POLYMERIC PEEL-OFF COATING COMPOSITIONS AND METHODS OF USE THEREOF

Abstract

Compositions are provided for protecting exterior surfaces of automobiles and other products, or components of products, against abrasion, abrasive dust, water, acid rain, etc. Methods of producing protective compositions where the degree of adhesion of the composition may be simply governed are also provided. One composition comprises an acrylic copolymer, a heat reactive acrylic latex polymer, and a wax. The composition may additionally comprise a pigment and/or a thickener. Other compositions comprise a poly(carboxylic acid), a poly ether, and optionally a pigment. The compositions dry on the exterior surfaces to form a tough flexible coating that can be removed by mechanical peeling.
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Polymeric Peel-Off Coating Compositions and Methods of Use Thereof
CROSS REFERENCE TO RELATED APPLICATIONS
This is a continuation-in-part of U.S. patent application serial number 07/330,053, filed on October 27, 1994, which is incorporated herein by reference for all purposes.

BACKGROUND OF THE INVENTION
This invention relates to surface protective coatings and more specifically to peel-off (peelable) coatings effective for protecting exposed surfaces of various products and components. In particular, the coatings are suitable for protection of vehicles and vehicle components. This invention also relates to a method for producing peel-off coatings with variable degrees of adhesiveness.

The surface paint finishes of new vehicles are subject to a variety of injuries both during the assembly process and during transportation from the assembly plant to retail locations. These finishes are especially prone to damage in the first month following manufacture because the paint has not had sufficient time to cure. Typical sources of damage include acid rain, bird droppings and "rail dust", a cloud of hard, abrasive particles which rises from a rail bed as a train passes over the rails. Rail dust is an especially difficult problem for car manufacturers as many cars are transported from assembly plants or dockyards to retail markets by rail. The damage inflicted on the vehicles' surface finish during transit can be quite severe, even requiring shipment back to the assembly plant for complete repainting.

In addition to new vehicles, other products are also subjected to abrasive and deleterious conditions during transit, and during fabrication and assembly into other products. For instance, storm windows and other glass products must be specially protected to avoid scratching and marring during road and rail transit. Deck cargo is also susceptible to surface damage caused by salt water and other factors. Similarly, many products must be protected during fabrication or assembly by downstream manufacturers. For example, plastic laminates such as Formica® and other materials with high-gloss finishes such as bathroom fixtures and chrome plated or brass surfaces must be protected not only during shipping, but during installation or assembly into other products.
Various approaches have been utilized to protect the exposed surfaces of vehicles, vehicle components, and other products during manufacture and transportation. The simplest approach, physical protection with solid coatings (e.g., covering the vehicle or component with plastic or canvas) is effective, but it is labor intensive and therefore prohibitively expensive for mass shipments. Plastic sheeting, for example, is as much as ten times more expensive to use than chemical coating solutions due to higher material costs and the amount of labor needed to properly apply the sheetings. In addition it is difficult, time consuming and sometimes virtually impossible to apply solid sheet coatings to complex or convoluted surfaces.

Solution-type protective compositions are known, but have not found widespread use because of the damage which may possibly occur to the underlying or adjacent surfaces. These compositions are often difficult to remove from certain surfaces (e.g. underlying plastics). Also, traditional chemical methods suffer from high cost and the health and environmental dangers posed by solvent-based solutions and coatings.

Aqueous emulsion type coatings are also easily applied and eliminate the problems associated with various organic solvent systems. The most widely used are polyvinyl acetate emulsions or acrylic resin emulsions. These emulsions, however, are defective with respect to heat stability, resistance to water and stability in storage, and low drying velocity after application. For example, those disclosed in Japanese Patent Publication No. 14770/73 which are prepared by adding floury materials such as calcium carbonate and titanium dioxide, silicone resin and an aqueous emulsion of paraffin wax are defective in their poor stability when stored for a long time, and also in their low drying velocity after application. In addition many coatings tend to cross-link, particularly after exposure to sunlight (UV radiation) or elevated temperature, and become very difficult to remove.

It is therefore clear that a composition providing a protective coating of surfaces is needed which allows for easy, inexpensive and safe application and removal. Such a coating composition should provide for good water and heat resistance, rapid drying after application, good storage stability, and easy removal after long term exposure to adverse conditions (e.g., heat, moisture, and radiation). Easy removal would be facilitated by a high level of tensile and tear strength as well as good flexibility and toughness. The ease of removal by peeling is also a function of the adhesion of the coating to the substrate and of the degree of convolution of the substrate. (It is also
often more difficult to peel coatings off of highly convoluted substrates.) A method of producing peelable coatings with varying adhesive qualities that would allow the production of coating to be optimized for particular applications would be greatly desired.

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SUMMARY OF THE INVENTION

This invention includes peel-off surface protective coating compositions, methods of protecting surfaces utilizing these compositions, and a method of producing peel-off compositions in which the substrate adhesiveness can be systematically varied. In one embodiment a surface protective coating composition of the invention preferably includes an acrylonitrile copolymer, a heat reactive acrylic latex polymer, and a wax. The acrylonitrile copolymer may be provided as an aqueous ammoniacal dispersion before drying, while the heat reactive latex polymer may be provided as an aqueous emulsion before drying. The composition may further comprise a thickener. The composition may also further comprise a pigment.

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In one preferred embodiment, the composition includes between about 50 and about 90 weight percent an acrylonitrile copolymer; between about 40 and about 10 weight percent of a heat reactive acrylic latex polymer; and between about 1 and about 20 weight percent, of a wax. If a pigment is present, the pigment may comprise between about 1 and about 20 percent, by weight, of the composition. If a thickener is present, the composition may comprise between about 0.2 and about 3 weight percent, of the thickener. Where lecithin is present, the composition may comprise between about 1 to about 20 percent by weight of the composition.

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In a still more preferred embodiment, the composition includes about 71 percent acrylonitrile copolymer; about 23 percent heat reactive acrylic latex polymer; about 3 percent wax; about 2 percent pigment; and about 0.6 percent thickener. In another more preferred embodiment, the composition includes about 56.7 percent acrylonitrile copolymer; about 18.6 percent heat reactive acrylic latex polymer; about 2.7 percent wax; about 1 percent pigment; about 0.4 percent thickener; and about 4.0 percent lecithin.

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In another embodiment, this invention provides for a "simplified" peelable coating composition. The "simplified" coatings are premised, in part, on the surprising discovery that vinyl-acrylic copolymer emulsions, typically used for interior and exterior paints, and vinyl acetate-ethylene emulsions, typically used as adhesives, may also be
used as peelable protective coatings in a wide variety of contexts. Thus, in one embodiment, this invention provides a method of protecting a surface involving applying to the surface a protective coating composition comprising an emulsion selected from the group consisting of a vinyl-acrylic copolymer emulsion and a vinyl acetate-ethylene emulsion. The emulsion is preferably an aqueous emulsion, more preferably Flexbond 325, Flexbond 380, or AirFlex 320. The coating composition can also include a pigment (e.g. TiO₂).

In another embodiment, this invention provides for a method of producing a water insoluble peelable polymer protective coating. The method includes combining a poly(carboxylic acid), or a copolymer comprising a poly(carboxylic acid), and a polyether in the presence of an inhibitor, a compound that interacts with and blocks (e.g., by forming a salt) free carboxyl groups, to form a polymer combination; and then removing the inhibitor to form a peelable polymer coating in which the polyether reduces the adhesion between the poly(carboxylic acid) and a substrate thereby producing a polymer coating which may be removed from the substrate by peeling. The adhesion of these coatings is governed by the ratio of the polyether to the poly(carboxylic acid), or to the poly(carboxylic acid) constituent(s) of a copolymer.

In a preferred embodiment the method provides for a polymeric poly(carboxylic acid), or a poly(carboxylic acid) component of a copolymer, comprising a minimum of about 0.3 carboxylic acid groups per 100 D molecular weight of the poly(carboxylic acid), or the poly(carboxylic acid) component of a copolymer. The polyether preferably comprises at least 0.5 ether groups per 100 D molecular weight. It is also preferred that the poly(carboxylic acid), whether alone or present in a copolymer, and the polyether each polymer have a molecular weight of 1000 D or more.

In a preferred embodiment of the method, the combining step will involve adjusting the ratio of the polyether to the poly(carboxylic acid), or to the copolymer comprising a poly(carboxylic acid), such that the molar ratio of ether groups of the polyether to the carboxyl groups of the poly(carboxylic acid), or the poly(carboxylic acid) component of a copolymer, is about 0.1 to about 0.5, more preferably about 0.2 to about 0.4 and most preferably about 0.25 to about 0.3. The combining step may involve mixing an aqueous emulsion of the polyether with an aqueous dispersion of the poly(carboxylic acid) or poly(carboxylic acid) copolymer.
Where the poly(carboxylic acid) is a poly(acrylic acid) copolymer and the polyether is a polyethylene glycol, the poly(acrylic acid) comprises about 96 weight percent of the composition and the polyethylene glycol comprises about 3 weight percent of the composition. This provides a weight ratio of polyethylene glycol to ethylene acrylic copolymer of about 0.031. As indicated, however, the method provides for compositions comprising a molar ratio of ether group to carboxylic acid group ranging from about 0.1 to about 0.5, and more preferably about 0.2 to about 0.4 are also suitable. These ranges correspond approximately to a weight ratio of about 0.012 to about 0.062 and about 0.024 to about 0.050 respectively for the ratio of Union Carbide 20M to Adcote®.

