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(71) Applicant: TATA CHEMICALS LIMITED [IN/IN]; Bombay House, 24 Homi Street, 400001 Mumbai (IN).

(72) Inventors: SENSARMA, Soumen; Tata Chemicals Limited, Innovation Centre, Ghotavde Phata, Urawde Road, Pirangut Industrial Area, Gate NO. 1139/1, Mulshi 412108 Pune (IN).

PANDEY, Someshwarnath; Tata Chemicals Limited, Innovation Centre, Ghotavde Phata, Urawde Road, Pirangut Industrial Area, Gate NO. 1139/1, Mulshi 412108 Pune (IN).

(74) Agent: AGARWAL, Sneha; Obhan & Associates, 501/7, Lane W-21A, Western Avenue, Sainik Farms, New Delhi 110 080 (IN).


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(54) Title: A MODIFIER FOR A COATING COMPOSITION

(57) Abstract: The present invention is directed to a modifier for improving the surface properties of a coating composition. The said modifier comprises of an inorganic nanoparticle having at least one hydroxyl functional group covalently bonded to a crosslinking agent, the crosslinking agent having a general formula (I): Z[R2XRiSi(R>3)]2 (I). The said crosslinking agent is further crosslinked with a polydialkysiloxane diol.
A MODIFIER FOR A COATING COMPOSITION

FIELD OF INVENTION

The present invention relates to a modifier for improving the surface properties of a coating composition. More particularly, the present invention relates to a modifier comprising inorganic nanoparticles bonded to a crosslinking agent, which is further crosslinked to a polydialkylsiloxane diol.

BACKGROUND

The use of inorganic particles in coating compositions is widely known to improve the surface properties of the coatings. Such coating compositions however are subjected to drawbacks such as - haziness, crater formation, brittleness etc. in the final coating. It is further desired that such coatings exhibit mar-resistance and resistance to environmental etching. Several methods of modifying the coating compositions have been devised to achieve one or more of these properties. To be commercially successful, a coating should provide as many favorable characteristics as possible. Accordingly, it is most preferable to produce a coating that has an optimum mix of characteristics with regard to various forms of damage resistance. One of such techniques employs modification of the inorganic particles such as silica by coating the particle surface with crosslinked polysiloxane coating. Herein, the inorganic particles are for example, grafted with a polysiloxane coating via a crosslinking agent. However, because the existing techniques represent a compromise, usually one or more properties are partially/ completely sacrificed to increase the other.

For example, EP 0832947 describes formation of a film forming binder system with improved scratch resistance. The binder system consists of a crosslinkable resin and crosslinking agent. The nanoscale fillers are made surface reactive by the use of dual functional crosslinking agent (carbamate or glycidyloxy silane) having reactive end groups which are reactive to the polymeric phase. Thus the covalent attachment of the nanoscale fillers to the polymer matrix is made possible in this procedure. One of the disadvantage of this process is that high loading of the reactive nanoscale fillers is required for gaining improved scratch resistance which also leads to high cost and brittleness of the coating.
US patent 5853809 describes use of silica particle modified with carbide molecules and used in clear coats. The inorganic organic hybrid mixture thus produced gives automotive coating system which gives scratch resistance. The nano particles thus produced require substantial amount of nano silica particles to obtain anti-scratch property while curing the film above 130 °C. Nano particles were modified with suitable functional agent and resin matrix binds chemically with nano particles which often lead to the brittleness in final coating.

US 7641972 describes modification of nano particles by use of trimethyl terminated polydimethylsiloxane hydride coupled with vinyl trimethoxysilane. It also teaches the reaction of silaplane based compound with caprolactone based monomer followed by further functionalization with isocyanatopropyltrimethoxysilane. The nano particles thus prepared is used for polyurethane based resin systems. The particle thus produced shows substantial enrichment of nano particles on the surface of the final film but unable to provide substantial surface hardness to obtain anti-scratch property at a relatively low temperatures. The film thus obtained also fails to exhibit, in particular, 0 hour mar resistance (i.e. immediately after baking).

WO 2006/1 14420 describes the modification of nano silica particle with the use of low chain polydimethylsiloxane and tetraethylorthosilicate and use the same for acrylic melamine and 2K based polyurethane system. The invention describes use of very low amount of silica in the final resin system to get the required surface hardness. However, incorporation of nano silica particles into the 2K based resin system develops craters and also the gloss of coating at 20 Deg reduces while comparing with blank system.

Further, for the reduction of crater formation and maintaining gloss of coatings it is essential that the crosslinked polydimethylsiloxane network carrying modified nanosilica particles must be compatible with the matrix. With the use of known crosslinkers such as tetraethylorthosilicate, octyl-triethoxy silane etc. there is no improvement in the reduction of crater formation without compromising on desired properties.

Thus, there is a need to devise modifiers for coating compositions which exhibit scratch and mar resistance without embrittlement, haziness, crater formation. It is also
desired that such coatings have properties such as recoatability while requiring lesser loading of inorganic particles. It is further desirable that such modifier system exhibits the afore-said properties with both the 1K (one-component) and 2K (two-component) coating compositions based on polyurethane/ acrylic melamine or epoxy resin etc.

