot rating is a measure of how well the coating composition is cross-linked early in the curing of the coating composition. Water spot damage on the coating composition indicates that the cure is not complete

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and further curing of the coating composition is needed before the coating composition can be wet sanded, buffed, or moved from the spray booth. The water spot rating is determined as follows. Panels coated with the test coating compositions were laid on a flat surface and deionized water was applied with a pipette at 1 hr. timed intervals. A drop of about 1.25 cm in diameter was placed on the panel and allowed to evaporate. The spot on the panel was checked for deformation and discoloration. The panel was wiped lightly with cheesecloth wetted with deionized water followed by lightly wiping the panel dry with the cloth. The panel was then rated on a scale of 1 to 10. A rating of 10 is best – no evidence of spotting or distortion of discoloration; rating 9 – barely detectable; rating 8 – slight ring; rating 7 – very slight discoloration or slight distortion; rating 6 – slight loss of gloss or slight discoloration; rating 5 – definite loss of gloss or discoloration; rating 4 – slight etching or definite distortion; rating 3 – light lifting, bad etching, or discoloration; rating 2 – definite lifting; and rating 1 – dissolving of the coating composition.

Table 5 shows the cure improvement found in Coating C because of the addition of the ketal group (Ketal Composition B) compared to Coating A without substantially harming potlife. Coating B versus Coating C is a comparison of the unprotected material (B) versus protected material (C). Coating C has better potlife at equal solids (75%) with similar cure.

Table 5

TEST	Coating A	Coating B	Coating C
% Solids	75	75	75
NCO/OH	1.40	1.03	1.03
Gardner-Holt 0 hr.	A	A	A
Gardner-Holt 1 hr.	A	E	B
Gardner-Holt 2 hr.	A	G	B
Cotton Tack Free Time (in hr.)	>7	5	6
BK3 (in min.)	458	465	283
Water Spot Rating after 4 hr.	1	8	8

EXAMPLE 7

For each of the coating compositions D-E, Portions 1, 2, and 3 were mixed together to form the coating composition as shown in Table 6.

Each of the coating compositions was applied with a doctor blade over a

- 5 separate phosphated cold roll steel panel primed with a layer of PowerCron® Primer supplied by PPG, Pittsburgh, Pa., to a dry coating thickness of 50 μ m, and air dried at ambient temperature conditions.

Table 6

Description	Coating D	Coating E
Portion 1		
IBOA/HEMA Acrylic-Unprotected Hydroxyl	30	0
Ketal Composition C (from Example 3)	0	30
Butyl Acetate	3.52	6.54
Flow Additive ¹	0.3	0.35
Catalyst Solution ²	1.5	5.27
Portion 2		
Tolonate® HDT ³	10.74	11.14
Portion 3		
25% Sulfonic Acid ⁴ in Isopropanol	0	0.76

¹20% BYK® 301 flow additive in propylene glycol monomethyl ether acetate supplied by BYK-Chemie

²1% di butyl tin dilaurate in methyl ethyl ketone supplied by Elf-Atochem North America, Inc. (Philadelphia, Pa.)

³Isocyanurate trimer of hexamethylene diisocyanate supplied by Rhodia, Inc. (Cranbury, N.J.)

⁴Aromatic Sulfonic acid; Nacure® XP-211 in isopropanol supplied by King Industries

The coating compositions were tested for BK3 time, BK4 time, water spot rating, Persoz Hardness, Fischer Hardness, MEK solvent resistance, viscosity, and time to gel.

- 20 BK3 time and water spot rating tests were performed as described in Example 5.

The dry time of a coated layer of the composition was also measured as BK4 surface dry time under ASTM test D5895.

- 25 The change in film hardness (Persoz Hardness) of the coating was measured with respect to time by using a Persoz hardness tester Model No. 5854 (ASTM D4366), supplied by Byk-Mallinckrodt, Wallingford, Conn. The number of oscillations (referred to as Persoz number) was recorded.

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Fischer Hardness was measured using a Fischerscope® hardness tester (the measurement is in N/mm²).

