⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 148 718**
A2

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **84630169.5**

㉒ Date of filing: **09.11.84**

(51) Int. Cl.⁴: **B 05 D 7/26**, B 05 D 5/06

㉚ Priority: **28.11.83 US 555721**

㊸ Date of publication of application: **17.07.85**
Bulletin 85/29

(84) Designated Contracting States: **BE DE FR GB IT NL SE**

(71) Applicant: **INMONT CORPORATION, 1255 Broad Street,**
Clifton New Jersey 07015 (US)

(72) Inventor: **Panush, Sol, 28670 Oak Crest Drive,**
Farmington Hills Michigan 48018 (US)

(74) Representative: **Schmitz, Jean-Marie et al, Office**
Dennemeyer S.à.r.l. 21-25 Allée Scheffer P.O. Box 41,
L-2010 Luxembourg (LU)

(54) *Color tinted clear coat coating system.*

(57) A coating system is described imparting durable and aesthetically pleasing coatings to metal substrates such as automotive finishes. Pigment containing base coats are overcoated with transparent topcoats containing a low pigment to binder ratio of a pigment the same as, complementary to, or divergent from the pigment in the base coat. The resultant coated article has improved chromaticity, clarity and depth of color in addition to significant improvement in properties and aesthetic appearance over conventional coatings in this area. Optionally, a low pigment to binder ratio of the same pigments can be included in the primer layer to further improve durability of color and aesthetic appearance.

ACTORUM AG

Technical Field

The field of art to which this invention pertains is coating compositions and particularly multi-coat coating systems and the resultant coated articles.

Background Art

Multi-coat coating systems are now well known in the coating industry. U. S. Patent 3,639,147 describes such a system for use as an automotive paint. When multi-coat coating systems have previously been applied, it has been difficult to obtain coatings having uniformly high gloss while at the same time maintaining good color, and durability.

In the automotive industry two significant systems are utilized in the painting of automobiles. One topcoat system which utilizes thermoplastic resins is known as the acrylic lacquer system. In this system the base polymers are the homopolymers of methyl methacrylate and copolymers of methyl methacrylate and acrylic acid, methacrylic acid, alkyl esters of acrylic acid or methacrylic acid, vinyl acetate, acrylonitrile, styrene and the like. The acrylic lacquer topcoats have been acknowledged to have outstanding aesthetic properties. Another outstanding topcoat system used in the automotive industry is the thermosetting acrylic resin system as described in U. S. Patent 3,375,227, issued March 26, 1968.

These topcoat systems have outstanding chemical resistance, outstanding resistance to cracking and crazing among other outstanding properties, but to the expert paint formulator, the thermosetting acrylic resins have not, in the past, quite provided the aesthetic properties obtained in the acrylic lacquer systems. In these systems pigmented base coat composition is applied to the metal substrate to hide metallic blemishes and provide the aesthetically pleasing colors desired followed by the application of an unpigmented layer of polymer which imparts a "deep" color appearance to the base coat and durability to this pigmented base coat. This system, however, is not without its problems. Aesthetic quality of the coating is totally dependent on the application of the base coat. The clear topcoat magnifies any weakness in this base coat including the highlighting of any color deficiencies of the base coat. The clear coat also acts as a magnifying mirror for ultraviolet radiation which can accelerate rather than retard any degradation of the base coat due to exposure to ultraviolet radiation. In addition, many of these coating systems in use today utilize metal particles in the base coat to provide an aesthetically pleasing metallic appearance. However, problems have occurred with the use of metallic pigments resulting in color loss in the base coat. Use of a three coat system can correct some of these problems. However, this is not an acceptable solution in the industry. Additional coating steps can only aggravate already insurmountable application control problems.

Accordingly, what are needed in this art are improved coating compositions and coating systems which are aesthetically pleasing as well as durable and easy to control.

Disclosure of Invention

A coating system is disclosed comprising a substrate material coated with at least two layers of polymer including a base coat and a transparent topcoat. Both the base coat and the topcoat are made up of pigmented thermosetting or thermoplastic resin. The pigment in the base coat is present in an amount of about 1% to about 20% by weight. The pigment in the topcoat is present in an amount less than that present in the base coat and comprises a pigment imparting the same color as, a color complementary to, or a color divergent from the color imparted by the pigment in the base coat. The utilization of such pigment combinations produces highlighted brilliance, chromaticity, and cleanliness of color to provide improved hiding and better exterior exposure and durability to the coating system.

Another aspect of the invention includes such a coating system including pigmentation of a primer layer beneath the base coat layer, the primer layer containing pigment in an amount less than that present in the base coat, the pigment being the same as, complementary to or divergent from the color imparted by the pigment in the base coat.

Another aspect of the invention includes a method of applying the pigmented base coat and topcoat described above. After the coatings have been applied, a heating step is performed to drive off the solvent and/or cure the resin layers.

Another aspect of the invention includes applying the base coat and topcoat as described above on top of a preapplied pigmented primer layer which has been dried or cured.

By utilizing the compositions and processes of this invention, not only are truer, more brilliant colors produced but colors more durable to the elements as well.

The foregoing, and other features and advantages of the present invention, will become more apparent from the following description.