5

SUMMARY

The present invention is directed to a modifier for improving the surface properties of a coating composition. The said modifier comprises of an inorganic nanoparticle having at least one hydroxyl functional group covalently bonded to a crosslinking agent, the crosslinking agent having a general formula (I):

$$Z[\text{R}_2\text{XR}_1\text{Si}({\text{R}})_3]_2$$

(I)

where:

\[
\begin{align*}
\text{R} &= \text{OMe, OEt} \\
\text{R}_1 &= (\text{CH}_2)_x, \text{where } x = 1 \text{ to } 4 \\
\text{X} &= \text{NHCOO} \\
\text{Z} &= \text{polydialkylsiloxane.}
\end{align*}
\]

The said crosslinking agent is obtained by reacting hydride terminated polydialkylsiloxane having a molecular weight equal to or less than 450 Da with a reaction product of an alkenol and an isocyanatoalkyl-trialkoxysilane. Herein, the alkenol has a general formula (II):

$$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{OH}$$

(II)

where \( n = 2 \) to 5;

and the isocyanatoalkyl-trialkoxysilane has a general formula (III):

$$X,\text{R},\text{Si}({\text{R}})_3$$

(III)

where:

\[
\begin{align*}
\text{X}_i &= \text{OCN} \\
\text{R}_i &= (\text{CH}_2)_x, \text{where } x = 1 \text{ to } 4 \\
\text{R} &= \text{OMe, OEt.}
\end{align*}
\]

The crosslinking agent thus obtained is further crosslinked with a polydialkylsiloxane diol having a molecular weight equal to or less than 450 Da.
The present invention also discloses a coating composition comprising the aforesaid modifier. The present invention is also directed towards a modifier kit for a coating composition. The said modifier kit comprises a first component comprising of the aforesaid modifier and a second component comprising a polyether-modified polydialkysiloxane, such that the first component and the second component are to be added to the coating composition to obtain a modified coating composition.

DETAILED DESCRIPTION

To promote an understanding of the principles of the invention, reference will be made to the embodiment and specific language will be used to describe the same. It will nevertheless be understood that no limitation of scope of the invention is thereby intended, such alterations and further modifications in the described product and such further applications of the principles of the inventions as disclosed therein being contemplated as would normally occur to one skilled in art to which the invention relates.

The present disclosure generally relates to a modifier for improving the surface properties of a coating composition. More particularly, the modifier of the present disclosure comprises an inorganic nanoparticle having at least one hydroxyl functional group covalently bonded to a crosslinking agent, the crosslinking agent having a general formula (I):

\[ Z[R_2X, Si(R)]_2 \] (I)

where:

R = OMe, OEt;
R_i = (CH_2)_x, where x = 1 to 4;
X = NHCOO;
R_2 = alkyl substituent having 4 to 7 carbon atoms, polyether, polyester;
Z = polydialkylsiloxane.

The said crosslinking agent is obtained by reacting hydride terminated polydialkysiloxane having a molecular weight equal to or less than 450 Da with a reaction product of an alkenol and an isocyanatoalkyl-trialkoxysilane. Herein, the alkenol has a general formula (II):

\[ CH_2=CH(CH_2)_nOH \] (II)
where \( n = 2 \) to \( 5 \);

and the isocyanatoalkyl-trialkoxysilane has a general formula (III):

\[
X,R,\text{Si}(R)_3 \quad \text{(III)}
\]

where:

\( X = \text{OCN}; \)

\( R_i = (CH_2)_x \), where \( x = 1 \) to \( 4 \);

\( R = \text{OMe}, \text{OEt}. \)

The crosslinking agent is further crosslinked with a polydialkylsiloxane diol having a molecular weight equal to or less than 450 Da.

Herein, the hydroxyl groups present in the alkenol having the general formula II reacts with the isocyanate group present in the isocyanatoalkyl-trialkoxysilane having the general formula III to form alkoxy silane encapped alkene. The thus obtained alkoxy silane encapped alkene is further reacted with hydride terminated polydialkylsiloxane in presence of platinum catalyst to form alkoxy silane terminated polydialkylsiloxane with urethane linkages in the chain. Thus, the crosslinking agent having the general formula I is obtained.

The alkoxy silane groups present on both the terminals of the crosslinking agent reacts with the hydroxyl functional groups present in the inorganic nanoparticles as well as that on the polydialkylsiloxane diol to obtain crosslinked polysiloxane network with embedded inorganic nanoparticles, the modifier disclosed herein. The reaction Scheme 1 illustrates the preferred embodiment of the present invention wherein the crosslinking agent is formed by reacting the reaction product (1) obtained by reaction of but-3-ene-l-ol (A) and 3-isocyanatopropyl-trimethoxysilane (B), with hydride terminated polydimethylsiloxane (C). The crosslinking agent (2) thus obtained is further crosslinked to polydimethylsiloxane diol (D) and silica nanoparticles to form crosslinked polysiloxane network with embedded silica nanoparticles, the modifier.
In accordance with a preferred embodiment, the isocyanatoalkyl-trialkoxy silane may be selected from 3-isocyanatopropyl-trimethoxysilane and 3-isocyanatopropyl-triethoxysilane and is more preferably 3-isocyanatopropyl-trimethoxysilane. As three reactive groups are present on the isocyanatoalkyl-trialkoxy silane, the resultant crosslinking agent has six reactive groups present thereon. This provides higher crosslinking density when the crosslinking agent is cured with polydialkylosiloxane diol.
In accordance with an aspect, the alkenol may be selected from any alkenol having a general formula (II):

\[
CH_2=CH(CH_2)_nOH \quad (II)
\]

where \( n = 2 \) to 5.

