



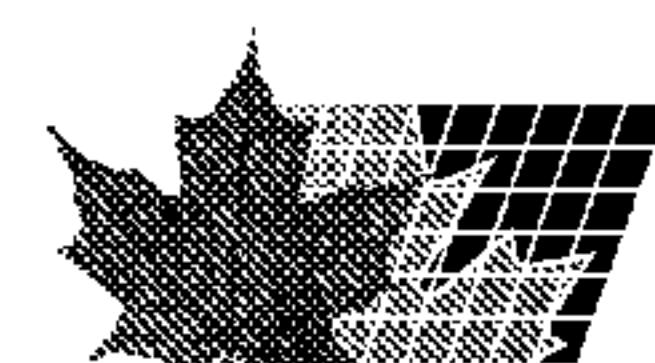
(86) Date de dépôt PCT/PCT Filing Date: 2002/12/27
(87) Date publication PCT/PCT Publication Date: 2004/06/27
(45) Date de délivrance/Issue Date: 2008/11/04
(85) Entrée phase nationale/National Entry: 2004/05/04
(86) N° demande PCT/PCT Application No.: IB 2002/005768
(87) N° publication PCT/PCT Publication No.: 2004/058905

(51) Cl.Int./Int.Cl. *C09D 131/04* (2006.01),
C09D 129/04 (2006.01), *C09D 161/04* (2006.01),
C09D 161/28 (2006.01), *C09D 163/00* (2006.01),
C09D 167/00 (2006.01), *C09D 175/04* (2006.01)
(72) Inventeur/Inventor:
BHATTACHARYA, DHRUBO, IN
(73) Propriétaire/Owner:
ROTOMAC ELECTRICALS PVT. LTD., IN
(74) Agent: MARKS & CLERK

(54) Titre : COMPOSITIONS ET METHODE POUR L'ENDUCTION EN CONTINU DE BANDES A AMORCAGE
AUTOMATIQUE
(54) Title: SELF-PRIMING COIL COATING COMPOSITIONS AND METHOD

(57) **Abrégé/Abstract:**

The invention discloses self-priming coating composition based on a vinyl terpolymer, a monomeric or oligomeric alkoxy amino resin cross linker and a multi component combination of two or more coresins selected from (a) oligomeric saturated polyester resin, (b) oligomeric unsaturated polyester resin dissolved in an unsaturated monomer with a free radical initiator (c) oligomeric bifunctional phenolic resole resin, (d) oligomeric epoxy resin, and (e) low molecular weight polyurethane resin, wherein said vinyl terpolymer is predominantly polyvinyl formal with polyvinyl alcohol and polyvinyl acetate as two other co-polymers. The composition can be applied as a clear coat or as a pigmented composition with addition of pigment on ferrous and non-ferrous metallic substrate and is particularly suitable for continuous coil coating lines for both dark and light colour metal coatings. The invention also concerns a method of coating ferrous and non-ferrous metallic substrate by applying the said coating composition on a surface and coated articles so produced.



ABSTRACT

The invention discloses self-priming coating composition based on a vinyl terpolymer, a monomeric or oligomeric alkoxy amino resin cross linker and a multi component combination of two or more coresins selected from , (a) oligomeric saturated polyester resin, (b) oligomeric unsaturated polyester resin dissolved in an unsaturated monomer with a free radical initiator (c) oligomeric bifunctional phenolic resole resin , (d) oligomeric epoxy resin, and (e) low molecular weight polyurethane resin, wherein said vinyl terpolymer is predominantly polyvinyl formal with polyvinyl alcohol and polyvinyl acetate as two other co-polymers. The composition can be applied as a clear coat or as a pigmented composition with addition of pigment on ferrous and non-ferrous metallic substrate and is particularly suitable for continuous coil coating lines for both dark and light colour metal coatings. The invention also concerns a method of coating ferrous and non- ferrous metallic substrate by applying the said coating composition on a surface and coated articles so produced.

FPP2767

SELF-PRIMING COIL COATING COMPOSITIONS AND METHOD

FIELD OF THE INVENTION

5

This invention relates to chromate free self-priming coating compositions based on a polymeric material, particularly a vinyl terpolymer of polyvinyl formal, polyvinyl alcohol and polyvinyl acetate used as film
10 former and a binder with a cross-linker such as an alkoxy-amino resin with various multi-component combinations of co-resins such as saturated polyester, unsaturated polyester with an unsaturated monomer, epoxy, phenolic and polyurethane resins. The heat reactive coating compositions can be applied on ferrous or non-ferrous metallic
15 substrates. The rapid curing nature coupled with high flexibility and resistance to wear, abrasion, chemicals, staining, corrosion and dry heat makes it most ideal for continuous metal coil coating lines. These can be formulated both as a clear coat as well as a pigmented coating in a range of colors in a blend of volatile organic solvents. The coatings are self-
20 priming in nature and can be applied as a topcoat directly on the metal surface without any primer thereby making the coating method most cost effective. The absence of any primer helps to avoid toxic materials, especially chromate salts normally accompanying a primer and thereby makes the coating environment friendly.

25

BACKGROUND OF THE INVENTION

Pre-coated metals generated in continuous coil coating lines processing
30 rolled stock such as cold rolled steel, hot dip galvanized steel, stainless steel, tin plated steel and aluminum, constitutes a major industrial activity

FPP2767

today. Steel, excluding hot rolled steel, is increasingly being coated in this manner. The organic products normally employed for this purpose are based on silicones, polyesters, epoxies, polyurethanes, acrylics and combinations thereof, PVC plastisols and fluorocarbons. Most of these products are solvent based i.e. contain a volatile organic solvent, though some are also available as powdered resin to be applied as powder coatings. Generally these products require their specific primers as these lack the ability to adhere directly to substrates in the short oven dwell times of continuous coil coating lines.