Best Mode For Carrying Out The Invention

While any substrate material can be coated with the coating compositions according to the present invention, including such things as glass, ceramics, asbestos, wood, and even plastic material depending on the specific drying and/or curing requirements of the particular composition, the coating system of the present invention is particularly adapted for metal substrates, and specifically as an automotive paint finish system. The substrate may also be bare substrate material or can be conventionally primed, for example to impart corrosion resistance. Exemplary metal substrates include such things as steel, aluminum, copper, magnesium, alloys thereof, etc.

All substrates (metal and non-metal) require a primer to fill blemishes, seal the substrate and provide a bonding base for the enamel.

(a) Metal Substrates - Primary primer functions are to seal substrate from moisture and provide a bonding base for the enamel.

(b) Non-Metal Substrates - Primary primer functions are to seal the substrate from solvent or polymer attack of the enamel and provide a bonding base for the enamel.

The vehicle and pigment compositions of primers are specifically designated to perform these functions. The primer vehicle is any conventional vehicle used in this art such as the polymers listed below used in the base coats and topcoats which are epoxy- or phenolic- modified for improved corrosion resistance. Primers historically have been relegated to the specific color areas:

(a) Grays - Light to Dark
(b) Muddy Red-Browns - Taupe

Due to the existing colors of the primers the base coat enamels must be pigmented to produce absolute hiding (any show through of the primers will produce a grayed, less chromatic color).

Producing high chromaticity base coat colors with the required hiding severely limits pigment selection and color ranges eliminating many deep, rich and highly chromatic colors (metallic and non-metallic). The color tinted clear coat according to the present invention provides an aesthetic chromaticity and brilliance; it also provides an ultraviolet screener which reduces the penetration of these degrading rays. This additional ultraviolet screen provides a medium through which one can reduce the pigment concentration of the base coat providing the primer color is complementary to the base coat color.

The primer to perform its primary function must contain specific pigments at controlled levels and have good hiding. Producing a colored primer that is complementary to a specific base coat allows the reduction of pigment loading in the base coat. The overall effect, at this point, is a rich, clean and highly chromatic color. Applying a color tinted clear coat will provide highlights the same as, complementary or divergent to the base coat.

The total finished color is corrosion resistant, color durable and highly chromatic -- all of which is accomplished by totally and synergistically uniting of the primer, base coat and color tinted clear coat into one completely ultraviolet hiding system.

The clear and base coats prevent the ultraviolet rays from reaching the primer. The primer provides the primary hiding and the base color for a less-than-hiding base coat. The final system is a durable, high gloss, highly chromatic color with optimum purity and depth.

The polymer components of the composition can be varied to suit the temperature tolerance of the substrate material. For example, the components can be so constituted for air drying (i.e., ambient), low temperature cure (e.g., 150°F-180°F), or high temperature cure (e.g., over 180°F).

The base coat material comprises any suitable film forming material conventionally used in this art including acrylics, alkyds, polyurethanes, polyesters and aminoplast resins. Although the base coat can be deposited out of an aqueous carrier, it is preferred to use conventional volatile organic solvents such as aliphatic, cycloaliphatic and aromatic hydrocarbons, esters, ethers, ketones and alcohols including such things as toluene, xylene, butyl acetate, acetone, methyl isobutyl ketone, butyl alcohol, etc. When using volatile organic solvents, although it is not required, it is preferred to include from about 2% to about 50% by weight of a cellulose ester and/or wax (e.g., polyethylene) which facilitates quick release of the volatile organic solvent resulting in improved flow or leveling out of the coating. The cellulose esters used must be compatible with the particular resin systems selected and include such things as cellulose nitrate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose acetate propionate, and mixtures thereof. The cellulose esters when used are preferably used in about 5% to about 20% by weight based on film forming solids.

The acrylic resins in the base coat may be either thermoplastic (acrylic lacquer systems) or thermosetting. Acrylic lacquers such as are described in U. S. Patent 2,860,110 are one type of film forming composition useful according to this invention in the base coat. The acrylic lacquer compositions typically include homopolymers of methyl methacrylate and copolymers of methyl methacrylate which contain among others, acrylic acid, methacrylic acid, alkyl esters of acrylic acid, alkyl esters of methacrylic acid, vinyl acetate, acrylonitrile, styrene and the like.

When the relative viscosity of the acrylic lacquer polymer is less than about 1.05, the resulting films have poor solvent resistance, durability and mechanical properties. On the other hand, when the relative viscosity is increased above the 1.40 level, paints made from these resins are difficult to spray and have high coalescing temperatures.

Another type of film forming material useful in forming the base coat of this invention is a combination of a cross-linking agent and carboxy-hydroxy acrylic copolymer. Monomers that can be copolymerized in the carboxy-hydroxy acrylic copolymer include esters of acrylic and methacrylic acid with alkanols containing 1 to 12 carbon atoms, such as ethyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, lauryl methacrylate, benzyl acrylate, cyclohexyl methacrylate, and the like. Additional monomers are acrylonitrile, methacrylonitrile, styrene, vinyl toluene, alpha-methyl styrene, vinyl acetate, etc. These monomers contain one polymerizable ethylenically unsaturated group and are devoid of hydroxyl and carboxylic groups.

The cross-linking agents used in combination with the hydroxy-carboxy copolymers are those compositions which are reactive with hydroxy and/or carboxylic acid groups. Examples of such cross-linking agents are polyisocyanates (typically di- and/or tri- isocyanates) polyepoxides and aminoplast resins. Particularly preferred cross-linking agents are the aminoplast resins.