In accordance with a preferred embodiment, the alkenol is but-3-ene-1-ol. The alkenol may be prepared by any known method or may be obtained from any commercial source. In accordance with an embodiment, a mixture of two or more alkenols having the general formula II may be used.

In accordance with an embodiment, the hydride terminated polydialkylsiloxane has an alkyl substituent having 1 to 8 carbon atoms. The hydride terminated polydialkylsiloxane has an average number of siloxane groups (n) between 1 to 10. The hydride terminated polydialkylsiloxane has two terminal hydride groups attached thereon.

In accordance with a preferred embodiment, hydride terminated polydialkylsiloxane is hydride terminated polydimethylsiloxane having the general formula (IV), where \( 1 \leq n \leq 10 \):

\[
\begin{align*}
\text{H-Si-O} & \text{Si-O} \text{Si-H} \\
\text{CH}_3 & \text{CH}_3 \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3 \text{CH}_3 \\
\end{align*}
\]

\quad \text{(IV)}

The hydride terminated polydialkylsiloxane may be prepared by any known method or may be obtained from any commercial source. In accordance with an aspect, low molecular weight hydride terminated polydialkylsiloxane having a molecular weight equal to or less than 450 Da is used in the present invention. Use of shorter hydride terminated polydialkylsiloxane or low molecular weight hydride terminated polydialkylsiloxane with alkene group provides a rapid transfer of hydride group onto the double bond of alkenol group and thereafter reaction with isocyanatoalkyl-trialkoxysilane with alkenol. It also allows achieving higher crosslinking density when reacted with polydialkylsiloxane diol.

In accordance with an embodiment, the polydialkylsiloxane diol has an alkyl substituent having 1 to 8 carbon atoms. The polydialkylsiloxane diol has an average
number of siloxane groups \((r)\) between 1 to 10. In accordance with a preferred embodiment, polydialkylsiloxane diol is polydimethylsiloxane diol having the general formula \((V)\), where \(1 \leq r \leq 10:\)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{HO} \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{OH} \\
\text{CH}_2 \\
\end{array}
\]

\((V)\)

The polydialkylsiloxane diol may be prepared by any known method or may be obtained from any commercial source. Herein, the polydialkylsiloxane diol having a molecular weight equal to or less than 450 Da is used. Using the low molecular weight polydialkylsiloxane diol further enables achieving higher crosslinking density, as desired in the present invention.

In accordance with an aspect, the use of flexible polydialkylsiloxane (a soft polymer) based crosslinking agent introduces softness in the resultant coating and thus prevents the brittleness of the final coating. Due to the presence of polydialkylsiloxane there is increase in flexibility of the crosslinked polysiloxane network and reduction in the crater formation on the surface when blended with \(1K/2K\) coating system. Also, there is increase in homogeneity of the coating composition on the surface. Polydialkylsiloxane renders further advantages such as the long chain of polydialkylsiloxane leads to the phase separation between the inorganic nanoparticle and polydialkylsiloxane. Further, the absence of true chemical bond between the inorganic nanoparticles and coating matrix leads to migration of inorganic nanoparticles towards the surface of the coating and hence renders glass like properties to the coating thereby providing abrasion resistance, mar resistance and scratch resistance to the coating. The inorganic nanoparticles migrates towards the coating surface also because of low bulk density. Migration of inorganic nanoparticles to surface of coating during curing provides further advantages such as lesser amount of inorganic nanoparticles in the range of 1 to 6 wt% based on total weight is required to achieve the desired surface properties. Further, the inorganic nanoparticles present on surface of coating provide anchoring points thereby allowing ability to recoat the surface with the coating composition.
In accordance with an embodiment, the amount of inorganic nanoparticles in the modifier of the present invention is in the range of 1 to 6 wt% based on total weight.

In accordance with an embodiment, the isocyanatoalkyl-trialkoxy silane is reacted with the alkenol in the molar ratio of 1:1. In accordance with a further embodiment, the reaction product obtained by reacting isocyanatoalkyl-trialkoxy silane with alkenol is reacted with the hydride terminated polydialkylsiloxane in a molar ratio of 2:1.

In accordance with a related embodiment, the molar ratio of the crosslinking agent and the polydialkylsiloxane diol is in a range of 0.1 to 1.4 and is preferably 0.9.