The products used for metal pre-coating in continuous coil coating lines ranging from vinyl plastisols and fluorocarbons to other thermosetting resins as stated in prior art have a limitation in that these do not generally offer a combination of high scratch hardness with good flexibility. This combination is most desirable since the pre-coated metal sheets have to undergo fabrication involving rigorous forming and flexing operations in engineering, appliance and construction industries. Hardness of thermosetting coatings depends on the density of cross-links achieved during cure. As this density increases, the material hardens but begins to lose its flexibility. Contrarily, a coating that is inherently flexible such as plastisol, has poor thermal resistance and hardness. Polyesters have been extensively studied in this regard to obtain the desired combination of hardness and flexibility. A survey of such compositions (US Patent nos. 4140729, 4734467, 5322884) reveals that it is very difficult to resolve these conflicting demands in coatings on hard metallic substrates. Increasing the aromatic content and/or inorganic pigment level increases the hardness but lowers the flexibility. Increasing the molecular weight of linear aliphatic chains has the opposite effect on cured resin properties

though this is restricted by requirement of resin compatibility with the amino cross-linkers. A combination of these approaches has been generally employed in polyester resin compositions. Coil coating compositions based on thermosetting alkyds using drying/semi-drying oils have also not been successful in providing a combination of hardness and flexibility.

The primers normally used for these products contain large amounts of inorganic additives and corrosion inhibiting compounds. Such additives in some cases include chrome based compounds, which are considered to be toxic and harmful. Additionally priming of metal substrate is expensive and time consuming, as this adds another operation to the coating scheme besides increasing the cost of removal of the paint during stripping operation. It also adds to the overall thickness of the coating, which may be undesirable in certain applications. Self-priming coatings with good barrier characteristics and dielectrics offer excellent corrosion protection in thin films. A quick curing, self-priming polyester has been proposed for coil coating (US Patent No. 4071578) that is quite flexible, passing a 1T bend test, but offers a maximum pencil hardness of only H-.

The co-pending PCT publication no. WO/2003/093380 by the same applicant describes a self-priming coating formulation based on a linear vinyl terpolymer containing acetyl, hydroxyl and formal pendant groups on the vinyl backbone and an oil based alkyd co-resin. Another co-pending PCT publication no. WO/2004/024835 by the same applicant describes a self-priming coating composition based on such vinyl terpolymer with a saturated oligomeric polyester co-resin and an alkoxy amino resin cross linker. The former composition is highly scratch and abrasion resistant

FPP2767

with pencil hardness of at least 6H and extremely flexible (passes 0T bend test). However it requires high peak metal temperature (PMT) of around 240-250°C for complete cure and darkens somewhat during the exposure. The latter composition cures at a lower PMT of 230°C without darkening to provide a flexible (0T) and hard coating with a scratch hardness of at least 6H. However, both these compositions have a limitation in that the solids content of solvent bearing pigmented compositions, with viscosities amenable to coil coating, are in the range of 30-40% by weight.

The present work has focused on the reduction of the PMT and therefore the energy input in the curing process as well as the enhancement of solids in coating compositions to reduce solvent emissions during drying while retaining the basic attributes of the coating earlier obtained.

The inventor of the instant invention has unexpectedly found that when the linear vinyl terpolymer containing hydroxyl, acetyl and formal groups, along with an alkoxy amino cross-linker resin, is used in multi-component combinations of co-resins of low molecular weight selected from the group consisting of saturated polyester, unsaturated polyester with an unsaturated monomer, a bi-functional phenolic resole, epoxy and polyurethane resins, the resulting composition ensures incorporation of more solids at low viscosity along with other desirable properties including high scratch hardness and abrasion resistance, high flexibility and low PMT for cure.

The vinyl macromolecule offers limited sites for cross-linking through its reactive pendant hydroxyl groups and thereby a lightly cross-linked matrix where a long linear polymer is interlinked with short chains of the

FPP2767

co-resins is obtained which is tough as well as hard and possesses excellent thermal and chemical resistance. All the compositions exhibit excellent flow and adhesion on a variety of ferrous and non-ferrous substrates such as cold rolled steel, galvanized steel, stainless steel and
5 aluminum and cure within 50 seconds at PMT ranging from 210 to 230°C in off-line ovens. Further, incorporation of larger proportions of low molecular weight co-resins in the composition also helps to increase the solids content to a level of 40% or higher and thereby overcome one of the limitation of the prior art compositions described above. It will be
10 obvious to someone skilled in the art that such properties offer important advantages in a variety of coil coating applications for both light and dark colored coated metals.

OBJECTS OF THE INVENTION

15

The first object of the invention is to provide quick curing polymeric coating compositions that cure at PMT of 210-230°C and are suitable for continuous coil coating lines.

20

The second object of the invention is to provide polymer coatings, which have high degree of flexibility and surface hardness at the same time.

25

The third object of the invention is to provide environment friendly chromate free self-priming corrosion resistant colored coating compositions containing minimum 40% solids including the binder and
pigments.

30

Another object of the invention is to provide a coating method for coating a ferrous or non-ferrous metallic substrate by using primer free corrosion resistant coatings.

FPP2767

Yet another object of the invention is to apply the coating composition of the invention as an under coat followed by one or more top coat(s) of polyester, epoxy, amino, alkyd and polyurethane coatings.

- 5 Yet another object of the invention is to provide coated articles at least one surface of which is coated by applying the coating composition according to the invention.