The polyisocyanates when reacted with hydroxyl bearing polyester or polyether or acrylic polymers will yield urethane films useful in the process of this invention in both the base coat and topcoat. The isocyanate (-NCO) - hydroxyl (-OH) reaction takes place readily at room temperature, so that ambient and low temperature cure is possible.

Among other base coats which are typically used in the processes of the present invention are those commonly known as alkyd resins which are defined to include fatty acid or oil containing esterification products. The methods for preparing these resins are well known in the art.

The preferred alkyd resins useful in this invention are those containing from about 5 to about 65 weight percent of fatty acid or oil and having an hydroxyl equivalent to carboxy equivalent ratio of from about 1.05 to 1.75. Alkyd resins having less than about 5% fatty compound are classified as the "oil-less" alkyd resins or polyester resins described hereinafter. On the other hand, alkyd resins containing greater than 65% of a fatty compound exhibit poor baking properties, poor chemical resistance and unsatisfactory adhesion to either the base coat or the substrate. When the hydroxyl to carboxyl equivalent ratio is less than about 1.05 gelation can result during polymer preparation while resins prepared having a ratio in excess of 1.75 have low molecular weights and therefore poor chemical resistance.

These alkyd resins can also be used as the topcoat of this invention. When this is the case it is preferred that the oil or fatty acid portion of the alkyd resin contain a light colored baking oil or fatty acid such as coconut or dehydrated castor oils or fatty acids. Furthermore, when these resins are used as topcoats they can be reacted with various acrylic or ethylenically unsaturated monomers as described above to produce vinyl modified alkyd resins.

Curing of these alkyd resins can be accomplished by blending with any of the previously described cross-linking agents in the same weight ratios as are used with carboxy-hydroxy copolymers.

Included among the various fatty acids and oils useful in preparing these alkyd resins are the fatty acids derived from the following oils; castor, dehydrated castor, coconut, corn, cottonseed, linseed, oticica, perilla, poppyseed, safflower, soybean, tung oil, etc., and the various rosins containing tall oil fatty acids. Useful polyols include the various glycols, such as ethylene glycol, propylene glycol, neopentyl glycol, butylene glycol, 1,4 butanediol, hexylene glycol, 1,6 hexanediol, the polyglycols such as diethylene glycol or triethylene glycol, etc.; the triols such as glycerine, trimethylol ethane, trimethylol propane, etc., and other higher functional alcohols such as pentaerythritol, sorbitol, mannitol, and the like. Acids useful in preparing the alkyd resins of this invention include mono-functional acids such as rosin acids, benzoic acid, para-tertiary butyl benzoic acid and the like; the poly-functional acids such as adipic acid, azelaic acid, sebacic acid, phthalic acid or anhydride, isophthalic acid, terephthalic acid, dimerized and polymerized fatty acids, trimellitic acid, and the like.

Yet another useful base coat is prepared using non-aqueous dispersions such as are described in U. S. Patents 3,050,412; 3,198,759; 3,232,903; 3,255,135. Typically these dispersions are prepared by polymerizing a monomer such as methyl methacrylate in the presence of a solvent in which polymers derived from the above monomer are insoluble and a precursor which is soluble in the solvent. Non-aqueous dispersions can have a relative solution viscosity as previously defined of about 1.05 to 3.0. Dispersions having a relative solution vicosity in excess of about 3.0 are difficult to spray and have high coalescence temperatures while dispersions with relative solution viscosity less than about 1.05 have poor resistance, durability and mechanical properties. The monomers useful in preparing the above-dispersed copolymers or homopolymers are those listed previously as useful in forming the carboxy-hydroxy acrylic copolymers.

In another instance the base coat film can be produced from resins known as polyesters or "oil-less" alkyd resins. These resins are prepared by condensing non-fatty containing polyols and polyacids. Included among the useful polyacids are isophthalic acid, phthalic acid or anhydride, terephthalic acid, maleic acid or anhydride, fumaric acid, oxalic acid, sebacic acid, azelaic acid, adipic acid, etc. Mono-basic acids such as benzoic, para-tertiary butyl benzoic and the like can also be utilized. Among the polyalcohols are the diols or glycols such as propylene glycol, ethylene glycol, butylene glycol, 1,4 butanediol, neopentyl glycol, hexalene glycol, 1,6 hexanediol, and the like; the triols such as trimethylol ethane, trimethylol propane and glycerine and various other higher functional alcohols such as pentaerythritol.

Any of the above-recited polymers may be used as the topcoat, as long as it provides a transparent film. The term "transparent film" is defined as a film through which the base coat can be seen. The outstanding feature of the topcoat is the significant improvement in the durability which is provided to the overall coating composition.

Utilizing the compositions of the present invention offers a means of combining the desirable properties of a combination of resin systems. For example, in automotive finishes the pigment control properties of acrylic lacquers can be combined with the chemical resistance properties of thermosetting acrylic resins by applying a thermosetting acrylic clear coat over a pigmented thermoplastic acrylic lacquer base coat (although acrylic lacquers may be used for both layers). Likewise, in appliance finishes the chemical resistance of polyester resins can be combined with the lower cost of thermosetting acrylic resins by applying a polyester clear topcoat over a pigmented thermosetting acrylic base coat. Although any of the above-mentioned thermoplastic materials may be used to form the transparent topcoat, better durability is achieved if the topcoat is one of the above-cited thermosetting materials, i.e., the material containing the cross-linking agents.