The method may also involve combining a pigment with the poly(carboxylic acid), or copolymer comprising a poly(carboxylic acid), and the polyether. Where a pigment is present it comprises about 1 percent to about 10 percent, more preferably about 1 percent to about 5 percent, and most preferably about 1 percent to about 3 percent, by weight, of the composition.

This invention also provides for the water insoluble peelable polymer protective coatings made according to this method. As indicated above, these coatings comprise a poly(carboxylic acid) and a polyether where the ratio of the polyether to the poly(carboxylic acid) is selected such that the molar ratio of the ether groups of the polyether to the carboxylic acid groups of the poly(carboxylic acid) ranges from about 0.1 to about 0.5, more preferably from about 0.2 to about 0.4, and most preferably about 0.25 to 0.3. The poly(carboxylic acid) may be an ethylene acrylic copolymer, while the polyether may be polyethylene glycol. The composition may additionally comprise a pigment. In one preferred composition the poly(carboxylic acid) is an ethylene acrylic copolymer, the polyether is polyethylene glycol and the ratio of polyether to poly(carboxylic acid) is selected such that the ratio of the ether groups of the polyether to the carboxyl groups of the ethylene acrylic copolymer is about 0.1 to about 0.5. Particularly preferred is a composition comprising about 96 percent by weight ethylene acrylic copolymer, about 3 percent by weight polyethylene glycol, and about 1 percent by weight a pigment. One preferred pigment is titanium dioxide.

All weight percentages refer to the dry weight of the active material. Commercial products may contain water addition to the active material. The coatings of
this invention are compounded as aqueous solutions. Water may therefore comprise up to about 60 percent by weight of the composition before drying.

A preferred method of protecting surfaces according to this invention includes steps of applying the coating compositions to the surface to be protected in a substantially continuous film. The compositions are then dried to form a tough, yet flexible coating that may be subsequently removed from the surface by mechanical peeling when the coating is no longer required. By "substantially continuous film" it is intended to mean herein a film generally lacking pinholes through which water, oil, paint, dust, or other materials could reach the underlying surface. In a particularly preferred embodiment, the peel-off coatings of this invention are used to protect components of automobiles or automobile surface finishes.

The method can additionally include removing the protective composition from the protected surface. In a preferred embodiment, the composition is removed by peeling. The coatings of this invention will form a peelable film on a wide variety of surfaces. Thus, the protected surface can be a surface of an article of manufacture selected from the group consisting of a motor vehicle, motor vehicle components, bathroom and plumbing fixtures (e.g., sink, a bathtub, faucets, drains, chrome trim, etc.), glass (formed or in sheets), tools and machinery, marble (real or cultured), plexiglass and other plastics (formed, molded or sheet), laminates (e.g., Formica®, Wilson Art®) window and door assemblies, household appliances, aluminum components (e.g., tanks, wheels, trim), furniture (metal, plastic, or wood), plated or chromed parts (e.g., trim, moldings, bumpers), instrument panels, shelves, cabinets, and artwork (e.g. statues and sculptures).

In another embodiment, this invention provides for an article of manufacture having a surface coated with any of the above-described protective coating compositions, where the composition has dried to form a peelable protective coating. Coated articles of manufacture include, but are not limited to, any of the above-described articles of manufacture.

Finally, in another embodiment, this invention provides a method of transporting an article of manufacture. The method involves coating the article of manufacture with an of the protective coating compositions of this invention; transporting the article; and then removing the protective coating composition after transporting the article. In a preferred embodiment, the protective coating is removed by mechanical
peeling. The protective coating can be applied by any convenient means, and is preferably applied by spraying. This method of transporting is suitable for virtually any article of manufacture as described herein.

A further understanding of the nature and advantages of the invention described herein may be realized by reference to the remaining portions of the specification.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 illustrates removal of the protective coating from the surface of an automobile by peeling.

**DETAILED DESCRIPTION**

This invention provides improved surface protective coating compositions and methods for protecting surfaces utilizing these coatings. The coating compositions produce a film which adheres well to a surface to be protected, with few or no pinholes. Further, the coating film may be removed easily by simple mechanical peeling (i.e., by hand, or with the aid of a peeling tool).

In another embodiment, this invention provides for "simplified" peelable coatings comprising essentially a single component and therefore requiring little or no compounding.

This invention also provides for a method of producing peelable protective coatings that have varying degrees of adhesiveness to their substrates to which they are applied. This permits optimization of the coating to use in specific applications reflecting the complexity of the surface and the ease with which polymers adhere to the surface.

**Ambient Temperature Curing Peelable Protective Coating**

In an "ambient-temperature-curing" embodiment the surface protective coating composition of the invention preferably includes an acrylonitrile copolymer, a heat reactive acrylic latex polymer and a wax. Preferred acrylonitrile copolymers are chosen to simultaneously provide good surface adhesion, toughness, good solvent resistance (especially against water and oils), and high tensile and tear strength to facilitate subsequent removal by peeling. Additionally, flexibility is required to prevent cracking with temperature changes, surface deformation, and during peel-off. Such acrylic copolymers are commercially available, and a preferred copolymer suitable for
use in this invention is Carboxet® PL958 (B.F. Goodrich, Cleveland, Ohio, USA). Of course, other commercial acrylic copolymers may be substituted for Carboxet®. Such substitutions are well known to those of skill in the art and include, for example UCAR 441. In the ambient-temperature curing embodiment, the peelable protective coating will comprise between about 50 to 90 percent, more preferably between about 55 to about 75 percent, and most preferably about 71 percent or about 57 percent, by weight an acrylonitrile copolymer.

It was a surprising discovery of the present invention, that compounding of an acrylonitrile copolymer with a heat reactive acrylic latex polymer, and a wax provides a peel-off coating with substantially higher water resistance, tensile and tear strength, and longterm chemical stability (e.g. resistance to cross-linking) than known peel-off acrylic copolymers in their recommended formulations (e.g. Carboxet® PL958 when formulated as recommended in the Carboxet Technical Information Sheet).

Without being bound to a particular theory, it is believed that addition of a heat reactive acrylic latex polymer imparts significantly improved water resistance (both impermeability and resistance to dissolution). Such heat reactive acrylic latex polymers are commercially available and include, but are not limited to, materials such as Hycar® polymers (available from B.F. Goodrich, Cleveland Ohio, USA). Specific heat reactive acrylic latex polymers suitable for use in this invention include Hycar® 2679. The heat reactive latex polymer will be present at about 40 to 10 percent, more preferably about 30 to about 15 percent, and most preferably about 23 percent or about 18 percent by weight the of the protective coating composition.

Water impermeability is improved by the presence of a wax in the composition. It is believed that the wax helps to fill pinholes in the coating once it is applied to a surface and also prevents ozonolysis thereby increasing chemical stability of the coating composition. Additionally, the wax may facilitate separation from the underlying surface when the coating is later peeled off. Numerous waxes are suitable for use in this invention and include natural wax emulsions, synthetic waxes, silicones, and lecithin. Anionic wax emulsions are particularly suitable for use in this invention. One particularly preferred wax emulsion is an anionic wax emulsion comprising #1 carnauba and synthetic wax (e.g., #110 available from Michelman, Cincinnati, Ohio, USA). The wax may be present at about 1 to about 20 percent, more preferably about 3 to about 10 percent, and most preferably about 3 percent, by weight of the polymeric composition.
Similarly, lecithin may be present at about 1 to about 20 percent, more preferably about 2 to about 10 percent, and most preferably about 3 to 4 percent, by weight of the polymeric composition.

The composition may also include a pigment. The pigment is largely used for coloration. However, without being bound to a particular theory, it is believed that the pigment may also contribute to longterm chemical stability of the composition through ultraviolet-blocking. In addition, the pigment may contribute to mechanical strength and stability of the composition (when dried as a film) by acting as a filler. Finally, it is believed that the pigment also helps to decrease the water sensitivity of the composition.

The pigment is a finely divided material which contributes to optical and other properties of the coating. The pigment is insoluble in the coating medium (e.g. the aqueous dispersion) and is typically mechanically mixed with the coating and deposited when the coating dries. The physical properties of the pigment are not changed by incorporation in and deposition from the coating. Preferred pigments are inorganic "white" pigments although colored and certain organic pigments are also suitable. Inorganic white pigments suitable for this invention include, but are not limited to, titanium dioxide, white lead, zinc oxide, calcium carbonate, lithopone (a mixture of zinc sulfide and barium sulfate), zinc sulfide and antimony oxide. Titanium dioxide (e.g., Ti-Pure® R-902, DuPont Chemicals, Wilmington, Delware, USA) is particularly suitable for the present invention because of its high efficiency (unit opacity/weight). The pigment may be present at about 1 to about 20 percent, more preferably about 1 percent to about 5 percent, and most preferably about 2 percent, by weight, of the composition.