SUMMARY OF THE INVENTION

10

The present invention provides a self-priming, rapid curing, chromate free, corrosion resistant coating composition comprising:

- 15 a) a linear vinyl terpolymer made up predominantly of polyvinyl formal with polyvinyl alcohol and polyvinyl acetate as the two other co-polymers with three randomly distributed functional groups along the vinyl backbone, comprising acetyl, formal and hydroxyl;
- 20 b) a monomeric or oligomeric alkoxy amino resin and
- c) multi-component combinations of two or more of the resins selected from the group consisting of:
- i) an oligomeric saturated polyester resin,
- 25 ii) an oligomeric unsaturated polyester resin dissolved in an unsaturated monomer and containing a free radical initiator with high activation energy,

FPP2767

- iii) an oligomeric bi-functional phenolic resole resin,
- iv) a low molecular weight epoxy resin and
- v) a low molecular weight polyurethane resin;

- 5 d) a mineral acid catalyst;
- e) a blend of organic solvents and optionally
- f) one or more driers, and one or more chromate free inorganic pigment and/or organic dyes;

10

The said alkoxy amino resin in oligomeric form has an average degree of polymerization of no more than three.

15

The unsaturated monomer in which said unsaturated polyester resin is dissolved is preferably diallyl phthalate (DAP) or diallyl isophthalate (DAIP).

The free radical initiator used with the unsaturated polyester is preferably Dicumyl Peroxide (DCPO).

20

The said coating compositions may be suitably pigmented with inorganic pigments and/or organic dyes to obtain pigmented coatings in a choice of attractive colors with low to medium gloss.

25

The invention also provides a method of coating ferrous or non-ferrous metal substrates by applying the composition according to invention on the surface of the said substrate in desired thickness and curing the same.

FPP2767

The invention further provides a coated article comprising a ferrous or a non-ferrous metallic substrate of which at least one surface is coated with the coating compositions according to the invention.

5 DETAILED DESCRIPTION OF THE INVENTION

A linear vinyl terpolymer, namely polyvinyl formal, polyvinyl alcohol and polyvinyl acetate with three functional groups randomly distributed along the vinyl backbone offers cross-linking sites through the hydroxyl
10 groups. The density of cross-links may be controlled by the number and placement of hydroxyl groups on the vinyl backbone of polymer. This polymer possesses a rare combination of mechanical, thermal, chemical and dielectric properties. The functional groups along with its vinyl backbone confer to this polymer the properties of adhesion, toughness,
15 chemical inertness and heat stability while the long linear chains contribute to the outstanding flexibility. The spatial structure of this thermoplastic material helps to form a closely packed molecular structure, which in turn provides excellent barrier characteristics when coated on a wide array of substrates. The hydroxyl groups are fully
20 accessible to cross-linking with reactive functional groups of co-resins and this makes the thermoplastic polymer heat curable in the presence of a mineral acid. The chain length distribution of a poly disperse polymer is made such as to permit film formation, migration by diffusion to the substrate and development of the required cohesive strength in the
25 coating. Specifically, the terpolymer used in the invention has weight average molecular weight ranging between 15,000 and 80,000 preferably between 20,000 and 50,000. The content of polyvinyl alcohol, polyvinyl acetate and polyvinyl formal of the vinyl terpolymer used for the

FPP2767

invention is 6-15%, 9-15% and 70-84% respectively by weight and preferably 6.0-7.5%, 10-13% and 80-83% respectively by weight.

The said terpolymer useable in the composition may be produced by simultaneous hydrolysis and formalization of polyvinyl acetate in acetic acid media. For this purpose polyvinyl acetate of the required molecular weight (28,000-140,000) and of low to very low branching frequency is dissolved in acetic acid and formalin (37% formaldehyde aqueous solution) at room temperature. Dilute sulfuric acid (N/10 normality) is added to this solution with agitation. The contents are well stirred, heated to 75°C and maintained at this condition for 20-24 hours. The whole process is conducted in a homogenous solution state. By regulating quantities of acetic acid, water and formaldehyde, the required composition of the functional groups of the vinyl backbone viz. acetyl, hydroxyl and formal may be obtained. Typically for one part of polyvinyl acetate, 1.65 parts of acetic acid, 0.55 part of water and 0.45 part of formalin (37% formaldehyde solution in water) is used to obtain a composition comprising 6.0 - 6.5 % polyvinyl alcohol, 11.0-12.0 % polyvinyl acetate and 81.5-83.0 % polyvinyl formal. The extent of reaction is determined by the percentage of hydroxyl and acetyl groups in the extracted polymer and the reaction is terminated at the desired point by neutralizing the acid catalyst with a dilute alkali. The polymer is next precipitated from solution by adding water as non-solvent, washed and dried. The simultaneous hydroxyl and formalization reactions prevent the development of blocky sequences on vinyl chain in a homogenous media and thus helps to get a random terpolymer. The T_g of the terpolymer so produced ranges between 100 - 115°C.

FPP2767

The amino formaldehyde resin is obtained by the condensation reaction of formaldehyde and a poly functional amine with the former used in excess in the presence of an alkali catalyst and the product is alkylated (butylated or methylated) after condensation with the corresponding
5 alcohol. The alkoxy amino resin used in the present invention is a low molecular weight melamine formaldehyde resin that is methylated by etherifying its methylol groups with methanol to increase its stability and solvency in organic media. It contains heat reactive methoxy - methyl and methylol groups and approximately 96 % solids.