In all instances where the above methods and compositions are used extremely high gloss films result. In fact, where with a normal two coat system a 60° gloss in excess of 90-95 is difficult to obtain, using the process of this invention gloss readings in excess of 100 are readily obtained.

The amount of pigment in the base coat generally comprises about 1% to about 20% by weight, preferably about 7.5% to about 15% and typically about 10% by weight. Examples of pigments which can be used according to the present invention in the primer layer, base coat and/or topcoat are shown in Table 1.

TABLE 1

Pigment	Same	Complementary	Divergent
Nickel Titanate Yellow	Nickel Titanate	Chrome Yellow Chrome Titanate (Buff) Anthrapyrimidine Yellow	Phthalocyanine Blue (Red and Green Shade) Opaque Red Oxide Flavanthrone Yellow
Chrome Titanate Buff	Chrome Titanate	Nickel Titanate Yellow Opaque Yellow Iron Oxide Anthrapyrimidine Yellow	Opaque Red Iron Oxide Quinacridone (Red to Violet) Phthalocyanine Blue (Red and Green Shade)
Chrome Yellow	Chrome Yellow	Anthrapyrimidine Yellow Phthalocyanine Green (Yellow Shade) Isoindolinone Yellow	Quinacridone (Red to Violet) Opaque Red Iron Oxide Phthalocyanine Blue (Red and Green Shade)
Flavanthrone Yellow	Flavanthrone	Molybdate Orange Opaque Red Iron Oxide Transparent Red Iron Oxide	Chrome Yellow Quinacridone (Red to Violet) Phthalocyanine Blue (Red and Green Shade)
Anthrapyrimidine Yellow	Anthrapyrimidine	Chrome Yellow Opaque Yellow Iron Oxide Phthalocyanine Green (Yellow Shade)	Molybdate Orange Quinacridone (Red to Violet) Flavanthrone Yellow

Pigment	Same	Complementary	Divergent
Isoindolinone Yellow	Isoindolinone	Chrome Yellow	Phthalocyanine Blue (Red and Green Shade)
		Nickel Titanate Yellow	Opaque Red Iron Oxide
		Transparent Yellow Iron Oxide	Quinacridone (Red to Violet)
Metal Chelated Azo (Copper, Nickel, etc.)	Metal Chelated Azo	Phthalocyanine Green (Blue and Yellow Shade) Chrome Yellow Transparent Yellow Iron Oxide	Phthalocyanine Blue (Red and Green Shade) Molybdate Orange Perylene Maroon
Quinacridone Gold	Quinacridone Gold	Transparent Red Iron Oxide Quinacridone Maroon	Quinacridone Magenta Phthalocyanine Blue (Red and Green Shade)
		Transparent Yellow Iron Oxide	Perylene Red
Molybdate Orange	Molybdate Orange	Quinacridone Red	Opaque Red Iron Oxide
		Mono Azo Chrome Yellow	Phthalocyanine Blue Metal Chelated Azo
Imidazole Orange	Imidazole	Transparent Red Iron Oxide Perylene Maroon Quinacridone Magenta	Transparent Yellow Iron Oxide Chrome Yellow Quinacridone Gold

Pigment	Same	Complementary	Divergent
Mono Azo Orange	Mono Azo	Quinacridone (Red to Violet) Molybdate Orange Chrome Yellow	Metal Chelated Azo Phthalocyanine Blue (Blue and Green Shade) Nickel Titanate Yellow
Perylene Red - Opaque	Perylene - Opaque	Quinacridone Magenta Mono Azo Orange Opaque Red Iron Oxide	Transparent Red Iron Oxide Quinacridone Violet Opaque Yellow Iron Oxide
Perylene Maroon - Transparent	Perylene - Transparent	Transparent Red Iron Oxide Quinacridone Magenta Indanthrene Blue	Transparent Yellow Iron Oxide Quinacridone Violet Carbazole Dioxazine
Quinacridone Maroon	Quinacridone Maroon	Transparent Red Iron Oxide Quinacridone Gold Perylene Maroon	Phthalocyanine Blue Isoindolinone Yellow Opaque Yellow Iron Oxide
Quinacridone Red	Quinacridone Red	Molybdate Orange Perylene Red - Opaque Phthalocyanine Blue (Red Shade)	Anthrapyrimidine Yellow Quinacridone Gold Phthalocyanine Green (Blue and Yellow Shade)
Quinacridone Magenta	Quinacridone Magenta	Transparent Red Iron Oxide Molybdate Orange Perylene Maroon	Perylene Red Chrome Yellow Metal Chelated Azo