In accordance with an embodiment, the inorganic nanoparticle is selected from the group comprising of silica, alumina, titania, zirconia, clay and mixtures thereof. In accordance with a preferred embodiment, silica nanoparticles are used. Further, the silica nanoparticles may be present either in powder or solution form. In accordance with a related embodiment, silica nanoparticles may be obtained from commercial source. Preferably, sols of silica are used. It could be aqueous based silica sol (aquasol) or any polar/ non-polar solvent based silica sol. The polar solvent may be any alcohol and non-polar solvent can be butyl acetate, methoxy propyl acetate, heptanone, Methyl ether ketone. In accordance with a related embodiment, silica nanoparticles have a particle size in the range of 1-60 nm and is preferably 5-20 nm. The pH of aqueous based sol which is used in the present invention may range from 2 to 4 with particle size distribution (PSD) of 5 to 60 nm and silica loading of 20 to 35 wt%. The alcohol based silica sol could have pH 3 to 4 with PSD of 5 to 60 nm and silica loading of 20 to 35 wt%. The non polar solvent based silica sol has a PSD of 5 to 60 nm with silica loading 20 to 35 wt%.

Alternatively, silica nanoparticles may be obtained by controlled hydrolysis of tetraethylorthosilicate, methyl trimethoxy silane, ethyl trimethoxy silane or any other suitable derivative of siloxane compounds in presence of mild acid.

In accordance with an aspect, sol containing inorganic nanoparticles having free hydroxyl groups is used. In accordance with a preferred embodiment, the hydroxyl groups on the inorganic nanoparticles are made hydrophobic by at least partial esterification with
organic solvents such as ethanol, butanol etc. Any known technique may be used to esterify inorganic nanoparticles.

In accordance with an aspect, a modifier kit for a coating composition is also disclosed. The said modifier kit comprises a first component comprising of the modifier, as described above and a second component comprising a polyether-modified polydialkylsiloxane, such that the first component and the second component are to be added to the coating composition to obtain a modified coating composition.

In accordance with a preferred embodiment, the polyether-modified polydialkylsiloxane is polyether-modified polydimethylsiloxane. In accordance with a related embodiment, when the modifier is added to the coating composition, the amount of polyether-modified polydialkylsiloxane is 0.02% to 0.5% of total weight. The polyether-modified polydialkylsiloxane serves to reduce the surface tension of the coating composition upon curing. The modifier when used along with polyether modified polydimethylsiloxane exhibits synergistic action to render complete mar resistance to the cured coating composition at 0 hour.

In accordance with an aspect, a coating composition comprising the modifier of the present invention is also disclosed. In accordance with an aspect, a polyether modified polydialkylsiloxane is also added to the coating composition.

The modifier as described in the present disclosure may be used with any thermally, radiation curable 1K / 2K coating compositions. In accordance with an embodiment, the modifier may be used as filler for any polypropylene, polyurethane, nylon, PBT, polyimide, polyether ether ketone, Polyethylene terephthalate, PPT, polyesters, polyamide, polyacrylate, polyether, polysulphone based polymer systems. The coating composition may further comprise certain additives such as UV-absorbers, defoamers, plasticizers, adhesion promoters, light stabilizers, anti-oxidants, colouring agent, flow controllers/ enhancers, catalysts, wetting agents, leveling agents, sag control agent, organic solvent etc.
The coating composition according to the invention may be used for coating automotive parts, various other substrates such as wood, metal, alloys, ceramic and plastic.

In accordance with an aspect, a method of preparing the modifier of the present invention is disclosed. The said method comprises of adding to a dispersion of inorganic nanoparticles, the crosslinking agent and the polydialkylsiloxane diol in the desired molar ratio, followed by heating the reaction mixture so obtained at the an elevated temperature in the range of 80 to 150°C for a time period in the range of 30 minutes to 4 hours. Preferably, the reaction mixture is heated at 130°C for 3 hours. In accordance with a further preferred embodiment, the molar ratio of the crosslinking agent and the polydialkylsiloxane diol is in a range of 0.1 to 1.4. Herein, the dispersion of inorganic nanoparticles is prepared by first esterifying the inorganic nanoparticles with an organic solvent followed by dispersion in a desired solvent.

The crosslinking agent of the present invention is prepared by first reacting the alkenol and the isocyanatoalkyl-trialkoxy silane, the alkenol having the general formula (II):

\[ \text{CH}_2=\text{CH}((\text{CH}_2)_n\text{OH}) \quad (II) \]

where \( n = 2 \) to 5;

the isocyanatoalkyl-trialkoxy silane having the general formula (III):

\[ \text{X} \text{R} \text{Si}(\text{R})_3 \quad (III) \]

where:

\( \text{X} \text{I} = \text{OCN} \);

\( \text{R} \text{I} = (\text{CH}_2)_x \), where \( x = 1 \) to 4;

\( \text{R} = \text{OMe, OEt} \);

in the presence of dibutyltin dilaurate (DBTDL) at an elevated temperature in the range of 60 to 100°C and preferably at 85 °C for a predetermined time period. Preferably, the reaction is carried out for one hour. The reaction product thus obtained is reacted with the hydride terminated polydialkylsiloxane having a molecular weight equal to or less than 450 Da in the presence of a platinum catalyst at an at an elevated temperature in the range of 60 to 100 °C and preferably at 85 °C for a predetermined time period. Preferably, the reaction is carried out for one hour.
In accordance with an embodiment, the isocyanatoalkyl-trialkoxysilane is reacted with the alkenol in the molar ratio of 1:1. In accordance with a further embodiment, the reaction product obtained by reacting isocyanatoalkyl-trialkoxysilane with alkenol is reacted with the hydride terminated polydialkylsiloxane in a molar ratio of 2:1.