In another embodiment, the composition may include a thickener. The thickener may be utilized to regulate the viscosity and film thickness of the protective coating composition. Preferred thickeners show little or no water sensitivity. Thus silicone based thickeners are particularly suitable for this invention. Acrylic thickeners selected for low water sensitivity (e.g., Carbopol® EP1) are also suitable, as are associative thickeners. Alkali-swallowable acrylic emulsion thickeners capable of imparting shear-thinning characteristics (e.g., Carbopol® EP1) are particularly preferred for use in this invention. The thickener may be present at about 0.2 to 3 percent, more preferably at about 0.2 percent to about 1 percent, and most preferably at about 0.6 percent, by weight, of the composition.
The coating, while applied as a liquid, will form a substantially continuous solid sheet when dried. Drying may be accomplished at room temperature (i.e. by air drying). At a thickness of 3 mils (3/1000 inch) the coatings will typically dry in about one hour at an ambient temperature of 70°F. However, dry time may be reduced to just a few minutes using heat (e.g., using infra red heat lamps, hot air blowers, oven baking, or other heat sources). The coating is preferably stable up to a temperature of at least 300°F.

Simplified Peelable Protective Coating

In another embodiment, this invention provides a simplified peelable protective coating. The simplified peelable coatings are premised, in part, on the discovery that vinyl-acrylic copolymer emulsions typically used for interior and exterior paints, and vinyl acetate ethylene emulsions, typically used as adhesives, and compositions comprising such emulsions, can also be used as peelable protective coatings on a wide variety of surfaces. The emulsions, and compositions thereof, produce a film which adheres well to a surface to be protected, with few or no pinholes. Further, the coating film may be removed easily by simple mechanical peeling (i.e., by hand, or with the aid of a peeling tool).

It was a surprising discovery that the vinyl-acrylic copolymer emulsions and vinyl acetate ethylene emulsions can be used as removable (peelable) coatings. Vinyl-acrylic copolymer emulsions (e.g., Flexbond 325, or 380 from Air Products and Chemicals, Inc.) are typically used as principle components of interior and exterior paints (see, e.g. Flexbond 325 Technical Data Sheets available from Air Products, and Chemicals, Inc., Allentown, Pennsylvania, USA). As paint film formers, the vinyl-acrylic copolymer emulsions are designed to adhere strongly to the underlying surface and to resist subsequent removal. Easy peelability is not seen as a desirable property in a paint by those of skill in the art.

Similarly, vinyl-acetate ethylene emulsions (e.g., AirFlex™ emulsions by Air Products, and Chemicals, Inc.) are typically used as adhesives. In particular, they are used as adhesives where good water resistance is desired. Again, prior to this invention one of skill would not view these adhesive compositions as suitable candidates for peelable protective coatings.
The vinyl-acrylic copolymer emulsions and vinyl acetate ethylene emulsions can be used as peelable coatings "straight out of the can" with essentially no further compounding. The emulsions adequately wet and adhere to the surfaces to which they are applied and yet can be easily peled off without the use of releasing agents.

Thus in one preferred embodiment, the coatings use the emulsion in the form provided by the manufacturer and thus require no compounding at all.

In other preferred embodiments, e.g., where pigments or other components are added to the basic emulsion, compounding requires only simple admixing the components (or aqueous solutions, dispersions, etc. thereof) at substantially atmospheric pressure so as to form a substantially homogeneous mixture. Thus an advantage of the present invention is the relatively simple formulation and therefore low labor costs in producing the coatings.

Preferred emulsions for use in the methods of this invention include vinyl-acrylic emulsions typically used in paints and vinyl acetate-ethylene emulsions typically used for adhesives. Particularly preferred emulsions are aqueous emulsions and are well known to hose of skill in the art. Preferred vinyl-acrylic copolymer emulsions include, but are not limited to Flexbond 149, 150, 153, 165, 185, 325, 825, or 845 (Air Products and Chemicals, Inc.), with Flexbond 325 and Flexbond 380 being most preferred. Preferred vinyl acetate-ethylene emulsions include Airflex emulsions (e.g., 320, 400, 400H, 440, 440H, 401, 405, 410, 420, 421, etc.) and the like, with Airflex 320 being most preferred.

While it was a discovery of this invention that the above-described emulsions provide suitable peelable coatings without additives, the coating compositions may contain a variety of other materials such as cosolvents and coalescers, antioxidants, antiozonates, UV stabilizers, colorants, defoamers, corrosion inhibitors, and the like. In one preferred embodiment, the coating compositions can be compounded with a pigment. As described above, the pigment primarily provides coloration, however, it may also contribute to longterm chemical stability of the composition through ultraviolet-blocking. Suitable pigments are described above. When a pigment is present is can comprise up to about 30%, preferably up to about 10%, more preferably up to about 5% and most preferably up to about 2%, by weight of the coating composition.

In some contexts, it is desirable to add releasing agents to facilitate the peelability of the film. Suitable releasing agents include, but are not limited to natural
and synthetic waxes, wax emulsions (e.g., #110 available from Michelman, Cincinnati, Ohio, USA), lecithin, and surfactants with a hydrophile-lipophile balance (HLB) ranging from about 8 to about 10.

The coating composition can additionally include a thickener. Preferred thickeners show little or no water sensitivity. Suitable thickeners are well known to those of skill in the art and include, but are not limited to, Carbopol® EP1 Rohm & Haas 825, Montmorillonite, EZ-1, BFG, and the like. The thickener may be present at up to about 30%, by weight of the composition, but it is preferably present at up to about 5%, more preferably at up to about 3%, and most preferably at up to about 1%, by weight of the composition.

The "simplified" coating composition can be formulated with additional film formers in addition to the vinyl-acrylic copolymer or vinyl acetate-ethylene. Additional film formers suitable for use in this invention include, but are not limited to vinyl chloride copolymers (e.g. Carbobet 1957, B.F. Goodrich, Cleveland, Ohio, USA), acrylic latex (e.g., 1324, B.F. Goodrich), acrylic copolymer emulsions (e.g., Hycar 2679, B.F. Goodrich), and styrene acrylic copolymers (e.g., Carboset 958, B.F. Goodrich). When used, the additional film formers can be present at up to about 90 percent, by weight of the coating, however, in a preferred embodiment, they are present at less than about 50 percent, more preferably less than about 20 percent and most preferably less than about 10 percent, by weight of the composition.

The vinyl-acrylic copolymer and vinyl acetate-ethylene emulsions, while applied as a liquid, will form a substantially continuous solid sheet when dried. Drying may be accomplished at room temperature (i.e. by air drying). However, dry time may be reduced using heat (e.g., using infra red heat lamps, hot air blowers, oven baking, or other heat sources).

The vinyl-acrylic copolymer and vinyl acetate-ethylene emulsions used in the practice of the methods of his invention can be peeled off a wide variety of surfaces. These include, but are not limited to, metal, glass, plastic, painted wood, marble, laminate, plated surfaces, and the like.
Method of Producing Peelable Protective Coatings Having Varying Adhesive Properties

In another embodiment, this invention provides a method of producing peel-off protective coatings in which the adhesion between the coating and a surface to which the coating is applied may be continuously varied by a simple variation in the ratio of the two primary constituents of the coating. These coatings are based on the interaction between a polymer containing a multiplicity of ether groups, referred to herein as a polyether (e.g., poly(ethylene oxide), and a polymer comprising a multiplicity of carboxyl groups, referred to herein as a poly(carboxylic acid) (e.g., poly(acrylic acid)). As used herein the term poly(carboxylic acid) also includes copolymers in which at least one constituent polymer is a poly(carboxylic acid).

It has long been known that homopolymers of poly(ethylene oxide) and poly(acrylic acid), while completely soluble in water, immediately precipitate when they are combined together (Smith et al. Industrial & Engineering Chem., 51: 1361-1364 (1959). It was also recognized that the addition of an inhibitor gives an aqueous homogeneous solution which can be cast and insolubilized by drying. Id. Smith et al., suggested that these reactions are mediated by hydrogen bonding between the ether groups in the polyethylene oxide and the free carboxyl groups in the poly(acrylic acid) and suggested that this mechanism may be a generalized to poly(carboxylic acids) and polyethers.

It is a surprising discovery of the present invention that this same mechanism may be utilized to produce peelable protective coatings. In general, the method involves combining a poly(carboxylic acid), or a copolymer comprising a poly(carboxylic acid), and a polyether in the presence of an inhibitor to form a polymer combination; and then removing the inhibitor to form a peelable polymer coating.