10

Saturated polyester resin used in some of the compositions described later may be made from saturated carboxylic acids and anhydrides such as adipic, succinic, sebacic, phthalic, isophthalic or terephthalic and alcohols such as ethylene glycol, diethylene glycol, triethylene glycol,
15 neopentyl glycol, propylene glycol and cyclohexane dimethanol or a combination thereof. The preferred chain length of the oligomeric resin lies between 2 and 5. The resin is produced by esterification to high conversion, a mix of a molar excess of alcohols over acids/anhydrides using a catalyst such as triphenyl phosphite and removing the water of
20 condensation through an azeotropic solvent such as toluene. The polyester solids are obtained in solution in the azeotropic solvent. The polyester resin chosen in this invention was made from adipic and isophthalic acids and propylene and neopentyl glycols in toluene solvent and contains 82% solids. The unsaturated polyester resin may be
25 produced by replacing partly or wholly, saturated acids/anhydrides by unsaturated diacids/ anhydrides like maleic or fumaric, and esterifying these with the alcohols listed earlier. Control of the degree of unsaturation in the polyester backbone is vital since excessive

FPP2767

unsaturation will not permit complete cure through free radical polymerization in the short oven dwell times of coil coating resulting in poor hardness, chemical and UV resistance of the coating. This is evident from compositions that use wholly unsaturated polyesters with or without
5 other co-resins together with the vinyl polymer and the amino resin cross-linker. However excellent results are obtained when saturated and completely unsaturated polyesters are used together. Often a Diels Alder adduct made from cyclopentadiene and the unsaturated acid/anhydride is used to regulate the unsaturation in the chain and to improve the thermal
10 resistance of the polyester. Two kinds of unsaturated polyester resin were used in the illustrative examples for the present invention. The first one used only maleic anhydride and diethylene glycol to yield completely unsaturated polyester while the other partially unsaturated composition used maleic anhydride and dicyclopentadiene with ethylene glycol. All
15 these recipes were processed to high conversion (acid value of 6 to 9) and the semi-solid mass was dissolved in DAP or DAIP, used here as a reactive diluent monomer. DAP/DAIP monomer is the ideal choice as it is low in odor, toxicity and volatility. A free radical initiator with a high energy of activation such as DCPO is added to the solution. The two
20 unsaturated polyesters have been designated as UP 1, UP 2 respectively in the illustrative examples. The preferred molecular weight of these polyesters should not exceed 4000 daltons. During high temperature cure a part of the DAP/DAIP monomer copolymerizes with the unsaturated maleate in the polyester and thus increases the solids during solidification
25 and cure. This is a slow reaction, hence unsaturation levels should be low. Apart from free radical cure, involving the unsaturation in its chain, the polyester also condenses with reactive functional groups on co-resins

FPP2767

and the pendant hydroxyls of the vinyl polymer through its reactive terminal functional groups, mainly hydroxyls.

The bi-functional phenolic resole may be made from p-substituted phenols such as p-cresol, p-tertiary amyl phenol, p-tertiary butyl phenol, or bis-phenol A, used singly or in combination and formaldehyde. The formaldehyde is used in molar excess and the condensation proceeds in the presence of an alkaline catalyst with an azeotropic solvent such as xylene, used to remove the water of condensation and the water contained in formalin, and to solubilize the solids. Care should be taken to remove water to improve storage stability of resole based formulations in the organic solvent blend. The maximum chain length preferred for this invention is 4. P-tertiary amyl phenol and bis-phenol A were used in the present invention with formalin in a molar ratio of 1:1.95 with sodium hydroxide catalyst and the solids content ranged from 65-70 % by weight. The resole contains methylol terminal groups that condense with hydroxyls on the vinyl polymer and other co-resins. It was used along with a) saturated polyester and b) epoxy resins together with the vinyl polymer and the amino resin cross-linker to obtain highly flexible, chemically and thermally resistant and hard coating compositions. However the resole when used with unsaturated polyester even with a low level of unsaturation resulted in a hard coating with poor flexibility.

Low molecular weight liquid epoxy resins made from bisphenol A and epichlorohydrin with epoxide equivalent ranging from 150-300 are preferred as these may be added in larger proportions within reasonable levels of viscosity. The epoxy resin used in the examples was Epon 830 of Shell. The epoxy resin has reactive epoxide and hydroxyl groups. Curing was effected by condensation of the hydroxyls with those of the

FPP2767

vinyl polymer and other co-resins. No hardeners that activate cure through the epoxide were employed since these affected the storage stability of the coating composition. This epoxy has an epoxide equivalent weight of 190-210 and was used in combination with saturated polyester resin together with the vinyl polymer and the amino resin, to yield compositions with excellent color retention, flexibility, hardness and chemical resistance. However, when used with phenolic resin, the color retention during cure was found to be poorer though the coating had excellent flexibility, hardness and chemical resistance.

10

Thermoplastic polyurethane resin may be used in combination with polyester, phenolic and epoxy resins, together with the vinyl polymer and the amino resin, and provides excellent gloss and chemical resistance to the cured coatings. It however should not be used at high levels since this lowers the hardness of cured coatings. It contains heat reactive terminal hydroxyl and isocyanate groups, which condense with the hydroxyl groups of these co-resins and those of the vinyl polymer. Estane 5715 of Noveon, a polyester based polyurethane resin with a solution viscosity of 40-70 cps in MEK (20% solids) containing largely reactive terminal hydroxyls was used in the examples with saturated polyester and a glossy, extremely flexible, chemically resistant coating was obtained.