The modifier once prepared may be dispersed in water, solvents etc. to obtain a dispersion thereof or separated in the form of solid particles such as powder, flakes etc. for storage and transportation.

In accordance with a further aspect, a method of preparing the coating composition comprising the modifier described above is also disclosed. The said method comprises of adding to the coating composition, the modifier of the present invention in a predetermined quantity. In accordance with an embodiment, the polyether-modified polydialkylsiloxane is also added to the coating composition in a predetermined quantity.

In accordance with a preferred embodiment, the amount of the modifier added to the coating composition is in the range of 3 to 20 % by weight based on the total weight and that of the polyether-modified polydialkylsiloxane is in the range of 0.02% to 0.5% by weight based on the total weight.

Any known method of coating the coating composition prepared in accordance with the present invention may be used. These include, for example, spray coating, dip coating, roll coating, curtain coating, and the like. Although various methods of curing may be used, heat curing is preferred. The coating composition prepared in accordance with the present invention when coated on plastics generally cure at 70°C and at 120-140°C for metallic parts. The curing time will vary depending on the particular components used, and physical parameters such as thickness of the layers etc.

Examples

The following examples are provided to explain and illustrate the preferred embodiments of the process of the present invention and do not in any way limit the scope of the invention as described and claimed:
Example 1: Synthesis of modifier in accordance with the present invention.

Materials used:
1. Hydride terminated polydimethylsiloxane (Mn ~ 450, Gelest);
2. Bis(3-hydroxypropyl) polydimethylsiloxane (Mn -380, Nanjing SiSiBSilicoes Co., Ltd.);
3. Isocyanatopropyltrimethoxysilane (Gelest);
4. dibutyltin dilaurate (DBTDL,95%, Aldrich);
5. Aqueous silica sol (snowtex-O, PH-2-4, 23 wt % silica,Nissan Chemical America corporation);
6. Polyether modified polydimethylsiloxane (BYK-333, BYK chemie Co.).
7. Thinner, Lacquer (acrylic / polyester polyol) and Hardner (HMDI) obtained from commercial source.
8. Absolute Ethanol(Merck), Isopropanol (Merck) and Butanol (sd-fine chemicals), methoxypropyl acetate from commercial source.
9. But-3-ene-1-ol (Sigma-Aldrich)
10. Hexachloroplatinic acid (S D Fine Chem, India)
11. Modaflow acrylic flow additive
12. 10% BYK 310 in Methoxy propyl acetate (MPA)

The synthesis of modifier was carried out in three steps:

Step 1: Dispersion of aqueous silica sol into an organic solvent such as methoxy propyl acetate after esterification with alcohols such as butanol etc.

20 grams of aqueous silica sol was taken in a 100 milliliter round bottom flask attached with a condenser. The assembly was circulated with rütrogen gas through schlenk line. To the round bottom flask were added 60 grams of isopropanol and 40 grams of butanol along with addition of 0.06 g of n-propyltrimethoxysilane. The solution was evaporated using rotavapor at 30°C to make volume of solution around 40 grams. Further 30 gramsof methoxy propyl acetate was added to the round bottom flask and heated at 130°C for one hour. The solution was further concentrated to 36 grams using rotavapor.
Step 2: Preparation of crosslinking agent

In the reaction process 0.615 grams of 3-iscryanatopropyl-trimethoxysilane was taken in a completely dry preheated 25 milliliter two necked round bottom flask with a magnetic pellet. Nitrogen gas was flushed for 2 minutes through the flask and it was connected to dried condenser with nitrogen inlet which was further connected to schlenk line for maintaining the nitrogen atmosphere. 235 milligrams of 10 % DBTDL in heptanone was added to the flask followed by drop-wise addition of but-3-ene-1-ol (0.215 g) over 10 minutes maintaining temperature of the reaction mixture at 85°C. The reaction was carried out over a period of one hour. The reaction was confirmed by the disappearance of isocyanate peak at 2270 cm⁻¹. After the reaction had subsided, the temperature of the round bottom flask under nitrogen was decreased to 50°C and catalytic amount of hexachloroplatinic acid was added to the flask. Further 0.825 g of hydride terminated polydimethylsiloxane was added drop-wise to the reaction mixture and temperature was raised to 85°C and the reaction was continued for one hour. The success of the reaction was confirmed by the disappearance of Si-H peak in Infrared spectra at 2163cm⁻¹.