Pigment	Same	Complementary	Divergent
Quinacridone Violet	Quinacridone Violet	Perylene Maroon Carbazole Dioxazine	Iron Blue Transparent Yellow Iron Oxide
		Transparent Red Iron Oxide	Phthalocyanine Green (Blue and Yellow Shade)
Thio Indigo Maroon	Thio Indigo	Quinacridone Violet Indanthrene Blue	Quinacridone Red Opaque Red Iron Oxide
		Perylene Maroon	Anthrapyrimidine Yellow
BON Red	BON Red	Molybdate Orange Quinacridone Red	Perylene Maroon Phthalocyanine Green
		Perylene Red	Flavanthrone Yellow
Phthalocyanine Blue - Red	Phthalocyanine Blue - Red	Iron Blue	Phthalocyanine Green (Yellow Shade)
		Indanthrene Blue	Anthrapyrimidine Yellow
		Quinacridone Red	Molybdate Orange
Phthalocyanine Blue - Green	Phthalocyanine Blue - Green	Phthalocyanine Green (Blue Shade)	Molybdate Orange
		Iron Blue Chrome Yellow	Indanthrene Blue Carbazole Dioxazine
Indanthrene Blue	Indanthrene Blue	Phthalocyanine Blue - Red Shade Carbazole Dioxazine Quinacridone Magenta	Isoindolinone Yellow Mono Azo Quinacridone Red

Pigment	Same	Complelmentary	Divergent
Carbazole Dioxazine	Carbazole Dioxazine	Indanthrene Blue	Phthalocyanine Green (Yellow Shade)
		High Color Carbon Black	Transparent Yellow Iron Oxide
		Iron Blue	Molybdate Orange
Carbon Black	Carbon Black	Iron Blue	Isoindolinone Yellow
		Transparent Red Iron Oxide	Quinacridone Red
		Phthalocyanine Blue (Red Shade)	Perylene Red
Lampblack	Lampblack	Opaque Red Iron Oxide	Metal Chelated Azo
		Quinacridone Violet	Chrome Yellow
		Carbazole Dioxazine	Thio Indigo Maroon
High Color Carbon Black	High Color Carbon Black	Iron Blue	Carbon Black
		Carbazole Dioxazine	Lampblack
			Phthalocyanine Green (Blue and Yellow Shade)
Opaque Red Iron Oxide	Opaque Red Iron Oxide	Opaque Yellow Iron Oxide	Quinacridone (Red to Violet)
		Chrome Titanate Yellow	Phthalocyanine (Blues and Greens)
		Lampblack	Perylene Red and Maroon
Opaque Yellow Iron Oxide	Opaque Yellow Iron Oxide	Opaque Red Iron Oxide	Blues (Phthalocyanine and Iron)
		Chrome Titanate Yellow	Perylene (Red and Maroon)
		Chrome Yellow	Mono Azo

Pigment	Same	Complementary	Divergent
Transparent Red Iron Oxide	Transparent Red Iron Oxide	Quinacridones (Red to Violet) Perylene Maroon Indanthrene Blue	Mono Azo Orange Opaque Yellow Iron Oxide Chrome Titanate Yellow
Transparent Yellow Iron Oxide	Transparent Yellow Iron Oxide	Quinacridone Gold Phthalocyanine Green - Extra Yellow Metal Chelated Azo	Opaque Red Iron Oxide Nickel Titanate Yellow Imidazole Orange
Phthalocyanine Green - Blue	Phthalocyanine Green - Blue	Phthalocyanine Blue - Green Shade Transparent Red Iron Oxide Iron Blue	Indanthrene Blue Quinacridone (Red to Violet) Perylene Red and Maroon
Phthalocyanine Green - Yellow	Phthalocyanine Green - Yellow	Metal Chelated Azo Transparent Yellow Iron Oxide Opaque Yellow Iron Oxide	Phthalocyanine Blue (Red and Green Shade) Iron Blue Mono Azo
Phthalocyanine Green - Extra Yellow	Phthalocyanine Green - Extra Yellow	Metal Chelated Azo Transparent Yellow Iron Oxide Chrome Yellow	Thio Indigo Maroon Carbazole Dioxazine Flavanthrone Yellow

Both the base coat and the topcoat can be applied by any conventional method in this art such as brushing, spraying, dipping, flow coating, etc. Typically spray application is used, especially for automotive finishing. Various types of spraying can be utilized such as compressed air spraying, electrostatic spraying, hot spraying techniques, airless spraying techniques, etc. These can also be done by hand or by machine.

As stated above prior to application of the coating materials of the present invention a conventional corrosion resistant primer has already been applied. Primers can be applied in two basic processes.

(a) Spray Application - Air or rotational atomized with or without electrostatic assistance.

(b) Electrodeposition.

Depending on the type of primer, film builds and cure schedules will vary. Some examples are as follows:

(a) Film Builds - 0.7 to 1.2 Mils.

(b) Cure Schedules - 20 to 30 Minutes at 250°F to 400°F.

To this primed substrate is applied the base coat. The base coat is typically applied from about 0.4 mil to about 2.0 mils and preferably about 0.5 mil to about 0.8 mil. This thickness can be applied in a single coating pass or a plurality of passes with very brief drying ("flash") between applications of coats.

Once the base coat has been applied the transparent overcoat is applied after allowing the base coat to flash at ambient temperature for about 30 seconds to about 10 minutes, preferably about 1 to about 3 minutes. While the base coat can be dried for longer periods of time, even at higher temperatures, a much improved product is produced by application of the transparent topcoat after only a brief flash. Some drying out of the base coat is necessary to prevent total mixing of the base coat and topcoat. However, a minimal degree of base coat/topcoat interaction is desirable for improved bonding of the coatings. The topcoat is applied thicker than the base coat (preferably about 1.8 to 2.3 mils) and can also be applied in a single or multiple pass. Pigment control is retained in the base coat while it is being overcoated. This is evidenced by lack of "strike-in" or migration of the two films (the base coat and topcoat) into each other. When "strike-in" occurs, pigments move from the base coat into the topcoat, the film compositions become intermixed at the interface and the baked coating composition has a dusty appearance rather than a clear "depth" appearance. By this invention substantially no "strike-in" occurs, and the coatings have outstanding clearity and depth. However, sufficient wetting takes place at the interface so that no problems of delamination and solvent release from either coating are obtained.