The MEK Solvent Resistance Test was performed by rubbing a coated panel (100 times) with an MEK (methyl ethyl ketone) soaked cloth using a rubbing machine, and excess MEK was wiped off. The panel was then rated from 1-10. Rating of 10 means no visible damage to the coating, 9 means 1 to 3 distinct scratches, 8 means 4 to 6 distinct scratches, 7 means 7 to 10 distinct scratches, 6 means 10 to 15 distinct scratches with slight pitting or slight loss of color, 5 means 15 to 20 distinct scratches with slight to moderate pitting or moderate loss of color, 4 means scratches start to blend into one another, 3 means only a few undamaged areas between blended scratches, 2 means no visible signs of undamaged paint, 1 means complete failure, that is, bare spots are shown. The final rating was obtained by multiplying the number of rubs by the rating.

Viscosity was measured on an ICI cone & plate viscometer in centipoises at 10,000 sec⁻¹ shear rate and/or in seconds using a Zahn #2 cup viscometer.

Time to Gel is the time it takes for a liquid coating to gel. The results of the tests are shown in Table 7.

Table 7

Test	Coating D	Coating E
Weight Solids (Theoretical)	65	65
ICI Viscosity (cps)	160	30
Time to Gel	84 min.	> 5 hr.
BK3 TIME (min.)	138	269
BK4 TIME (min.)	> 600	> 600
APP - WET	Good	Good
APP/Clarity -DRY	Good	Good
Water Spot Rating after 1 d.	9	8
MEK Rub after 1 d. at Room Temperature	850	750
Persoz Hardness after 1 d. at Room Temperature	77	33
Fischer Hardness after 1 d. at Room Temperature	16.1	11.58
Fischer Hardness after 7 d. at Room Temperature	73.5	41.1

- Comparing coatings D to E shows the significant advantages of using polymers with protected hydroxyl groups over the use of more conventional acrylics with hydroxyl groups in coatings. Coating E has significantly lower viscosity and longer time to gel than coating D with comparable cure.

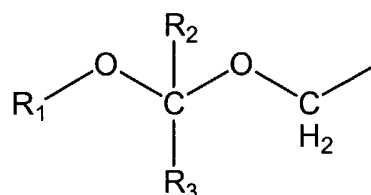
Claims

We Claim:

1. A coating composition comprising:

- 5 (a) a poly(meth)acrylate containing at least two hydroxyl groups blocked by hydrolyzable ketal groups; and
 (b) at least one polyisocyanate compound.

2. The coating composition of claim 1, wherein the hydrolyzable
 10 ketal groups are



wherein R₁ is an alkyl substituent of 1 to 6 carbon atoms; and
 R₂ and R₃ are, independently, alkyl substituents of 1 to 6 carbon
 atoms or cyclic substituents of 4 to 7 carbon atoms.

15

3. The coating composition of claim 1, wherein from about 30% to
 100% of the hydroxyl groups of the poly(meth)acrylate are blocked by
 hydrolyzable ketal groups.

20 4. The coating composition of claim 1, wherein the
 poly(meth)acrylate has a number average molecular weight from about
 200 to about 50,000.

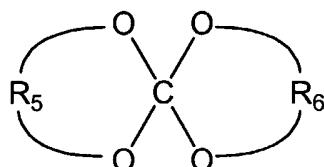
25 5. The coating composition of claim 1, wherein the at least one
 polyisocyanate compound is present in a molar equivalent ratio to the
 poly(meth)acrylate of from about 0.5 to about 5.

30 6. The coating composition of claim 1, further comprising at least
 one of a pigment, a filler, a solvent, a catalyst, and a conventional additive.

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7. The coating composition of claim 1, further comprising at least one of a spiroorthocarbonate compound and an amide acetal compound.

8. The coating composition of claim 7, wherein the
5 spiroorthocarbonate compound is



wherein R₅ and R₆ are, independently, hydrocarbylene or substituted hydrocarbylene bridging groups that have at least two bridging carbon atoms.