Step 3: Reaction of the sol formed in step 1 with a mixture of crosslinking agent prepared in the step 2 and Polydimethylsiloxane diol in a molar ratio of 0.9 to obtain modifier of the present invention.

The step 3 involves reaction of the sol formed in step 1 with a mixture of crosslinking agent prepared in the step 2 and Bis(3-hydroxypropyl) polydimethylsiloxane(M₆=380) in a molar ratio of 0.9 respectively. In a round bottom flask, 36 grams of the dispersion of silica nanoparticles in methoxy propyl acetate and 1.41 grams of crosslinking agent formed in step 2 was added along with 0.62 g of Bis(3-hydroxypropyl) polydimethylsiloxane maintaining the molar ratio of 0.9. The reaction was carried out at 130°C for 3 hours. Further, the reaction product was concentrated to 20 grams on a rotavapor by removing excess solvent and centrifuged to get a clear stable organosol containing silica particles embedded in crosslinked polysiloxane network.
Preparation of coating composition including modifier of present invention

Example 2: Testing on 2K polyurethane based system:

5 2K Polyurethane (PU) metallic base coat:

2K PU base coat with blazing silver contains mixture of two acrylic polyol resins with one having the solid content of 54.5% and other one having 50%. Hydroxyl value of one of the film forming polyol resin is 80 and other one is 30 respectively. Apart from these the formulations also contains component of wax dispersion, Cellulose acetate butyrate and antisettling additives. Hexamethylenediisocyanate (HMDI) was used as hardener and thinner used was a mixture of xylene, solvent C9 and butyl acetate (55:30:15). Mixture of non leafing type aluminum pigments are used to get desire color such as silver effect or sparkling effect.

15 Top Clear coat formulation:

The top clear coat was formed using the following materials:
Polyacrylatepolyol : 73.2 g;
Defoamer : 0.09g;
HALS : 0.37 g;
UV absorber : 0.73g;
Glycol ether ester solvent : 11.0 g;
Butyl diglycolacetate : 1.83g;
Duranate 22A/75PX (NCO content 16.5% and solid content 75%) as catalyst used stoichiometrically
BYK 310-Silicon flow additive: 0.094 g;
Modaflow Acrylic flow additive : 0.013 g
Silica sol : 8.5 g in methoxypropyl acetate;
BYK 333 (polyether-polydimethylsiloxane) : 0.069 g;
Dibutyltin dilaurate : 0.009 g .

Application of 2K coating system to Acrylonitrile Butadiene Styrene (ABS) and metal sheet (MS) panels
ABS and metallic panels were washed with iso-propanol and allowed to dry. The 2K polyurethane metallic base coat comprising metallic silver was applied on both the panels with thickness 20 to 25 microns followed by flash off time of 5 minutes. Then top clear coat as prepared above (application viscosity 22 sec) was sprayed on the panels to achieve thickness 25 to 35 micron. After flash off time of 5 minutes, the panels were baked at 80 °C for 30 minutes.

**Perfomance analysis - Instruments Used**

Pencil hardness was tested using Mitsubishi Uni-H pencil (pressure proofed high density lead). Scratch / mar behavior was tested using automatically electrically operated model as per BS-3900 part Es I.S. 101-1964. Pencil Hardnesss was tested using 720 N pencil scratch hardness tester from Sheen using pencils 9B to 9H (ISO 15184 / BS 3900 - E19). Scratch test was carried out by using 'SHEEN' UK Make Automatic Electric operated Scratch Hardness Tester (Ref: 705).

Various samples of the above coating composition were prepared to determine and compare the effect of the modifier of the present invention on various properties of the resulting coating composition. Preparation of various samples of coating composition including the modifier of the present invention is illustrated below:

**Sample 1:** 2 grams of polyacrylate polyol resin with hydroxyl value 56 (obtained from Berger Paints) was taken and 0.3 grams of hardener was mixed to it along with 0.6 grams of thinner. 0.4 grams of modifier (sol) prepared in example 1 was added to the mixture to enable the concentration of the silica nanoparticles on PU coating to be 7.55% after drying and mixing. The coating was casted on a clean glass panel. The panel was kept for five minutes in fuming hood and was further maintained in hot oven at 70°C for 30 minutes.

**Sample 2:** 2 grams of polyacrylate polyol resin was taken and 0.3 grams of hardener was mixed to it along with 0.6 grams of thinner. 0.4 grams of modifier (sol) prepared in example 1 was added to the mixture to maintain the concentration of the silica nanoparticles on PU coating to be 7.55% after drying and mixing. The coating was casted
on a clean glass plate. The panel was kept for five minutes in fuming hood and further maintained in hot oven at 70°C for 30 minutes.

**Sample 3:** In 2 grams of 1K resin (acrylic melamine) was added 0.4 grams of modifier (sol) prepared in example 1 along with 0.6 grams of thinner to maintain the concentration of the silica nanoparticles on the dried coating at around 4.39%. The coating was casted on a panel. After coating, the panel was left for 5 minutes. Finally, it was baked at 130°C in hot oven for 30 minutes.