Once the topcoat is applied the system is again flashed for 30 seconds to 10 minutes and the total coatings are then baked at temperatures sufficient to drive off all of the solvent in the case of thermoplastic layers and at temperatures sufficient to cure and cross-link in the case of thermosetting layers. These temperatures can range anywhere from ambient temperature to about 400°F. Typically in the case of thermosetting material temperatures of about 225°F to about 280°F (e.g., 250°F) are used, (e.g., for about 30 minutes).

The following examples are illustrative of the principles and practice of this invention although not limited thereto. Parts and percentages where used are parts and percentages by weight.

Example

A base coat polymer composition was prepared by blending 144 parts of the copolymer formed by reacting 47 parts of butyl methacrylate, 37 parts of styrene, 15.75 parts of hydroxypropyl methacrylate and 0.25 part of methacrylic acid with 176 parts of xylene and butanol (in a weight ratio of 85/15). A pigment base was selected from the pigments recited under the heading Base Coat in Table 2. This pigment base was blended with the base coat polymer composition in an amount sufficient to produce substrate hiding at a 0.5 mil film thickness.

Bonderized steel panels primed with a cured corrosion resistant primer were sprayed with the base coat paint composition to a film thickness of 0.5 mil on dry film basis. After a flash of approximately 2 minutes at room temperature, an additional 0.5 mil film of the base coat paint composition again as measured on a dry film basis was applied by spraying. After a 2 minute flash at room temperature, a clear (transparent) topcoating (pigmented as set forth in Table 2) was applied by spraying to a film thickness on a dry basis of 1 mil. The transparent topcoating composition was prepared by blending 144 parts of the copolymer solution described above at 45 percent nonvolatiles with 58 parts of 60 percent nonvolatile solution of butylated methylol melamine. This topcoating composition was applied by spraying to a dry film thickness of 2 mils over the base coat described in the Example to a metal substrate. After a 2-5 minute flash time at room temperature, the coating was baked at 190°F for 15 minutes. The coating was then sanded with 600 sand paper and water to smooth the coating and to remove surface imperfections. After rinsing with mineral spirits, the coating was baked at 250°F for 30 minutes. The resulting coating had reflowed before curing, the sanding marks had disappeared and the coating also had a pleasing aesthetic appearance, exhibiting superior polychromatic effects.

The following pigment combinations were used in the composition of the base coat and topcoat according to the Example. In all cases the resultant coating had excellent properties for use as an automotive paint. (P/B indicates pigment to binder ratio).

TABLE 2

Base Coat	Clear Coat
100% RT-759-D (Quinacridone Red)	100% RT-759-D at .001 P/B, .006 P/B, .012 P/B 100% 088VN at .006 P/B (Transparent Yellow Iron Oxide) 100% RT-9000 at .006 P/B (Transparent Red Iron Oxide)
50% F3RK70 (Mono Azo Red)/ 50% RT-759-D (Quinacridone Red)	100% RT-759-D at .001 P/B, .006 P/B, .012 P/B 100% 088VN at .006 P/B 100% RT-9000 at .006 P/B
100% RT-959-D (Quinacridone Red)	100% RT-959-D at .012 P/B
100% XRT-859-D (Quinacridone Red)	100% XRT-859-D at .012 P/B
100% R-6719 (Quinacridone Magenta)	100% R-6719 at .012 P/B
100% E3B (Quinacridone Magenta)	100% E3B at .012 P/B
100% 3BRF (Cyclic Azo)	100% 3BRF at .012 P/B
100% X-3218 (Chrome Yellow)	100% X-3218 at .012 P/B
100% L-3135 (Molybdate Orange)	100% L-3135 at .012 P/B
100% F3RK70 (Mono Azo Red)	100% F3RK70 at .012 P/B
75% L-3135 (Molybdate Orange)/ 25% R-658 (Quinacridone Magenta)	75% L-3135/25% R-658 at .012 P/B
100% Orasol RL	100% Orasol RL at .012 P/B

Base Coat	Clear Coat
100% BP1300 (High Color Carbon Black)	100% BP1300 at .012 P/B
100% #7370 (Chrome Titanate Buff)	100% #7370 at .012 P/B
100% XLO-NP (Opaque Yellow Iron Oxide)	100% XLO-NP at .012 P/B
100% HFR (Mono Azo Brown)	100% HFR at .012 P/B
100% FA7286	100% FA7286 at .012 P/B
100% 70C (Chrome Yellow)	100% 70C at .012 P/B
100% 6RL (Isoindolinone)	100% 6RL at .012 P/B
100% RV-6902 (Quinacridone Violet)	100% RV-6902 at .012 P/B
100% 4183H	100% 4183H at .012 P/B
100% HF4B	100% HF4B at .012 P/B
60% L6700 (Phthalocyanine Blue)/ 40% 4028AR (Iron Blue)	60% L-6700/40% 4028AR at .012 P/B
70% X-3218 (Chrome Yellow)/ 30% 264-8142 (Phthalocyanine Green)	70% X-3218/30% 264-8142 at .012 P/B

If identical pigmentation is used in the clear coat and the base coat chromaticity, clarity and depth are improved while providing an improved film that protects the pigment over stressed base coat through absorption and reflection of ultraviolet radiation. The preferred pigment to binder weight ratio in this clear coat is about 0.012:1 although comparable results were obtained at pigment to binder ratios of 0.002:1 to 0.30:1.