Homopolymers and copolymers comprising poly(carboxylic acids) are generally known for their water solubility and their adhesive properties. Thus, they are typically used as simple adhesives or as components of polymer mixtures to promote the permanent bonding of the polymer mixture to a substrate. Thus, poly(carboxylic acids) and poly(carboxylic acid) copolymers, are often used in permanent coatings on substrates such as fabrics, metals and the like. These coating are typically very durable, extremely difficult to remove, often highly water sensitive, and typically make poor peel-off coatings.
Conversely, polyethers, while also water soluble, typically are very rigid polymers once cured and typically show very poor substrate adhesion. The publication by Smith et al. indicates that reaction of homopolymers of poly(carboxylic acids) in the absence of an inhibitor produces a gelatinous precipitate, while reaction of the two components in the presence of an inhibitor produces a polymeric composition suitable for casting and the production of polymer sheets. There was no indication that the combination of polyethers and poly(carboxylic acids) could produce a polymer composition having the flexibility, tensile strength, tear resistance, water resistance and adhesive characteristics required to produce a satisfactory peelable coating.

In addition, the compositions described by Smith et al. showed high levels of extractibles suggesting that they had relatively low water resistance (high water sensitivity). It was a surprising discovery of the present invention that compositions having low water sensitivity could be produced by the combination of a poly(carboxylic) acid and a polyether.

The method of the present invention is premised on the discovery that blocking the carboxyl groups in a poly(carboxylic acid) or a copolymer in which one of the components is a poly(carboxylic acid) reduces the ability of the poly(carboxylic acid) or the copolymer to adhere to a substrate. Without being bound to a particular theory, it is believed that the adhesion of the poly(carboxylic acid) or the copolymer comprising the poly(carboxylic acid) to the substrate is a function of the ability of the compound to wet the substrate to which it is applied. This wetting ability is believed to be an effect of the number of free carboxyl groups. Thus, this invention is premised, in part, on the discovery that blocking of varying numbers of carboxyl groups permits the production of poly(carboxylic acid) containing polymers that have continuously variable adhesion to a particular substrate depending on the ratio of the blocking moiety to poly(carboxylic acid) polymer or copolymer.

Of course, the use of inhibitors, such as ammonia, to form ammonia salts and thereby block the carboxyl groups of poly(carboxylic acids) has long been known. Subsequent removal of these inhibitors (blocking groups), as by heating or through chemical reactions, typically results in a tightly bound adhesive or a rigid (often cast) polymer. This invention is premised on the recognition, that blocking the carboxyl groups through hydrogen bonding to a long chain (e.g., molecular weight greater than about 1000 D) polymer (e.g. to a polyether) can result in the production of polymeric
compositions suitable for use as peel-off protective coatings. Varying the percentage of hydrogen bound carboxyl groups (e.g., by varying the ratio of the poly(carboxylic acid), or the poly(carboxylic acid) constituent of a copolymer, to the polyether) varies the adhesiveness of the resulting composition. Thus decreasing the ratio of polyether to poly(carboxylic acid), or copolymer comprising a poly(carboxylic acid), increases adhesion of the resulting composition to a substrate, while increasing the ratio of polyether to poly(carboxylic acid), or to copolymer comprising a poly(carboxylic acid), decreases the adhesion of the poly(carboxylic acid) to the substrate.

From the foregoing discussion it can be seen that there is an optimum range for the ratio of polyether to poly(carboxylic acid), or copolymer comprising a poly(carboxylic acid), in order to provide a polymer composition that may be used as a peelable coating. If too little polyether is present, the composition will adhere too tightly to the substrate to allow subsequent peeling. Conversely, if too much polyether is present, the composition will not adhere sufficiently to protect the underlying substrate and will show an unacceptably high level of water sensitivity. In a preferred embodiment, the weight ratio of the polyether to the poly(carboxylic acid), or to the copolymer comprising a poly(carboxylic acid), will be adjusted such that the molar ratio of ether groups of the polyether to the carboxyl groups of the poly(carboxylic acid), or the poly(carboxylic acid) component of a copolymer, is about 0.1 to about 0.5, more preferably about 0.2 to about 0.4 and most preferably about 0.25 to about 0.3.

One of skill in the art will appreciate that the number of ether groups in the polyether and of the carboxyl groups in the poly(carboxylic acid) or poly(carboxylic acid) component of a copolymer will vary with the particular polymers utilized.

Conversion of molar ratios into appropriate weight ratios of the polyether to the poly(carboxylic acid), or copolymer comprising a poly(carboxylic acid), may easily be determined by using the ratio of the number of carboxylic acid groups per unit molecular weight of the poly(carboxylic acid), or of the copolymer comprising a poly(carboxylic acid) component, and the ratio of the number of ether groups per unit molecular weight of the polyether.

Thus, for example, if the number of carboxylic acid groups per 100 molecular weight of the poly(carboxylic acid) or copolymer comprising a poly(carboxylic acid) is 0.3, and the number of ether groups per 100 molecular weight of the polyether is 0.6, then a weight ratio of 0.25 polyether to 1.0 poly(carboxylic acid) or copolymer
comprising a poly(carboxylic acid) will yield a ratio of 0.5 ether groups/carboxylic acid group.

In one particularly preferred embodiment, the method provides for a composition comprising an ethylene acrylic copolymer such as Mortons Adcote 50T4983 EAA dispersion as the poly(carboxylic acid) and a polyethylene glycol, such as Union Carbide 20M, as the polyether, the ratio of carboxyl groups to ether groups varies from about 0.25 to about 0.30. This corresponds to a composition comprising approximately 96 percent, by weight, the ethylene acrylic copolymer and approximately 3 percent, by weight the polyethylene glycol thus providing a weight ratio of polyethylene glycol to ethylene acrylic copolymer of about 0.031. As indicated above, however, compositions comprising a molar ratio of ether group to carboxylic acid group ranging from about 0.1 to about 0.5, and more preferably about 0.2 to about 0.4 are also suitable. These ranges correspond approximately to a weight ratio of about 0.012 to about 0.062 and about 0.024 to about 0.050 respectively for the ratio of Union Carbide 20M to Adcote®.

In another preferred embodiment, the method is performed using Carboset® 560 or Aqua® 220 as the poly(carboxylic acid) and Carbowax® 20M as the polyether. The Carboset® ranges from about 90 percent to about 99 percent, more preferably from about 95 percent to about 98 percent, and most preferably about 97.6 percent, by weight of the composition. The Aqua® 220 ranges from about 90 percent to about 99 percent, more preferably from about 93 percent to about 97 percent, and most preferably about 95 percent, by weight of the composition. In particularly preferred embodiments, the composition comprises about 97.6 weight percent Carboset® 560 and 2.4 weight percent Carbowax 20M or about 95 weight percent Aqua® 220 and about 5 weight percent Carbowax 20M.

As indicated above, the term "poly(carboxylic acid)", as used herein, refers to a polymer comprising a multiplicity of carboxyl groups and to a copolymer comprising at least one polymer that comprises a multiplicity of carboxyl groups. Poly(carboxylic acids) suitable for the practice of this invention include maleic acid copolymers, acrylic acid homopolymers acrylic acid copolymers, carboxyl derivatives of cellulose, and silicones. In a preferred embodiment, the poly(carboxylic acids) or the poly(carboxylic acid) component of a copolymer will have a minimum of about 0.3 carboxylic acid groups per 100 Daltons molecular weight of polymer bearing a multiplicity of carboxyl acid groups. In addition, it is preferred that the molecular
weight of the polyether and of the polymer bearing a multiplicity of carboxyl groups be of the order of 1000 D or more.

Also, as indicated above, the term "polyether", as used herein, refers to polymers containing a multiplicity of ether groups. Polyethers suitable for the practice of this invention include poly(vinyl ethers), cellulose ethers and hydroxyethylated polymers. Other polyethers useful for this invention are the branched polymers normally obtained by hydroxyalkylation of active hydrogen compounds such as triols and higher polyols, where three or more reactive hydrogen atoms serve as initiators for chain growth. Examples of such polyfunctional "starters" are glycosides, starch, cellulose, vegetable gums, polyfunctional amines and amides.

In general the hydrogen bonding (association reaction) between the poly(carboxylic acid) and the polyether takes place independently of other functional groups that may occur as relatively minor components, although possibly as repetitive units, either attached to or within the backbone polyether chains such as a carboxylic ester, inorganic ester, acetal, hemiacetal, and amide. Permissible groups are almost unlimited and include, but are not limited to, hydroxyl, aldehyde, carboxyl, halogen, and alkoxy.