**Sample 4:** 2 grams of polyurethane resin with additive was taken and 0.3 grams of hardener was mixed to it along with 0.6 grams of thinner. 0.1 g of modifier (sol) prepared in example 1 was added the mixture to maintain the concentration of the silica nanoparticles on PU coating to be 2% after drying and mixing. The coating was casted on a clean glass plate. The plate was kept for five minutes in fuming hood and further maintained in hot oven at 70°C for 30 minutes.

**Sample 5:** 2 grams of polyurethane resin with additive was taken and 0.3 grams of hardener was mixed to it along with 0.6 grams of thinner. 0.2 grams of modifier (sol) prepared in example 1 was added to the mixture to maintain the concentration of the silica nanoparticles on PU coating to be 3.92% after drying and mixing. The coating was casted on a clean glass plate. The plate was kept for five minutes in fuming hood and further maintained in hot oven at 70°C for 30 minutes.

**Sample 6:** 2 grams of polyurethane resin with additive was taken and 0.3 grams of hardener was mixed to it along with 0.6 grams of thinner. 0.3 grams of modifier (sol) prepared in example 1 was added to the mixture to maintain the concentration of the silica nanoparticles on PU coating to be 5.77% after drying and mixing. The coating was casted on a clean glass plate. The plate was kept for five minutes in fuming hood and further maintained in hot oven at 70°C for 30 minutes.

Table 1 illustrates the findings of the scratch test after 24 hours of curing by pencil hardness measurement. As shown in Tables 1, the coatings having lesser percentage of silica nanoparticles on surface are clearer than the coatings having increased percentage of
silica nanoparticles. However, the coatings having increased percentage of silica nanoparticles on surface exhibited improved characteristics in terms of pencil hardness and also nail mark resistance as compared to the coatings having lesser percentage of silica nanoparticles on surface.

Table 1: Results of scratch test after 24 hrs of curing

<table>
<thead>
<tr>
<th>Description</th>
<th>Resin</th>
<th>Hardener</th>
<th>Sol</th>
<th>Thinner</th>
<th>Flash time</th>
<th>Curing time</th>
<th>Curing temp.</th>
<th>Appearance</th>
<th>Hardness</th>
<th>% of silica on dry film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>2 g</td>
<td>0.3 g</td>
<td>0.4 g</td>
<td>0.6 g</td>
<td>5 min</td>
<td>30 min</td>
<td>70°C</td>
<td>Slightly hazy</td>
<td>5H</td>
<td>7.55</td>
</tr>
<tr>
<td>Sample 2</td>
<td>2 g</td>
<td>0.3 g</td>
<td>0.4 g</td>
<td>0.6 g</td>
<td>5 min</td>
<td>30 min</td>
<td>70°C</td>
<td>Slightly hazy</td>
<td>5H</td>
<td>7.55</td>
</tr>
<tr>
<td>Sample 3</td>
<td>2 g</td>
<td>0 g</td>
<td>0.4 g</td>
<td>0.6 g</td>
<td>5 min</td>
<td>30 min</td>
<td>130°C</td>
<td>clear</td>
<td>4H</td>
<td>4.39</td>
</tr>
<tr>
<td>Sample 4</td>
<td>2 g</td>
<td>0.3 g</td>
<td>0.1 g</td>
<td>0.6 g</td>
<td>5 min</td>
<td>30 min</td>
<td>70°C</td>
<td>clear</td>
<td>3H</td>
<td>2</td>
</tr>
<tr>
<td>Sample 5</td>
<td>2 g</td>
<td>0.3 g</td>
<td>0.2 g</td>
<td>0.6 g</td>
<td>5 min</td>
<td>30 min</td>
<td>70°C</td>
<td>Slightly hazy</td>
<td>5H</td>
<td>3.92</td>
</tr>
<tr>
<td>Sample 6</td>
<td>2 g</td>
<td>0 g</td>
<td>0.3 g</td>
<td>0.6 g</td>
<td>5 min</td>
<td>30 min</td>
<td>70°C</td>
<td>Slightly hazy</td>
<td>5H</td>
<td>5.77</td>
</tr>
</tbody>
</table>

Example 3: Various samples of the coating composition were prepared to determine and compare the effect of the modifier of the present invention and the polyether-modified polydialkylysiloxane on various properties of the resulting coating composition. Preparation of various samples is illustrated below:

Sample 7 (Blank): 92 grams of acrylic polyol lacquer is taken and 15.9 grams of hardener is mixed to it along with 35 grams of thinner and mixed well and coating was drawn on MS plate as well as ABS panel.
Sample 8: About 92 grams of polyurethane lacquer is mixed with 15.9 grams of hardener along with 35 grams of a thinner (mixture of xylene, 85% and butyl acetate, 15%). To the above formulation, 8.5 grams of modifier (sol) of the present invention and 0.068 grams of polydimethylsiloxane-polyether based additive (BYK 333) is added to maintain the concentration of the silica nanoparticles on polyurethane film to be 4.01% upon mixing and drying.