15
20

The heat curable clear coats may be formulated by dissolving the polymer first in the solvent blend and then the resins together with a mineral acid catalyst are added to this solution. Compositions containing polyurethane and polyester were made by blending the molten polyurethane resin in the polyester and the adding this mix and the amino resin to the polymer solution. The basic attributes of the cured coating

25

FPP2767

remains unaffected by increasing the proportion of the vinyl polymer vis-à-vis the co-resins, but due to the high molecular weight of the polymer, viscosity of the compositions increases dramatically. This reduces the solids content of the liquid compositions. The same effect is observed on

5 increasing the molecular weight of the vinyl polymer. The proportion of the vinyl polymer is therefore minimized to the extent possible and its weight average molecular weight range is chosen between 20,000 and 50,000 to obtain the best balance of properties. Increasing the melamine resin content decreases the curing time of the composition and also

10 increases the hardness of the cured coating but adversely affects the flexibility. The most preferred level of melamine cross-linker is found to be 15-20 % of the total weight of the co-resins excluding the vinyl polymer. Components of the solvent blend may be selected from aliphatic alcohols such as methanol, ethanol, isopropanol, n-butanol, iso-

15 butanol and aromatics such as toluene, xylene. Other solvents such as diacetone alcohol, methyl ethyl ketone, methyl isobutyl ketone, and solvent naphtha may also be used as co-solvents/diluents in small proportions. Phosphoric acid or para toluene sulfonic acid may be used as the acid catalyst for these formulations. Phosphoric acid is preferred as

20 it provides much higher storage stability to these compositions. Many other combinations using these resins are possible in conjunction with the vinyl polymer. The heat curable clear coat systems may be pigmented to impart color in low to medium gloss to coated substrates. Titanium dioxide may be added for opacity and colored inorganic pigments and/or

25 organic dyes may be used for color. The pigment binding power of the polymer-resin system is quite high, however, a maximum of 50% of the polymer and resin content using titanium dioxide for a white coating, is suggested for optimum flexibility and corrosion resistance. This ensures

FPP2767

that the passivating nature of the cured film and its barrier characteristics are maintained with high flexibility. Blister resistance is obtained even with a low porosity of the film due to the passivation achieved on the metal interface. A range of corrosion inhibiting pigments may be selected comprising of inorganic and organic pigments which offer passive inhibition, for example, zinc molybdate and other molybdates, zinc phosphate, mica, tolyltriazole, complex organotitanate and other organic inhibitors which operate by passive inhibition. The incorporation of corrosion inhibiting pigments improves further the corrosion resistance of the coating. The pigments can be incorporated in the coating by first forming a mill base by conventional sand grinding or ball milling techniques, a concentrated solution of the polymer and resins of concentration 45-60% in the organic solvent blend, together with the pigments, and then blended with the remaining portion of solvents by high speed stirring to obtain a final solids content of 40-50 %. Other additives such as heat and light stabilizers may be added in small proportions to improve weatherability of these coatings. The coating, with or without pigments, dries by solvent evaporation on substrates such as cold rolled steel, hot dip galvanized steel, stainless steel, aluminum etc. when sprayed or flow coated on these surfaces. The rate of evaporation of the solvents especially at the cure temperatures used in metal pre-coat lines with peak metal temperatures ranging from 210-230° C may be adjusted by the choice of the solvents from the ones enumerated earlier. Specifically, a binary blend of xylene and butanol in a 60:40 weight ratio was found most suitable and was used for all compositions and those containing unsaturated polyester also contained DAP or DAIP as a reactive diluent. The small quantities of solvents contained in the co-resins have been accounted for in all the

FPP2767

formulations, or, the amount of solvent blend used in these includes the amount of solvents in these co-resins so that a 100% solids basis has been chosen for the co-resins. Cure time in the heated oven was fixed at 50 seconds and the PMT ranged from 210 to 230°C. The residence time may
5 further be reduced by increasing the acid catalyst level beyond 1% of the total weight of the liquid, chosen for all the examples herein.

The coating composition of the instant invention may be applied to ferrous and non-ferrous substrate including cold-rolled steel, hot dip
10 galvanized steel, stainless steel, tin plated steel, aluminum and other non-ferrous substrate in films of dry film thickness (DFT) ranging from 5-30 micrometers preferably 10-20 micrometers. The self-priming compositions are particularly suited to metal pre-coating process in coil coating lines because of its quick curing nature. These can be formulated
15 as free flowing one pack liquid that can be stored below 20°C for 6 (six) months.

The following examples of compositions are illustrative of the invention and are not intended to limit the scope of the invention as defined by the
20 appended claims.

The vinyl terpolymer as used in these examples are prepared by the process as described earlier with the weight content of polyvinyl alcohol, polyvinyl acetate and polyvinyl formal at 6.0-7.5%, 10-13% and 80-83%
25 respectively and a molecular weight between 25,000 and 30,000. It should be noted that a further increase of 7- 10 % in total solids is possible in all the listed examples by choosing the weight average molecular weight of the vinyl polymer to be around 20,000.

FPP2767**Example 1**

A clear coat composition may be made from the following ingredients in the assigned range of parts by weight:

INGREDIENTS	RANGE OF PARTS BY WEIGHT
Vinyl terpolymer	1.0
Melamine Resin (100% solids basis)	0.4 – 0.5
Polyurethane Resin	0.8 – 0.88
Saturated Polyester (100% solids basis)	1.3 – 1.87
Butanol	2.4 – 2.7
Xylene	3.6 – 4.0
Phosphoric Acid	0.1 – 0.15

5

Colored coatings may be made by incorporating a maximum of 50% of colored pigments and titanium dioxide, of the polymer and resin solids, in the above composition.

10 **Example 2**

A clear coat composition may be made from the following ingredients in the assigned range of parts by weight:

INGREDIENTS	RANGE OF PARTS BY WEIGHT
Vinyl terpolymer	1.2
Melamine Resin (100%solids basis)	0.35 – 0.44
Saturated Polyester (100%solids basis)	1.0 – 1.2
UP 1/ UP 2 (100% solids basis)	0.75 – 1.0
Butanol	2.65 – 3.3
Xylene	4.0 – 4.9
DAP	0.38 – 0.6
DCPO	0.01 – 0.015
Phosphoric Acid	0.1 – 0.15

Note : UP1 represents a completely unsaturated polyester made from maleic anhydride and diethylene glycol.