The term inhibitor, as used herein refers to molecules capable of bonding to and thereby blocking the carboxyl groups of the polycarboxylic acids. The bonds may be ionic, covalent or hydrogen bonds. Carboxyl group inhibitors are well known to those of skill in the art and include, but are not limited to ammonia, methyl amines, pyridine, triethylamine, alkalais, and the like. In a preferred embodiment, the inhibitor will be ammonia or an ammonia containing compound that forms an ammonia salt with the poly(carboxylic acid). The inhibitor may be exogenous to the poly(carboxylic acid) and polyether composition and added as a separate ingredient. Alternatively, such inhibitors are often present in the commercial forms of poly(carboxylic acids) to confer dispersion stability. Thus such polymers are often sold as aqueous ammoniacal dispersions of the polymer. For example, Morton's Adcote® is an ammoniacal dispersion of an ethylene acrylic acid copolymer.

The term "removal", as used herein with reference to the removal of inhibitors, refers to the elimination of the interaction of the inhibitor with the carboxyl groups on the poly(carboxylic acid). This may be accomplished by actual removal of the inhibitor group from the composition or by reacting the inhibitor with another group
thereby preventing its interaction with the poly(carboxylic acid). Methods of removing various inhibitors are well known to those of skill in the art.

The method of removal will typically reflect the particular inhibitor used and the particular poly(carboxylic acid). Thus, for example, the inhibitor may be removed by adding a chemical that reacts with the inhibitor thereby preventing the formation of a salt with the poly(carboxylic acid). More commonly however an inhibitor is removed by volatilizing it and removing it in vapor phase. Thus, for example, where the inhibitor is ammonia the preferred removal usually involves drying or "curing" the composition. While drying may be effected at room temperature, drying often is preferably performed at an elevated temperature. The drying temperature is determined by the volatility of the inhibitor, the thermal stability of the other constituents of the coating material, the thickness of the coating, the thermal stability of the underlying material, and rapidity of film formation (drying) that is sought. Typically a higher temperature provides more rapid drying. Thus, in a preferred embodiment, drying is typically accomplished at a temperature of at about 160°F to about 200°F.

In a particularly preferred embodiment, the inhibitor will be removed after the protective composition is applied to the object or surface to be protected. Thus, for example, where the external finish of an automobile is to be protected, the composition will be applied to the surface of the automobile to form a substantially continuous film. The film will then be heated, thereby volatilizing the inhibitor dehydrating the composition and thus drying the composition, thereby inducing film formation to produce an insoluble polymer film bound to the coated surface.

The method described above may further involve combining a pigment with the poly(carboxylic acid) homopolymer, or copolymer, and the polyether. As with the ambient-temperature curing composition described above, a pigment may be used in this method largely for coloration. However, without being bound to a particular theory, it is believed that the pigment may also contribute to longterm chemical stability of the composition through ultraviolet-blocking. In addition, the pigment may contribute to mechanical strength and stability of the composition (when dried as a film) by acting as a filler. Finally, it is believed that the pigment also helps to decrease the water sensitivity of the composition. Suitable pigments for use in this invention are described above, with titanium dioxide (e.g., Ti-Pure® R-902, DuPont Chemicals, Wilmington, Delaware,
USA) being most preferred for this invention because of its high efficiency (unit opacity/weight).

When a pigment is used in the above described method it typically comprises about 1 percent to about 10 percent of the composition, more preferably about 1 percent to about 5 percent of the composition and most preferably about 1 percent to about 3 percent of the composition.

This method of producing a peelable coating offers the additional advantage of eliminating incompatible phases in the composition. Unlike other coatings that utilize waxes to regulate the adhesion of the polymer to the substrate and often leave oily or other incompatible residues, a peelable coating whose adhesive property is regulated by its polyether composition has no incompatible phase and therefore leaves no residue after it is peeled off of the substrate which it has been protecting.

One of skill in the art will appreciate that the above described method may be practiced in a number of formulations reflecting the medium in which the components are supplied. Thus, for example, the method may be practiced using the combination of powdered components or conversely by the combination of aqueous emulsions or dispersions. In a preferred embodiment, the method will be practiced using aqueous ammoniacal dispersions of the respective components.

**Peelable Protective Coatings Comprising a Polyether and a Poly(Carboxylic Acid)**

In another embodiment, this invention provides for water insoluble peelable polymer protective coatings produced according to the method described above. Thus the compositions comprise a poly(carboxylic acid), or a copolymer comprising a poly(carboxylic acid), that forms hydrogen bonds with a polyether. In a preferred embodiment the ratio of the polyether to the poly(carboxylic acid), or poly(carboxylic acid) containing copolymer, will be adjusted such that the ratio of ether groups of the polyether to the carboxyl groups of the poly(carboxylic acid), or the poly(carboxylic acid) component of a copolymer, is about 0.1 to about 0.5, more preferably about 0.2 to about 0.4 and most preferably about 0.25 to about 0.3. In a particularly preferred embodiment, the poly(carboxylic acid) or the poly(carboxylic acid) present in a copolymer and the polyether each have a molecular weight of at least about 1000 Daltons. It is also preferred that the polyether comprise a minimum of about 0.5 ether groups per 100 D molecular weight. One preferred polyether is polyethylene glycol.
Similarly, preferred poly(carboxylic acids), or poly(carboxylic acids) in a copolymer, will comprise a minimum of about 0.3 carboxylic acid groups per about 100 D molecular weight of the carboxyl group bearing polymer. One preferred poly(carboxylic acid) is an ethylene acrylic copolymer. The composition may also comprise a pigment as in the method described above.

Poly(carboxylic acids), copolymers comprising poly(carboxylic acids) and polyethers generally suitable for the practice of this invention are described above in the description of the method of producing peelable protective coatings comprising a poly(carboxylic acid), or a copolymer comprising a poly(carboxylic acid), and a polyether. In particularly preferred compositions, the polycarboxylic acid is an ethylene acrylic copolymer and the polyether is a polyethylene glycol. A particularly suitable poly(carboxylic acid) copolymer is Mortons Adcote 50T4983 EAA dispersion while a particularly suitable polyether is a polyethylene glycol, such as Union Carbide 20M.

A particularly preferred composition comprising the ethylene acrylic copolymer and polyethylene glycol has a ratio of carboxyl groups to ether groups from about 0.25 to about 0.30. This corresponds to a composition comprising approximately 96 percent, by weight, the Mortons ethylene acrylic copolymer and approximately 3 percent, by weight the Union Carbide 20M polyethylene glycol. This composition provides a weight ratio of polyethylene glycol to ethylene acrylic copolymer of about 0.031. As indicated above, however, compositions comprising a molar ratio of ether group to carboxylic acid group ranging from about 0.1 to about 0.5, and more preferably about 0.2 to about 0.4 are also suitable. These ranges correspond approximately to a weight ratio of about 0.012 to about 0.062 and about 0.024 to about 0.050 respectively for the ratio of Union Carbide 20M to Adcote®.

In another preferred embodiment, the compositions comprise Carboset® 560 or Aqua® 220 as the poly(carboxylic acid) and Carbowax® 20M as the polyether. The Carboset® ranges from about 90 percent to about 99 percent, more preferably from about 95 percent to about 98 percent, and most preferably about 97.6 percent, by weight of the composition. The Aqua® 220 ranges from about 90 percent to about 99 percent, more preferably from about 93 percent to about 97 percent, and most preferably about 95 percent, by weight of the composition. In particularly preferred embodiments, the composition comprises about 97.6 weight percent Carboset® 560 and 2.4 weight percent
Carbowax 20M or about 95 weight percent Aqua® 220 and about 5 weight percent Carbowax 20M.

The poly(carboxylic acid)/polyether coatings of this invention, while applied as a liquid, will form a continuous solid sheet when dried. Drying is preferably accomplished by heating. The coatings are preferably dried by heating at a temperature of about 160°F to about 200°F. At a thickness of 3 mils (3/1000 inch) the coatings will typically dry in minutes at a temperature of 160°F. Heating may be accomplished by the use of heat lamps, hot air blowers, oven baking, or other heating means well known to those of skill in the art. In a preferred embodiment, the coating, once cured, is stable up to a temperature of at least 300°F.

Uses of the Ambient Temperature Coating and of the Continuously Variable Adhesion Coatings

The protective coatings of this invention are peel-off (peelable) coatings once cured. A peel-off coating is one that may be removed from the surface it coats simply by mechanical peeling. A peel-off coating must possess sufficient flexibility, tensile and tear strength so that it does not fracture during peeling. The required flexibility, tensile and tear strength is a function of the strength of adhesion of the coating to the underlying surface. In a preferred embodiment, the adhesive ability of the film is sufficient to keep it completely bound to the underlying substrate throughout the period of protection and yet remain fully peelable at the time of removal. It is particularly preferred that the peel-off coating peel without trouble or without being torn in pieces. The coating when peeled should not remain partially unpeeled, leaving portions adhering to the substrate.

The peelable protective coatings comprising a polyether and a poly(carboxylic acid) are advantageous in that the degree of adhesion of the cured coating can be varied by varying the amount of the poly(carboxylic acid) relative to the polyether. Where an easily removed coating is desired, e.g. a highly convoluted surface or a substrate material that itself is only weakly bonded to an underlying material, a low-adhesion coating may be produced by increasing the polyether content of the coating composition. Conversely, a protective coating that is not easily removed is desired, e.g. where it is difficult to achieve a bond between the coating and the substrate, or where the
coated object is subject to considerable mechanical contact, a high-adhesion coating may be produced by reducing the polyether content of the composition.