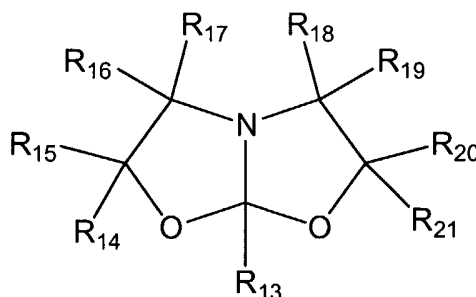
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9. The coating composition of claim 8, wherein R₅ and R₆ are, independently, -CR₇R₈-CR₉R₁₀-(CR₁₁R₁₂)_n-

wherein n is 0 or 1; and

R₇-R₁₂ are, independently, hydrogen, hydrocarbyl, or substituted
15 hydrocarbyl, provided that any two of R₇-R₁₂ vicinal or geminal to each other taken together may form a ring.

10. The coating composition of claim 7, wherein the amide acetal compound is



20

wherein R₁₃-R₂₁ are, independently, hydrogen, C₁ to C₂₂ alkyl, C₁ to C₂₀ alkenyl, C₁ to C₂₀ alkynyl, C₁ to C₂₀ aryl, C₁ to C₂₀ alkyl ester, or C₁ to C₂₀ aralkyl group; said alkyl, alkenyl, alkynyl, aryl, or aralkyl each optionally having at least one substituent selected from the group
25 consisting of halo, alkoxy, nitro, amino, alkylamino, dialkylamino, cyano, alkoxy silane and amide acetal (difunctional), and carbamoyl.

11. The coating composition of claim 1, further comprising at least one of an acrylic polymer, a polyester, a reactive oligomer, a non-alicyclic oligomer, a dispersed acrylic polymer, an aldimine, a ketimine, and a polyaspartic ester.

12. The coating composition of claim 1, wherein the coating composition is a clear coating composition, a pigmented composition, a basecoat composition, a monocoat composition, or a primer.

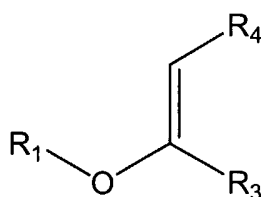
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13. A process for curing a coating composition comprising:

- (a) reacting by acid catalysis a poly(meth)acrylate containing at least two hydroxyl groups with at least one vinyl ether compound;
- (b) hydrolyzing the product of step (a) to unblock the poly(meth)acrylate containing at least two hydroxyl groups; and
- (c) reacting the unblocked poly(meth)acrylate containing at least two hydroxyl groups with at least one polyisocyanate compound.

20

14. The process of claim 13, wherein the at least one vinyl ether compound is



wherein R₁ is an alkyl substituent of 1 to 6 carbon atoms;

R₃ is an alkyl substituent of 1 to 6 carbon atoms or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond; and

R₄ is hydrogen, an alkyl substituent of 1 to 6 carbon atoms, or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond.

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15. The process of claim 14, wherein the at least one vinyl ether compound is 2-methoxypropene.

16. The process of claim 13, wherein from about 30% to 100% of the hydroxyl groups of the poly(meth)acrylate are blocked by hydrolyzable ketal groups.

17. The process of claim 13, wherein the poly(meth)acrylate has a number average molecular weight from 200 to 50,000.

10

18. A process for coating a substrate comprising:

- (a) applying a base coat to the substrate;
- (b) applying a clear coat over the base coat, wherein the clear coat comprises

15

- (i) a poly(meth)acrylate containing at least two hydroxyl groups blocked by hydrolyzable ketal groups, and

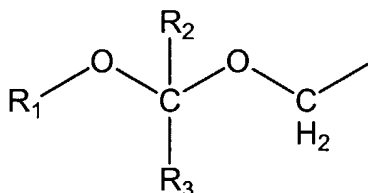
- (ii) at least one polyisocyanate compound;

(c) hydrolyzing the ketal groups of the poly(meth)acrylate containing at least two hydroxyl groups; and

20

(d) cross-linking the unblocked poly(meth)acrylates of step (c) through reaction with the at least one polyisocyanate compound.

19. The process of claim 18, wherein the hydrolyzable ketal groups are



wherein R₁ is an alkyl substituent of 1 to 6 carbon atoms; and

R₂ and R₃ are, independently, alkyl substituents of 1 to 6 carbon atoms or cyclic substituents of 4 to 7 carbon atoms.

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20. The process of claim 18, wherein from about 30% to 100% of the hydroxyl groups of the poly(meth)acrylate are blocked by hydrolyzable ketal groups.