The clear coats preferably range from 1.5 to 3 mils in thickness. Film builds below and above this range show significant colored deltas. The thickness of 2.0 mils is particularly preferred. With a 0.012 pigment to binder ratio more than adequate flexibility for the coating system is provided with this thickness.

Coating systems according to the present invention provide a high gloss, pure color and improved film over the base coat. This film provides chromaticity, clarity and depth not attainable with highly pigmented enamels. In fact, there is no need to use high pigmentation for hiding purposes with the coating system according to the present invention. The base coat provides the primary color while the clear coat provides aesthetic qualities through the availability of maximum vehicle (resin, based on the low pigment to binder ratio) to coat, suspend and wet the pigment. There is also unrestricted reflection and absorption of light yielding the optimum purity of the pigment without effecting the optimum gloss of the clear coat. The physical characteristics of the system are also a composite of the two coats, with the base coat providing the primary color durability and the low pigment to binder ratio clear coat providing ultraviolet and moisture protection. Combined they produce a final total coating system which is much stronger than a system with an untinted clear coat.

An untinted clear coat is a totally (100%) transparent film that allows unhindered penetration of ultraviolet wavelengths and moisture. The untinted clear coat can also act as an intermediate heat generator (i.e., catching sunlight in a magnifying glass to ignite paper, leaves, etc., positioned under the magnifing glass) which increases the energy of the solar wavelengths and bombarding the heavily pigmented base coat. This system (untinted clear) requires selected base coat pigmentation. These pigments must be durable and moisture resistant and subsequently severely limits the range of colors producible.

Using a color tinted clear coat significantly reduces the penetration of solar energy and moisture, providing an intermediate that absorbs, reflects, and refracts solar energy and moisture. The tinted clear becomes both a glamorizing and protective film permitting wider variations in base coat pigmentation and a more durable (stronger) system. The ultraviolet scattering normally provided by a clear coat is absorbed and reflected by the pigment in the clear coat resulting in lower and reduced ultraviolet rays reaching the base coat. The random, highly separated and unclustered pigment in the clear coat deprives the ultraviolet radiation of a mass to which all its energy can be transferred (i.e., the highly pigmented base coat) resulting in, where contact occurs, a moderately opaque surface that acts as an inconsequential inner face through which the rays pass resulting in a highly colored durable clear coat.

Because of this feature it is possible to produce base coat colors using less durable and less costly pigments while including in the clear coat a very low pigment to binder ratio high quality (automotive quality) pigment of the same, complementary or contradictory colors resulting in a durable, unique and inexpensive base coat-clear coat enamel system.

The above discussion is primarily directed to high solids, low volatile organic content (VOC) non-metallic colors. This invention has equal applicability to metallic colors. The aesthetics and durability are equal to those obtained with non-metallic systems. However, the base coat pigmentation requires careful consideration. The metal flakes in a color act as pure reflectors and because of the color reduction caused by the metal flake, most pigments will not possess the durability features they exhibit in mass tone or near mass tone colors.

Metallic pigmentations require an acute awareness and knowledge of the effect a metal flake has on the color and durability of colored pigments. Metal flakes are color reducers -- reducing the chromaticity and color value of the colored pigment(s) with which they are blended. Colored pigment (organic and inorganic) durability, in most cases, is dependent on two major factors:

(a) Their level (portion) of the pigment composition in a color.

(b) The synergistic or antagonistic effect of the other colored pigments in a color.

Non-metallic pigment compositions are generally, excluding colors where titanium dioxide is used, additive and synergistic -- all pigments contributing additive and supportive color and durability to each other.

In metallics the metallic flavor -- the metal flake -- is a subtractive antagonistic additive to almost every colored pigment. This necessitates the careful selection of:

(a) Metal flake to colored pigment ratios.

(b) Addition of other colored pigments selecting only those that are durability additive and synergistic to the primary colored pigment.

With the color tinted clear coat two options can be pursued to produce metallic colors and the aesthetics and durability of a non-metallic.

(a) A strong (durable) base coat pigmentation utilizing the color tinted clear coat to provide the desired highlights and undertone color shifts.

(b) A borderline (lacking color durability considered acceptable by both the paint supplier and purchaser) base coat pigmentation which produces a desired color with a durable (ultraviolet absorbing) colored pigment in the clear coat. These borderline durability base coats may be combined with a color tinted clear with a moderately increased pigment to binder ratio (e.g., 0.018) where the clear will provide at least 25% of the final color.

Whether non-metallic or metallic base coats are used, the color tinted clear coat will provide improved aesthetics, durability, chroma, purity, depth and undertone color shifts unattainable with pure, untinted, clear coats.

The color tinted clear coat which contributes aesthetics and durablity must be applied at controlled and specific film thicknesses. The color tinted clear coats being slightly opaque will alter the final color should the film vary from the prescribed parameters of 1.8 to 2.3 mils of cured color tinted clear coat. In the case of a "borderline" durability base coat, the "selective" increased pigment to binder clear coat which will provide at least 25% of the final color will be much more sensitive to excessive variations in the clear coat film thicknesses.