The coatings of this invention are designed to be easily compounded out of readily available precursors. Thus another advantage of this invention is the relatively simple formulation and therefore low labor costs in producing the coatings. The coating compositions of the invention are made by conventional means, typically including steps of simply admixing the components (or aqueous solutions, dispersions, etc. thereof) at substantially atmospheric pressure so as to form a substantially homogeneous mixture. Care should be taken when mixing polyacrylics to produce a clear film (i.e., the polyacrylics should be miscible) so that the coating's mechanical properties are uniform.

This invention also includes a method of protecting surfaces wherein a substantially continuous film of any of the above-described surface protective coating compositions (i.e., the "ambient-temperature-curing", the "simplified", or the "carboxylic acid/polyether" composition) is applied to the surface to be protected. Such surfaces may include the exterior painted portions of a motor vehicle (e.g., a truck or automobile), or other vehicle. Other suitable surfaces include, but are not limited to surfaces of various articles of manufacture such as motor vehicle components, bathroom and plumbing fixtures (e.g., sink, a bathtub, faucets, drains, chrome trim, etc.), glass (formed or in sheets), tools and machinery, marble (real or cultured), plexiglass and other plastics (formed, molded or sheet), laminates (e.g., Formica®, Wilson Art®) window and door assemblies, household appliances, aluminum components (e.g., tanks, wheels, trim), furniture (metal, plastic, or wood), plated or chromed parts (e.g., trim, moldings, bumpers), instrument panels, shelves, cabinets, and artwork (e.g. statues and sculptures).

The coating composition is applied by one of a variety of techniques. Preferred techniques include roller application, brushing, and spraying of the surface with the coating composition. In some cases, additional water may be added for easier application, such as a 10% dilution. Thereafter, the coating composition may be applied with a pressure pot sprayer, preferably first in a thin mist and, thereafter, in a flow coat or thicker substantially continuous film. The coating composition is sprayed primarily on the surface to be protected, although overspray will not pose significant problems since any overspray may be readily removed with, for example, a wet towel or sponge or after curing by simply peeling the coating off the oversprayed surfaces. The resulting
masking coating composition is from about 0.1 to about 30 mils thick, preferably about 0.5 to about 5 mils thick, with a preferred thickness of about 3 mils. Of course the thickness will vary depending on the requirements of the user. Thus, for example, where cost is a concern, thin coatings (~0.1 to 1 mil) are used. Conversely, where impact resistance is desired the coatings may have a thickness in excess of 30 mils.

In other preferred embodiments, the coating composition is applied in an aerosol form to a surface. In such embodiments, the composition is stored in a container pressurized with any of a number of propellants including such environmentally benign materials as dimethyl ether, nitrogen, or carbon dioxide. Alternatively, the composition can be stored in a pump-type spray can.

The coating composition is then permitted to dry. If the coating is an "ambient-temperature-curing" coating it may be allowed to dry at atmospheric temperatures and pressures. Typically a 3 mil coating will dry (to the touch) in about 1 hour at an ambient temperature of 70°F and a 30% humidity. The drying time may be shortened to several minutes by elevating the temperature. If the coating is an "elevated-temperature curing" coating (such as the poly(carboxylic acid)/polyether coatings) heat must be applied to effect curing. Typically the coating must be heated to an ambient temperature of about 160°F to about 200°F. Under these conditions, a 3 mil (thickness) coating will cure in a few minutes.

One of skill in the art will recognize that the coatings of this invention may be utilized as part of a method of transporting vehicles, or other articles of manufacture, which protects the exterior painted portions of the vehicle, or other article, from scratches, soiling, or chemical attack. Generally, any of the above-described surface protective coating compositions is applied to the surface to be protected, the vehicle is transported, and the protective coating is then removed from the surfaces by simple mechanical peeling as illustrated in Figure 1. For example, cars to be loaded onto auto-carriers (either road or rail) are first cleaned of surface debris and dust and then coated with either of the surface protective coating compositions of the invention as described above. The cars are then transported to their destination where the surface protective coating is removed by peeling. Peeling may be accomplished by hand or with the aid of mechanical devices.

In addition, the coatings of the present invention may be applied to protect sensitive finishes on most any item exposed to deleterious environmental factors. For
example, the compositions of this invention can be used to coat motor vehicle
components, bathroom and plumbing fixtures (e.g., sink, a bathtub, faucets, drains,
chrome trim, etc.), glass (formed or in sheets), tools and machinery, marble (real or
cultured), plexiglass and other plastics (formed, molded or sheet), laminates (e.g.,
Formica®, Wilson Art®) window and door assemblies, household appliances, aluminum
components (e.g., tanks, wheels, trim), furniture (metal, plastic, or wood), plated or
chromed parts (e.g., trim, moldings, bumpers), instrument panels, shelves, cabinets, and
artwork (e.g. statues and sculptures). The articles of manufacture can be coated for
protection during routine handling (e.g. during manufacture, assembly, or end use) or
during transport and/or outdoor storage (particularly during winter). Further, vehicle
windshields and finishes can be protected against accumulations of insects and other bugs
in environments where they are a problem. It has also been found that coatings prepared
according to the present invention can be used to protect against graffiti. The paint from
graffiti is simply peeled off with the protective coating.

A particularly useful application of the present invention is to protect
wheels and tires of vehicles during normal use. In these embodiments, the coating
composition is applied to the wheel and/or tire in the manner described above.
Typically, a black layer of brake dust accumulates on wheels during normal operation.
Because the wheels and tires are coated with the removable coating composition of this
invention, the brake dust (and other accumulated dirt) is easily removed by peeling off
the coating. The resulting clean wheel and tire can be re-coated with another layer of
the coating composition.

Any of the coating compositions of this invention can also be used
as a sacrificed layer to protect various items that are not necessarily associated with
transportation. For example, various building fixtures found in bathrooms and most
other rooms can be protected. Bathtubs, shower stalls, bathroom tiles and floors, etc.
are all adversely affected by steam, mineral deposits from water, and soap scum. Much
labor is expended by homeowners or maintenance personnel to remove bathroom
deposits. The acrylic-based removable coating compositions of this invention are used to
temporarily protect bathroom fixtures during normal use. When it is time to clean the
bathroom, the coating is simply peeled from the underlying surfaces thereby removing
the coating composition together with the accumulated dirt.
The coatings of this invention are tough, relatively thick, and provide a high degree of resistance to mechanical abrasion. They are therefore particularly suitable for protecting component parts during installation. Thus, for example, in bathroom components such as bathtubs, toilets, sinks and shower units are often damaged by contact with abrasives during installation. Workers often stand in or on these items and scratch their surfaces. Such damage is especially common when there is dirt or gravel in the tub and a worker standing in the tub, on top of the gravel grinds the gravel into the tub’s surface with his feet. Additionally, because these items are typically left outside on the job site, the coatings’ water resistant feature becomes very important.

Other fixtures that can be protected by this invention include banisters, electrical light switch plates, door knobs, windows, etc. Particularly preferred surfaces for coating include metals such as brass or chrome, ceramic, glass, and plastic laminates such as formica.

Similarly the coatings of this invention may protect component parts during assembly in an industrial setting. Thus, for example, component plastic bumpers may be coated to protect against scratching and other damage from the time they are produced, through the car assembly process, and until the car arrives at the dealership. The coatings may provide a rough easily gripped surface and therefore utilized to facilitate the gripping and manipulation of highly machined components without component scratching or other damage.

The coatings may also be used to maintain clean component parts until the time of use. Thus the coatings may be utilized to allow easy removal of accumulated layers of oil and grit, often present in factory environments, from metallic components awaiting assembly. The coating may be quickly peeled from the component just before use thereby removing the accumulated contaminating materials.

Because of their toughness, the coatings of this invention are also suitable for coating and protecting floor surfaces in highly trafficked areas. The compositions may be compounded with various particulate materials to enhance traction.

In addition, because of their stability to high temperatures (e.g. 200°F) for prolonged periods of time, the coatings of this invention are suitable for use as peelable paint-booth coatings.

Furniture may also be protected by the methods of this invention. In particular, lawn furniture and umbrellas can be protected by the coating compositions of
this invention. In preferred embodiments, an ultra-violet radiation blocker is added to the coating composition to protect outdoor furniture and umbrellas from the effects of sunlight. Automobile upholstery can also be protected by the methods of this invention.

It should be noted that many of the protected surfaces tend to flex during normal use. For example, tires continually compress as they roll. In addition, pliable lawn furniture stretches when used. For these applications, the coating compositions of this invention must be sufficiently pliable to ensure that they do not crack during flexure.