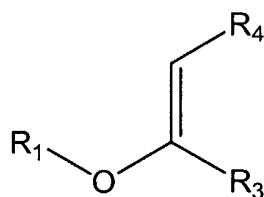
5 21. The process of claim 18, wherein the poly(meth)acrylate has a number average molecular weight from about 200 to about 50,000.

22. The process of claim 18, wherein the at least one polyisocyanate compound is present in a molar equivalent ratio to the
10 poly(meth)acrylate of from about 0.5 to about 5.

23. The process of claim 18, wherein the substrate is a motor vehicle or parts thereof.

15 24. A process for blocking the hydroxyl groups of poly(meth)acrylates comprising reacting by acid catalysis a poly(meth)acrylate containing at least two hydroxyl groups with at least one vinyl ether compound.

20 25. The process of claim 24, wherein the at least one vinyl ether compound is



wherein R₁ is an alkyl substituent of 1 to 6 carbon atoms;

25 R₃ is an alkyl substituent of 1 to 6 carbon atoms or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond; and

R₄ is hydrogen, an alkyl substituent of 1 to 6 carbon atoms, or a cyclic substituent of 4 to 7 carbon atoms including carbon atoms of the double bond.

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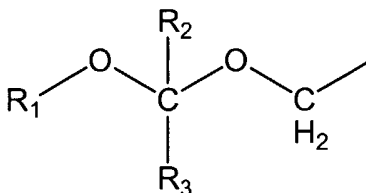
26. The process of claim 25, wherein the at least one vinyl ether compound is 2-methoxypropene.

27. The process of claim 24, wherein from about 30% to 100% of the hydroxyl groups of the poly(meth)acrylate are blocked by hydrolyzable ketal groups.

28. The process of claim 24, wherein the poly(meth)acrylate has a number average molecular weight from about 200 to about 50,000.

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29. A composition comprising a poly(meth)acrylate containing at least two hydroxyl groups blocked by hydrolyzable ketal groups comprising the formula



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wherein R_1 is an alkyl substituent of 1 to 6 carbon atoms; and R_2 and R_3 are, independently, alkyl substituents of 1 to 6 carbon atoms or cyclic substituents of 4 to 7 carbon atoms.

30. A substrate coated with the coating composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/008888

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L33/06 C08L75/04 C08F20/28

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 C08L C08F

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, PAJ, 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	US 5 241 002 A (OHASHI ET AL) 31 August 1993 (1993-08-31) claims 1-4	1-30
X	US 5 003 004 A (SIMMS ET AL) 26 March 1991 (1991-03-26) example comparison2 claims 1,8	1-30
A	US 5 571 884 A (GUO ET AL) 5 November 1996 (1996-11-05) examples 9-11 claims 1,4	1

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

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

31 May 2005

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/008888

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5241002	A	31-08-1993	JP	3099346 B2	16-10-2000
			JP	4041515 A	12-02-1992
			DE	69119151 D1	05-06-1996
			DE	69119151 T2	14-11-1996
			EP	0465835 A1	15-01-1992
			US	5194547 A	16-03-1993

US 5003004	A	26-03-1991	AT	84809 T	15-02-1993
			AU	591769 B2	14-12-1989
			AU	7155187 A	22-10-1987
			BR	8701765 A	02-02-1988
			CA	1323715 C	26-10-1993
			DE	3783642 D1	04-03-1993
			DE	3783642 T2	03-06-1993
			DK	198187 A	19-10-1987
			EP	0243120 A2	28-10-1987
			ES	2037710 T3	01-07-1993
			JP	7086161 B	20-09-1995
			JP	62252449 A	04-11-1987
			MX	168843 B	11-06-1993
			NO	871616 A	19-10-1987
			ZA	8702756 A	28-12-1988

US 5571884	A	05-11-1996	US	5475073 A	12-12-1995
			AT	177120 T	15-03-1999
			CA	2161819 A1	19-05-1996
			DE	69508038 D1	08-04-1999
			DE	69508038 T2	15-07-1999
			EP	0712872 A2	22-05-1996
			ES	2128000 T3	01-05-1999
			JP	8239429 A	17-09-1996
			US	5534598 A	09-07-1996
			US	5480943 A	02-01-1996
US	5525693 A	11-06-1996			