UP2 represents a partly unsaturated polyester made from maleic anhydride, dicyclopentadiene and ethylene glycol.

Colored coating compositions may be made by incorporating up to a maximum of 40 % of colored pigments and titanium dioxide, of the total weight of the vinyl polymer and the co-resins, in the above formulation.

Example 3

A specific white coating composition was made from the following ingredients in the assigned percentage parts by weight:

INGREDIENTS	% BY WEIGHT
Vinyl terpolymer	10.1
Melamine Resin (100% solids basis)	3.4
Saturated Polyester (100% solids basis)	8.8
UP 2 (100% solids basis)	8.8
Xylene	30.4
Butanol	20.3
Diallyl phthalate (DAP)	5.0
Dicumyl peroxide (DCPO)	1.3
Phosphoric Acid	1.0
Titanium Dioxide	10.9

Note : UP2 represents a partly unsaturated polyester made from maleic anhydride, dicyclopentadiene and ethylene glycol.

FPP2767**Example 4**

A clear coat composition may be made from the following ingredients in the assigned range of parts by weight:

INGREDIENTS	RANGE OF PARTS BY WEIGHT
Vinyl terpolymer	1.2
Melamine Resin (100% solids basis)	0.2 – 0.3
Saturated Polyester (100%solids basis)	0.9 – 1.0
Phenolic Resole (100%solids basis)	0.9 – 1.0
Xylene	3.4 – 3.7
Butanol	2.3 – 2.5
Phosphoric Acid	0.1– 0.15

- 5 Colored compositions may be made by incorporating up to a maximum of 40% of pigments including titanium dioxide, of the weight of the polymer and co-resins, in the above formulation.

Example 5

- 10 A clear coat composition may be made from the following ingredients in the assigned range of parts by weight:

INGREDIENTS	RANGE OF PARTS BY WEIGHT
Vinyl terpolymer	1.0
Melamine Resin (100%solids basis)	0.4 – 0.42
Saturated Polyester (100%solids basis)	0.9 – 1.0
Epoxy Resin	1.1 – 1.2
Xylene	3.6 – 3.8
Butanol	2.4 – 2.6
Phosphoric Acid	0.1 – 0.12

FPP2767

Pigmented versions of the above formulation may include up to a maximum of 50% of various pigments and titanium dioxide, of the weight of the vinyl polymer and the co-resins.

5 Example 6

A specific white pigmented composition was made from the following ingredients in the assigned percentage by weight:

INGREDIENTS	% BY WEIGHT
Vinyl terpolymer	9.47
Melamine Resin (100%solids basis)	4.16
Saturated Polyester (100%solids basis)	9.47
Epoxy Resin	11.4
Xylene	30.8
Butanol	20.5
Phosphoric Acid	1.2
Titanium Dioxide	13.0

10 Example 7

A clear coat composition may be made from the following ingredients in the assigned range of parts by weight:

INGREDIENTS	RANGE OF PARTS BY WEIGHT
Vinyl Terpolymer	1.0
Melamine Resin (100% solids basis)	0.25 – 0.3
Phenolic Resin (100% solids basis)	0.8 – 1.0
Epoxy Resin	1.0 – 1.1
Xylene	3.5 – 4.0
Butanol	2.3 – 2.7
Phosphoric Acid	0.1 – 0.15

FPP2767

Pigmented versions of the above formulation may be made by incorporating a maximum of 40% of pigments and titanium dioxide, of the weight of the vinyl polymer and the co-resins.

- 5 The non-volatile matter (NVM) of the clear coats listed above ranged from 32-37%. NVM of compositions containing DAP were measured at the PMT, that is, upon conversion into solids. It ranged from 42-50 % for pigmented compositions.
- 10 All the compositions were coated on dilute chromic acid treated aluminum, dilute hydrochloric acid treated cold rolled steel and untreated stainless steel and uniformly showed excellent flow and adhesion on these substrates. The coated panels were cured at PMT of 210-230°C for 50 seconds. All the compositions exhibited complete flexibility (passed
- 15 0T bend test). Hardness of the clear coats exceeded 4H for all formulations, while that for the white pigmented coats were nearly 6H or higher. The best color retention during cure was observed in compositions incorporating a) epoxy and polyester resins, and b) polyurethane and polyester resins. The epoxy based cured coatings also
- 20 exhibited the highest dry heat resistance of at least 150°C for sustained periods showing no color change at this condition while the other coatings did show a slight color change at this temperature though no deterioration in other properties was observed. All coatings showed excellent resistance to weak and strong acids, weak and strong alkalis,
- 25 organic solvents such as MEK, detergents, boiling water and staining.

FPP2767

TESTING METHOD

The testing methods used for different physiochemical characteristics are given below:

- 5 i) Scratch hardness - A pencil hardness index was used as is common in the industry.
- 10 ii) Solvent resistance – A cloth soaked with MEK was used to rub over coated surface for the prescribed number of times as per ASTM D-740. A minimum of 50 double rubs was used as a measure of pass.
- 15 iii) Flexibility - The coated substrate was folded on itself along a crease and an adhesive tape was used at the bend to examine any peel-off of the coating. All panels passed this OT bend test, which is the most rigorous examination of flexibility without any cracking or peel-off along the crease.
- 20 iv) Adhesion - ASTM 3359-76.
- 25 v) Resistance to boiling water - Edge protected coated panels were immersed in boiling water for 4 hours and the panels examined for blisters.
- vi) Chemical resistance – Resistance to chemicals was tested as per ASTM D 1308.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A self-priming, rapid curing, chromate free, corrosion resistant coating composition comprising:
 - a) a linear vinyl terpolymer made up predominantly of polyvinyl formal with polyvinyl alcohol and polyvinyl acetate as the two other co-polymers with three randomly distributed functional groups along the vinyl backbone comprising acetyl, formal and hydroxyl, offering cross-linking sites through the hydroxyl groups during cure, wherein the vinyl terpolymer comprises 6-15% by weight of the polyvinyl alcohol, 9-15% by weight of the polyvinyl acetate and 70-84% by weight of the polyvinyl formal;
 - b) a monomeric or oligomeric alkoxy amino resin;
 - c) multi-component combinations of two or more co-resins each consisting of:
 - i) an oligomeric saturated polyester resin;
 - ii) an oligomeric unsaturated polyester resin dissolved in an unsaturated monomer and containing a free radical initiator of high activation energy;
 - iii) an oligomeric bi-functional phenolic resole resin;
 - iv) an oligomeric epoxy resin; or
 - v) a low molecular weight polyurethane resin;
 - d) a mineral acid catalyst;
 - e) a blend of organic solvents; and optionally
 - f) one or more driers and chromate free inorganic pigments and/or organic dyes.
2. The coating composition as claimed in claim 1, wherein the percentages by weight of polyvinyl alcohol, polyvinyl acetate and polyvinyl formal of the vinyl terpolymer are 6.0-7.5%, 10-13% and 80-83% respectively.
3. The coating composition as claimed in claim 1 or 2, wherein the weight average molecular weight of said vinyl terpolymer is 15,000 to 80,000.
4. The coating composition as claimed in claim 3, wherein weight average molecular weight of said vinyl terpolymer is 20,000 to 50,000.

5. The coating composition as claimed in any one of claims 1 to 4, wherein the alkoxy amino resin is oligomeric with average degree of polymerization of no more than 3.
6. The coating composition as claimed in any one of claims 1 to 5, wherein methoxy melamine resin is used for cross-linking.
7. The coating composition as claimed in any one of claims 1 to 6, wherein the oligomeric saturated polyester has a chain length between 2 and 5.
8. The coating composition as claimed in any one of claims 1 to 7, wherein the oligomeric unsaturated polyester resin has a number average molecular weight not exceeding 4000 daltons.
9. The coating composition as claimed in any one of claims 1 to 8, wherein said unsaturated polyester resin is dissolved in diallyl phthalate or diallyl isophthalate.
10. The coating composition as claimed in any one of claims 1 to 9, wherein the free radical initiator used with the unsaturated polyester is dicumyl peroxide.
11. The coating composition as claimed in any one of claims 1 to 10, wherein the oligomeric phenolic resin has a chain length below 4.
12. The coating composition as claimed in any one of claims 1 to 11, wherein the saturated polyester resin is produced from adipic and isophthalic acids, and neopentyl and propylene glycols with triphenyl phosphite catalyst in toluene solvent.
13. The coating composition as claimed in any one of claims 1 to 12, wherein the unsaturated polyester resin used in the composition is either (a) a completely unsaturated polyester made from maleic anhydride and diethylene glycol, or (b) a partly unsaturated polyester made from maleic anhydride, dicyclopentadiene and ethylene glycol.

14. The coating composition as claimed in any one of claims 1 to 13, wherein the phenolic resole resin is produced from formalin, p-tertiary amyl phenol and bis-phenol A with a molar excess of formaldehyde over the substituted phenols.
15. The coating composition as claimed in any one of claims 1 to 14, wherein the epoxy resin is made from bisphenol A and epichlorohydrin and has an epoxide equivalent of 150-300.
16. The coating composition as claimed in claim 15, wherein the said epoxy resin has an epoxide equivalent weight of 190-210.
17. The coating composition as claimed in any one of claims 1 to 16, wherein the solvent blend comprises:
xylene, toluene, naphtha, isopropanol, butanol, ethanol, methanol, MEK, MIBK or diacetone alcohol, or any combination thereof.
18. The coating composition as claimed in any one of claims 1 to 17, wherein 60 parts of xylene and 40 parts of butanol by weight are used as solvent.
19. The coating composition as claimed in any one of claims 1 to 18, wherein the content of total solids in pigmented compositions is a minimum of 40% by weight.
20. The coating composition as claimed in any one of claims 1 to 19, wherein phosphoric acid is used as the catalyst.
21. The coating composition as claimed in claim 20, wherein 1% phosphoric acid used as the catalyst is 1% by weight of the composition.
22. The coating composition as claimed in any one of claims 1 to 21, which comprises 0-50% of the polymer and resin content of one or more chromate free inorganic pigments and/or organic dyes, and further comprises one or more corrosion inhibiting agents.

23. The coating composition as claimed in any one of claims 1 to 22, wherein one or more corrosion inhibiting agents each consisting of zinc or other molybdates, zinc phosphate, mica, tolyltriazole, complex organic titanates or other organic inhibitors which act by passive inhibition, or any combination thereof, are also comprised in the composition.

24. The coating composition as claimed in any one of claims 1 to 22 as a pigmented composition wherein titanium dioxide is comprised as the inorganic pigment.

25. The coating composition as claimed in claim 1, wherein the following ingredients are present in the listed range of parts by weight:

Ingredients	Range of parts by weight
Vinyl terpolymer	1.0
Melamine Resin (100% solids basis)	0.4 – 0.5
Polyurethane Resin	0.8 – 0.88
Saturated Polyester (100% solids basis)	1.3 – 1.87
Butanol	2.4 – 2.7
Xylene	3.6 – 4.0
Phosphoric Acid	0.1 – 0.15.