It should be noted that the coating composition also protects surfaces from the deleterious effects of ozone, the ubiquitous pollutant formed in smog. It is known that ozone attacks rubbers and other elastomers, causing them to crack. By applying the coating compositions of this invention, cracking associated with ozone is reduced.

**EXAMPLES**

The following examples are intended to illustrate the present invention and are not intended to limit the scope of the invention in any way.

**EXAMPLE 1**

**Ambient Temperature Curing Peelable Protective Coating**

The components of Formula 1 and Formula 2, listed in Table 1, where each combined at room temperature and at atmospheric pressure by slow stirring to form two surface protective coating compositions of this invention.
Table 1. Composition of two preferred ambient temperature curing peelable protective coatings.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formula 1 Amount (Wt. %)</th>
<th>Formula 2 Amount (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Acrylic Copolymer Emulsion (B.F. Goodrich Carboset® PL958)</td>
<td>56.7</td>
<td>70.80</td>
</tr>
<tr>
<td>Heat Reactive Acrylic Latex Polymer (B.F. Goodrich Hycar® 2679)</td>
<td>18.6</td>
<td>23.20</td>
</tr>
<tr>
<td>Wax (Michelman 110)</td>
<td>2.7</td>
<td>3.40</td>
</tr>
<tr>
<td>Titanium Dioxide (Dupont Ti-Pure® R902)</td>
<td>1.0</td>
<td>2.00</td>
</tr>
<tr>
<td>Thickener - Acrylic Polymer Emulsion (B.F. Goodrich Carbopol® EP1)</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Lecithin (Central soya, Lp-250)</td>
<td>4.0</td>
<td>--</td>
</tr>
<tr>
<td>Water</td>
<td>16.6</td>
<td></td>
</tr>
</tbody>
</table>

*All percentages refer to the dry weight of the active material. Listed commercial products may contain water addition to the active material.

The coatings were applied to test surfaces by dipping, spraying or brushing. Test surfaces included ceramic tile, panels finished with an automotive paint finish, various types of plastic, glass, and aluminum to form a 3 mil coating. The coating was allowed to dry at room temperature for about 1 hour. The dried coating showed a high degree of resistance to water and other solvents. The coating was subsequently removed from the test surface by peeling it off in essentially one piece.

EXAMPLE 2

Peelable Protective Coatings Comprising a Polyether and a Poly(Carboxylic Acid)

The components shown in Table 2 were combined at room temperature and at atmospheric pressure by slow stirring to form a suitable surface protective coating composition of the invention.
Table 2. A preferred peelable coating comprising a polyether and a poly(carboxylic acid).

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (Wt. %)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Acrylic Copolymer (Copolymer Dispersion Mortons 4883)</td>
<td>96.00</td>
</tr>
<tr>
<td>Polyethylene Glycol (Union Carbide 20M)</td>
<td>3.00</td>
</tr>
<tr>
<td>Titanium Dioxide (DuPont Ti-Pure ® R902)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*All percentages refer to the dry weight of the active material. Listed commercial products may contain water addition to the active material.

The coating was applied to various test surfaces as described in Example 1 and allowed to dry at a temperature of about 160° to 170°F. The dried coating showed a high degree of resistance to water and other solvents. The coating was subsequently removed from the test surface by peeling it off in essentially one piece.

EXAMPLE 3

"Simplified" Peelable Coating

A coating consisting of Flexbond 325 (Air Products, and Chemicals, Inc., Allentown, Pennsylvania, USA) or Flexbond 380 (Air Products and Chemicals, Inc.) was applied to a test surface by spraying. Test surfaces included ceramic tile, panels finished with an automotive paint finish, various types of plastic, glass, and aluminum to form a 5 mil coating. The coating was allowed to dry at room temperature for about 24 hours. The dried coating showed a high degree of resistance to water and other solvents. The coating was subsequently removed from the test surface by peeling it off in essentially one piece as illustrated in Figure 1.

The advantages of the invention will now be apparent. The invention provides a surface protective coating composition and a method of protecting surfaces which is easy and cost-effective. Using the method of the invention, large surface areas or many surfaces may be protected from damage quickly, easily, cheaply, and safely. Although certain embodiments and examples have been used to describe the invention, it will be apparent to those skilled in the art that various changes may be made to those embodiments and/or examples without departing from the scope of the invention. All patents and references are incorporated herein by reference for all purposes.
WHAT IS CLAIMED IS:

1. A method of protecting surfaces comprising applying a surface protective coating composition to said surface, said step of applying resulting in a substantially continuous film of said surface protective coating composition and said surface protective coating composition comprising:
   an acrylic copolymer;
   a heat reactive acrylic latex polymer; and
   a wax.

2. The method of claim 1, wherein said water solubilized acrylonitrile acrylic latex copolymer is an aqueous ammoniacal dispersion.

3. The method of claim 1, wherein said heat reactive latex polymer is an aqueous emulsion.

4. The method of claim 1, wherein said wax is selected from the group consisting of a natural wax emulsion, a polyethylene wax and lecithin.

5. The method of claim 1, wherein said coating composition further comprises a pigment.

6. The method of claim 1, wherein said composition further comprises a thickener.

7. The method of claim 1, wherein said applying comprises air drying said composition at room temperature.

8. The method of claim 1, wherein said acrylonitrile acrylic latex copolymer forms about 50 percent to about 90 percent of the composition by weight;
   said heat reactive acrylic latex polymer forms about 40 percent to about 10 percent of the composition by weight; and
said wax forms about 1 percent to about 20 percent of the composition by weight; and

9. The method of claim 8, wherein

said acrylonitrile acrylic latex copolymer forms about 71 percent of the composition by weight;
said heat reactive acrylic latex polymer forms about 23 percent of the composition by weight;
said wax forms about 3 percent of the composition by weight; and wherein said composition further comprises a pigment forming about 2 percent of the composition by weight and a thickener forming about 0.6 percent of the composition by weight.

10. The method of claim 8, wherein

said acrylonitrile acrylic latex copolymer forms about 56.7 percent of the composition by weight;
said heat reactive acrylic latex polymer forms about 18.6 percent of the composition by weight;
said wax forms about 2.7 percent of the composition by weight; and wherein said composition further comprises a pigment forming about 1.0 percent of the composition by weight; a thickener forming about 0.4 percent of the composition by weight; and lecithin forming about 4% of the composition by weight.

11. The method of claim 1, wherein said surfaces comprise surfaces of an automobile.

12. A method of protecting surfaces comprising applying a surface protective coating composition to said surface, said applying resulting in a substantially continuous film of said surface protective coating composition and said surface protective coating composition comprising:
a poly(carboxylic acid); and
a polyether;
wherein said protective composition may be removed by peeling.

13. The method of claim 12, wherein said poly(carboxylic acid) is an ethylene acrylic copolymer.

14. The method of claim 12, wherein said polyether is a polyethylene glycol.

15. The method of claim 12, wherein said composition further comprises a pigment.

16. The method of claim 12, wherein the amounts of the poly(carboxylic) acid and the polyether are adjusted such that the molar ratio of the ether groups of said polyether to the carboxyl groups of poly(carboxylic acid) is about 0.1 to about 0.5.

17. The method of claim 16, wherein said poly(carboxylic acid) is an ethylene acrylic copolymer; and said polyether is a polyethylene glycol.

18. The method of claim 17, wherein the ethylene acrylic copolymer forms about 96 percent of the composition by weight; the polyethylene glycol forms about 3 percent of the composition by weight; and wherein said composition further comprises a pigment forming up to about 1 percent of the composition by weight.

19. The method of claim 12, wherein said surfaces comprise surfaces of an automobile.

20. The method of claim 12, wherein said method further comprises the step of removing said protective coating composition when said protective coating is no longer required, said removing comprising peeling off said protective coating composition.
21. A peel-off surface protective composition comprising:
   a) an acrylonitrile copolymer;
   b) a heat reactive acrylic latex polymer; and
   c) a wax.

22. The composition of claim 21, wherein said wax is selected from the group consisting of a natural wax emulsion, a polyethylene wax and lecithin.

23. The composition of claim 21, further comprising a pigment.

24. The composition of claim 21, further comprising a thickener.

25. The composition of claim 21, wherein:
   said acrylonitrile acrylic latex copolymer forms about 50 to 90 percent of the composition by weight;
   said heat reactive acrylic latex polymer forms about 40 to 10 percent of the composition by weight; and
   said wax forms about 1 to 20 percent of the composition by weight.

26. The composition of claim 25, wherein
   said acrylonitrile acrylic latex copolymer forms about 71 percent of the composition by weight;
   said heat reactive acrylic latex polymer forms about 23 percent of the composition by weight;
   said wax forms about 3 percent of the composition by weight;
   said composition further comprising a pigment forming about 2 percent of the composition by weight and a thickener forming about 0.6 percent of the composition by weight.