The pigment to binder ratios of the color tintd clear coat are critical to the aesthetics of the final color. Base coat and clear coat pigmentations are singular when evaluated for color. While each contributes specific aesthetics, the final color is a product of their unity. A given color is the product of a base coat and clear coat pigmentation. The criticality of the color tinted clear coat is the pigment to binder ratio which if varied over a specific base coat will result in major total color deviations.

Coatings for the automotive industry are comprised of three (four with base coat/clear coat) separate and specific paints and each has a specific function to perform so that totally they produce durable and colorful automotive finishes.

(a) Electrodeposition Primer - Initial metal protection against oxidation and corrosion.

(b) Spray Primed - Additional metal protection, leveling surface and bonding substrate for colored coat.

(c) Color Coat - Covering to protect primer, aesthetics and durability.

(d) Clear Coat (Base Coat/Clear Coat Systems Only) - Add aesthetics and durability.

The primer coats are to protect the metals from oxidation. The color coat is to provide the aesthetics and an ultraviolet impervious barrier for the primers. The clear coat (base coat/clear coat system) provides the gloss and ultraviolet screen for the highly pigmented base coats.

Should light or moisture reach the primers the paint system will deteriorate rapidly and totally. Primers are pigmented for moisture protection and filling properties. Their pigments are highly sensitive to ultraviolet radiation. Therefore, the colored coat must provide a barrier of absolute hiding penetrating ultraviolet radiaton from reaching the primer(s).

In the base coat/clear coat systems this absolute hiding is not always attainable, especially in rich, bright colors (metallic and non-metallic). Utilizing the color tinted clear coat and its ability to scatter, absorb, refract and reflect light we can alter, to some degree, the pigmentation of the primer by introducing colored pigment(s) that would be complementary to the base coat pigments. Through this procedure substrate hiding could be obtained from the primer and base coat with full aesthetics. The color tinted clear coat with its same as, complementary or divergent color would provide the aesthetics and the ultraviolet hiding to protect the, now color coordinated, primer, with the end result -- rich, bright metallic and non-metallic colors with all the uniqueness durablity of a color tinted clear coat coating system.

Another feature of the color tinted clear coats according to the present invention is the use of color coordinated primer for those base coats in which the required hiding is not achievable. In these areas the color tinted clear coat will function as a diffuser for ultraviolet radiation, significantly reducing the possibility of primer failures related to UV visibility (non-hiding base coat).

Regardless of the system the tinted clear coat is used with, the total system will be at least equal in physical characteristics to base coat, clear coat systems while producing aesthetics (such as gloss, purity and depth) currently unattainable with such systems.

This system is also not moisture sensitive, uses relatively small particle sizes, is less sensitive to criticality of applications, maintains color trueness at all angles (face to flow color travel), can withstand the elements (i.e., sun exposure), does not operate with subtractive color effects when mixed with other pigments, allows low bake repair color matching, and resists settling and chemical (e.g., acid rain) attack.

It should be noted that while the compositions of the present invention are particularly adapted for original equipment manufacture coatings for automobiles, one of their advantages is the low bake matching use as refinish compositions as well. Whereas in original equipment manufacture the disclosed cellulose esters and/or wax are typically used, such are not universally required for example in refinish compositions. Also, where thermosetting polymer embodiments are preferred in the original equipment manufacture, in refinish either low temperature cure thermosetting materials (e.g., 150° to 180°F) or ambient temperature cure thermosetting or thermoplastic materials are preferred.

Although this invention has been shown and described with respect to detailed embodiments thereof, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

Claims

1. A substrate material coated with at least two layers of polymer including a base coat comprising a pigmented thermosetting or thermoplastic resin and a transparent topcoat comprising a pigmented thermosetting or thermoplastic resin, the pigment in the base coat being present in an amount of about 1% to about 20% by weight, the pigment in the topcoat being present in an amount less than that present in the base coat and in a pigment to binder weight ratio of about 0.002:1 to about 0.30:1, the topcoat having a thickness of about 1.5 to about 3.0 mils, and the pigment in the topcoat being the same color as, a color complementary to or a color divergent from the pigment in the base coat.

2. The coated substrate material of claim 1 wherein the clear coat is about 2.0 mils thick with a pigment to binder ratio of about 0.012:1.

3. The coated substrate material of claim 1 including a primer layer between the substrate and the base coat, the primer layer containing the same pigment as in the topcoat in a pigment to binder ratio of about 0.002:1 to about 0.30:1.

4. A method of coating a substrate with multiple layers of polymer comprisig applying at least one layer of a base coat comprising a pigmented thermosetting or thermoplastic resin, applying at least one layer of a transparent thermosetting or thermoplastic topcoat on the base coat, and drying or curing the applied coatings, both the base coat and topcoat containing pigment material, the pigment in the base coat being present in an amount of about 0.1% to about 20% by weight, the pigment in the topcoat being present in an amount less than that present in the base coat and in a pigment to binder ratio of about 0.002:1 to about 0.30:1, the thickness of the topcoat being about 1.5 to about 3.0 mils and the pigment in the topcoat being the same color as, a color complementary to, or a color diverent from the pigment in the base coat.

5. The method of claim 4 wherein the substrate is metal.