26. The coating composition as claimed in claim 1, wherein the following ingredients are present in the listed range of parts by weight:

Ingredients	Range of parts by weight
Vinyl terpolymer	1.2
Melamine Resin (100% solids basis)	0.35 – 0.44
Saturated Polyester (100% solids basis)	1.0 – 1.2
UP 1/ UP 2 (100% solids basis)	0.75 – 1.0
Butanol	2.65 – 3.3
Xylene	4.0 – 4.9
Diallyl phthalate (DAP)	0.38 – 0.6
Dicumyl peroxide (DCPO)	0.01 – 0.015
Phosphoric Acid	0.1 – 0.15

wherein UP 1 represents a completely unsaturated polyester made from maleic anhydride and diethylene glycol and UP 2 represents a partly unsaturated polyester made from maleic anhydride, dicyclopentadiene and ethylene glycol.

27. The coating composition as claimed in claim 1, wherein the following ingredients are present in the listed range of parts by weight:

Ingredients	Range of parts by weight
Vinyl terpolymer	1.2
Melamine Resin (100% solids basis)	0.2 – 0.3
Saturated Polyester (100% solids basis)	0.9 – 1.0
Phenolic Resole (100% solids basis)	0.9 – 1.0
Xylene	3.4 – 3.7
Butanol	2.3 – 2.5
Phosphoric Acid	0.1 – 0.15 .

28. The coating composition as claimed in claim 1, wherein the following ingredients are present in the listed range of parts by weight:

Ingredients	Range of parts by weight
Vinyl terpolymer	1.0
Melamine Resin (100% solids basis)	0.4 – 0.42
Saturated Polyester (100% solids basis)	0.9 – 1.0
Epoxy Resin	1.1 – 1.2
Xylene	3.6 – 3.8
Butanol	2.4 – 2.6
Phosphoric Acid	0.1 – 0.12 .

29. The coating composition as claimed in claim 1, wherein the following ingredients are present in the listed range of parts by weight:

Ingredients	Range of parts by weight
Vinyl Terpolymer	1.0
Melamine Resin (100% solids basis)	0.25 – 0.3
Phenolic Resin (100% solids basis)	0.8 – 1.0
Epoxy Resin	1.0 – 1.1
Xylene	3.5 – 4.0
Butanol	2.3 – 2.7
Phosphoric Acid	0.1 – 0.15.

30. The coating composition as claimed in claim 1 or 24, wherein it is formulated from the following ingredients in the assigned weight percentages:

Ingredients	% By weight
Vinyl terpolymer	10.1
Melamine Resin (100% solids basis)	3.4
Saturated Polyester (100% solids basis)	8.8
UP 2 (100% solids basis)	8.8
Xylene	30.4
Butanol	20.3
Diallyl phthalate (DAP)	5.0
Dicumyl peroxide (DCPO)	1.3
Phosphoric Acid	1.0
Titanium Dioxide	10.9

wherein UP 2 represents a partly unsaturated polyester made from maleic anhydride, dicyclopentadiene and ethylene glycol.

31. The coating composition as claimed in claim 1 or 24, wherein it is formulated from the following ingredients in the assigned weight percentages:

Ingredients	% By weight
Vinyl terpolymer	9.47
Melamine Resin (100% solids basis)	4.16
Saturated Polyester (100% solids basis)	9.47
Epoxy Resin	11.4
Xylene	30.8
Butanol	20.5
Phosphoric Acid	1.2
Titanium Dioxide	13.0.

32. A method of forming a coating on a ferrous or non-ferrous metallic substrate, which comprises:

- a) degreasing and treating the surface of said substrate on which coating is to be applied;
- b) preparing the coating composition as defined in claim 1 by dissolving the vinyl terpolymer in a blend of organic solvents, adding the amino resin and other co-resins with the acid catalyst to this solution and also free radical initiator, and, optionally, the drier(s), chromate free inorganic pigments and/or organic dyes;
- c) milling the contents to a homogeneous consistency;
- d) applying said coating composition by spray coating or roller coating method to attain the desired thickness and;
- e) curing coating so applied at a peak metal temperature of 210-230°C for 30-60 seconds.

33. The method as claimed in claim 32, wherein a white pigmented coating is prepared from the composition as defined in claim 31 or 32, to obtain a coating of 42-50% solids by weight.

34. The method as claimed in claim 32 or 33, wherein 0-50 % by weight of the resin and polymer content, of an inorganic pigment and/or organic dyes and other corrosion inhibiting agents other than chromates are added for preparing the said compositions.

35. The method as claimed in claim 32, 33 or 34, wherein 0-50 % by weight of the resin and polymer content, of titanium dioxide is added as the inorganic pigment.

36. The method as claimed in any one of claims 32 to 35, wherein the curing time is less than 60 seconds.
37. The method as claimed in any one of claims 32 to 36, wherein the thickness of the coating as applied is 5-30 micrometers.
38. The method as claimed in any one of claims 32 to 36, wherein the thickness of the applied coating is 10-20 micrometers.
39. The method as claimed in any one of claims 32 to 38, wherein said coating is applied directly on the surface of said substrate as a top coat.
40. The method as claimed in any one of claims 32 to 38, wherein said coating is applied directly on the surface of said substrate as an undercoat which is followed by application of top coat(s) based on one or more of resins each consisting of epoxy, polyurethane, alkyd, amino or polyester.
41. An article comprising:
- a) a ferrous or non-ferrous metallic substrate;
 - b) a coating applied to at least one surface of said substrate by a method as defined in any one of claims 32 to 40.
42. The article as claimed in claim 41, wherein said substrate is cold-rolled steel, hot dip galvanized steel, stainless steel, tin plated steel, aluminum or another non-ferrous substrate.