27. A method of producing a water insoluble peelable polymer protective coating, said method comprising:
combining a poly(carboxylic acid) and a polyether in the presence of an inhibitor to form a polymer combination; and removing said inhibitor to form a peelable polymer coating wherein said polyether reduces the adhesion between said poly(carboxylic acid) and a substrate thereby producing a polymer coating which may be removed from said substrate by peeling and wherein said adhesion is governed by the molar ratio of the carboxyl groups in said poly(carboxylic acid) to the ether groups in said polyether.

28. The method of claim 27, wherein said combining comprises adjusting the amounts of polyether and poly(carboxylic acid) such that the molar ratio of the ether groups in said polyether to the carboxyl groups of said poly(carboxylic acid) ranges from about 0.1 to about 0.5.

29. The method of claim 27, wherein said polymeric poly(carboxylic) acid is selected from the group consisting of maleic acid copolymers, acrylic acid homopolymers, acrylic acid copolymers, carboxyl derivatives of cellulose, carboxyl derivatives of silicones, polyvinyl oxides, and pyridines.

30. The method of claim 27, wherein said polyether is selected from the group consisting of poly(vinyl ethers), cellulose ethers, poly(ethylene oxides), and pyroliidine.

31. The method of claim 27, wherein said inhibitor is selected from the group consisting of ammonia, an alkalai, a pyridine, a methylamine, and a triethylamine.

32. The method of claim 27, wherein said combining step further comprises combining a pigment in said polymer combination.

33. The method of claim 27, wherein:
said poly(carboxylic acid) is an ethylene acrylic copolymer; and said polyether is a polyethylene glycol;
wherein the molar ratio of the ether groups of said polyether to the carboxyl groups of said ethylene acrylic copolymer is about 0.1 to about 0.5.

34. A peel-off surface protective composition comprising a poly(carboxylic acid) and a polyether where the ratio of the polyether to the poly(carboxylic acid) is selected such that the molar ratio of the ether groups of said polyether to the carboxyl groups of said poly(carboxylic acid) ranges from about 0.1 to about 0.5.

35. The composition of claim 34, further comprising a pigment.

36. The composition of claim 34, wherein:
said poly(carboxylic acid) is an ethylene acrylic copolymer; and
said polyether is a polyethylene glycol;
wherein the molar ratio of the ether groups of said polyether to the carboxyl groups of said ethylene acrylic copolymer is about 0.1 to about 0.5.

37. The composition of claim 36, wherein the ethylene acrylic copolymer forms about 96 percent of the composition by weight;
the polyethylene glycol forms about 3 percent of the composition by weight; and said composition further comprises a pigment present at about 1 percent of the composition by weight.

38. A method of protecting a surface, said method comprising:
applying to said surface a coating composition comprising an emulsion selected from the group consisting of a vinyl-acrylic copolymer and a vinyl acetate ethylene emulsion; and
drying said coating composition to form on said surface a substantially continuous film.

39. The method of claim 38, wherein said emulsion is an aqueous emulsion.
40. The method of claim 38, wherein said emulsion is selected from the
group consisting of FlexBond 325, FlexBond 380, and Airflex 320.

41. The method of claim 38, wherein said coating composition further
comprises a pigment.

42. The method of claim 38, wherein said applying is by a means
selected from the group consisting of a sprayer, a brush, a roller, and a doctor bar.

43. The method of claim 38, wherein said applying comprises air
drying said composition at room temperature.

44. The method of claim 38, wherein said method further comprises
removing said composition from said surface.

45. The method of claim 38, wherein said removing comprises peeling
said composition from said surface.

46. The method of claim 38, wherein said surface is a surface of an
article of manufacture selected from the group consisting of a motor vehicle, a motor
vehicle component, a bathroom fixture, a plumbing fixtures, a tool, a machine, a
laminated countertop, a table top, a window assembly, a door assembly, a stove, a
refrigerator, a microwave ovens, an aluminum tank, a wheel, furniture, a plated or
chromed part, a bumper, an instrument panel, a shelf, and a cabinet.

47. A composition comprising an article of manufacture having a
surface coated with a composition comprising an emulsion selected from the group
consisting of a vinyl-acrylic copolymer emulsion and a vinyl acetate-ethylene emulsion,
wherein said emulsion has dried to form a peelable protective coating.

48. The composition of claim 47, wherein said emulsion is an aqueous
emulsion.
49. The composition of claim 47, wherein said emulsion is selected from the group consisting of a motor vehicle, a motor vehicle component, a bathroom fixture, a plumbing fixtures, a tool, a machine, a laminated countertop, a table top, a window assembly, a door assembly, a stove, a refrigerator, a microwave ovens, an aluminum tank, a wheel, furniture, a plated or chromed part, a bumper, an instrument panel, a shelf, and a cabinet.

50. The composition of claim 47, wherein said emulsion is selected from the group consisting of FlexBond 325, FlexBond 380, and Airflex 320.

51. The composition of claim 47, wherein said composition further comprises a pigment.

52. The composition of claim 47, wherein said article of manufacture is selected from the group consisting of a motor vehicle, a motor vehicle component, a bathroom fixture, a plumbing fixtures, a tool, a machine, a laminated countertop, a table top, a window assembly, a door assembly, a stove, a refrigerator, a microwave ovens, an aluminum tank, a wheel, furniture, a plated or chromed part, a bumper, an instrument panel, a shelf, and a cabinet.

53. A method of transporting an article of manufacture, said method comprising the steps of:
   i) coating said article of manufacture with a protective coating composition comprising an emulsion selected from the group consisting of a vinyl-acrylic copolymer emulsion and a vinyl acetate-ethylene emulsion;
   ii) transporting said article; and
   iii) removing said protective coating composition after transporting said article.

54. The method of claim 53, wherein said removing is by mechanical peeling.

55. The method of claim 53, wherein said coating is by spraying.
56. The method of claim 53, wherein said protective coating composition further comprises a pigment.

57. The method of claim 53, wherein said article of manufacture is an automobile.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
   IPC(6) : Please See Extra Sheet.
   US CL : 524/145, 277, 279, 521, 523, 487; 428/520, 522, 523
   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)
   U.S. : 524/145, 277, 279, 521, 523, 487; 428/520, 522, 523

   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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>US, A, 3,653,894 (LEVY ET AL) 04 April 1972, columns 3-5 and examples.</td>
<td>1-11, 21-26, 38-52</td>
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<td>Y</td>
<td>US, A, 5,143,949 (GROGAN ET AL) 01 September 1992, columns 3-5 and examples.</td>
<td>12-20, 27-33, 34-37</td>
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☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

Date of the actual completion of the international search: 25 JANUARY 1996

Date of mailing of the international search report: 07 FEB 1996

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-2330

Authorized Officer
JEFFREY C. SMITH
Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet) (July 1992)
INTERNATIONAL SEARCH REPORT

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<tr>
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<td>This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:</td>
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<tr>
<td>1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:</td>
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<tr>
<td>2. ☐ Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:</td>
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<tr>
<td>3. ☐ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).</td>
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<td>This International Searching Authority found multiple inventions in this international application, as follows:</td>
</tr>
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<td>Please See Extra Sheet.</td>
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<th>Description</th>
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<td>1. ☐</td>
<td>As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.</td>
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<tr>
<td>2. ☐</td>
<td>As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.</td>
</tr>
<tr>
<td>3. ☐</td>
<td>As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:</td>
</tr>
<tr>
<td>4. ☐</td>
<td>No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:</td>
</tr>
</tbody>
</table>

Remark on Protest ☐ The additional search fees were accompanied by the applicant’s protest.  
☐ No protest accompanied the payment of additional search fees.
A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):
CO8L 33/02, 33/20, 91/08, 91/06; CO8K 5/01, 5/52; B32B 27/30, 27/32

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.
Group I, claim(s)1-11, drawn to a process of protecting surfaces employing a composition of an acrylic copolymer, an heat reactive acrylic latex polymer, and a wax,
Group II, claim(s)12-20, drawn to a process of protecting surfaces employing a composition of an poly(carboxylic acid) and a polyether
Group III, claim(s) 21-26, drawn to a peel-off surface protective a composition of an acrylonitrile copolymer, an heat reactive acrylic latex polymer, and a wax.
Group IV, claim(s) 27-33, drawn to a method of producing a peelable polymer protective coating.
Group V, claim(s)34-37, drawn to a peel-off surface protective composition of an poly(carboxylic acid) and a polyether.
Group VI, claim(s) 38-46, drawn to process of protecting surfaces employing a composition of an vinyl-acrylic copolymer and vinyl acetate ethylene emulsion.
Group VII, claim(s) 47-52, drawn to an article of manufacture.
Group VIII, claims 53-57, drawn to method of transporting.

The inventions listed as Groups I-VIII do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:
The special technical featureas defined in Group I is a composition of an acrylic copolymer, an heat reactive acrylic latex polymer, and a wax. The special technical feature of Group I is not novel as exhibited by LEVY (US 3,653,894). Groups II-VIII employ different compositions and/or processing conditions which do not correspond to the special technical feature of Group I.