Sample 9: 92 grams of acrylic polyol lacquer was mixed with silicone flow additive (0.4 wt%), acrylic flow additive (1.4 wt%), 15.9 grams of hardener (Duranate 22A) and 35 grams of a thinner (mixture of xylene and butyl acetate (85:15 w/w). To the above formulation 8.5 grams of dispersion of modifier (prepared in Example 1) along with 0.068 grams of BYK 333 was added to maintain the concentration of the silica nanoparticles on polyurethane film to be 4.01% upon mixing and drying.

Tables 2, 3 and 4 illustrate the findings of the test after 24 hours, 48 hours and 72 hours of curing respectively. As shown in Tables 2, 3 and 4, the coatings obtained using the modifier of the present invention exhibit improved characteristics in terms of pencil hardness and also nail mark.

**Table 2**: Performance after 24 hours maturation in air at room temperature (CRT) of the cured film at 80°C/30 minutes (25 minutes curing and 5 minutes heat up of the panel).

<table>
<thead>
<tr>
<th>SL NO</th>
<th>TEST ITEMS</th>
<th>SPECIFICATION</th>
<th>TYPE OF SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>W/O MODIFIER (Sample 7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>WITH MODIFIER (Sample 8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>WITH MODIFIER AND SILICONE FLOW + ACRYLIC FLOW ADDITIVE (Sample 9)</td>
</tr>
<tr>
<td>1.0</td>
<td>Gloss at 20°</td>
<td>Minimum 80 units</td>
<td>80 - 82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>84 - 85.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>84 - 86</td>
</tr>
<tr>
<td>2.0</td>
<td>Gloss at 60°</td>
<td>Minimum 90 units</td>
<td>92 - 96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>93 - 97.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>93 - 97</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td>Base Coat</td>
<td>Minimum Thickness</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td>-----------</td>
<td>-------------------</td>
</tr>
<tr>
<td>3.0</td>
<td>Dry Film Thickness (DFT)</td>
<td>Minimum 18 µm</td>
<td>20 - 23 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Minimum 30 µm</td>
<td>32 - 34 µm</td>
</tr>
<tr>
<td>4.0</td>
<td>Intercoat Adhesion</td>
<td>To pass as 100/100</td>
<td>Passes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No lifting of paint film from any square.</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>Scratch Hardness</td>
<td>To pass 1500 grm</td>
<td>Passes 1000 grm</td>
</tr>
<tr>
<td>6.0</td>
<td>Pencil Hardness</td>
<td>Tested on ABS Panel</td>
<td>To pass F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tested on MS Panel</td>
<td>To Pass F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Passed F+. Slight mark was observed with H.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Passed H. Slight mark was observed with 2H.</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>Nail Hardness</td>
<td>Checked on coating applied on both panel ABS and MS.</td>
<td>There should be no mark after moving the nail gently over the coating.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>Recoatability with same system</td>
<td>There should be no lifting, no loss of adhesion and gloss-shrinkage.</td>
<td>Passes</td>
</tr>
</tbody>
</table>
Table 3: Performance after 48 hours maturation in air at room temperature of the cured film at 80°C/30 minutes (25 minutes curing and 5 minutes heat-up of the panel).

<table>
<thead>
<tr>
<th>SL NO</th>
<th>TEST ITEMS</th>
<th>SPECIFICATION</th>
<th>TYPE OF SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>W/O MODIFIER (Sample 7)</td>
</tr>
<tr>
<td>1.0</td>
<td>Gloss at 20°</td>
<td>Minimum 80 units</td>
<td>81 - 83 84 - 85.5 84 - 86</td>
</tr>
<tr>
<td>2.0</td>
<td>Gloss at 60°</td>
<td>Minimum 90 units</td>
<td>92 - 96 95 - 97.5 93 - 97</td>
</tr>
<tr>
<td>3.0</td>
<td>DFT Base Coat</td>
<td>Minimum 18 µm</td>
<td>20 - 23 µm 19 - 24 µm 19 - 24 µm</td>
</tr>
<tr>
<td></td>
<td>DFT Clear Coat</td>
<td>Minimum 30 µm</td>
<td>32 - 34 µm 31 - 33 µm 30 - 35 µm</td>
</tr>
<tr>
<td>4.0</td>
<td>Intercom Adhesion</td>
<td>To pass as 100/100.</td>
<td>Passes Passes Passes</td>
</tr>
<tr>
<td>5.0</td>
<td>Scratch Hardness</td>
<td>To pass 1500 grm</td>
<td>Passes 1500 grm Passes 1800 grm</td>
</tr>
<tr>
<td>6.0</td>
<td>Pencil Hardness Tested on ABS Panel</td>
<td>To pass F</td>
<td>Passes B++ Passes H Passes H+ Slight mark was observed with 2H.</td>
</tr>
<tr>
<td></td>
<td>Pencil Hardness Tested on MS Panel</td>
<td>To Pass F</td>
<td>Passes F Passes H Passes 2H Slight mark was observed with 3H.</td>
</tr>
<tr>
<td>7.0</td>
<td>Nail Hardness Checked on coating applied on both panel ABS and MS.</td>
<td>There should be no *mark after moving the nail gently over the coating.</td>
<td>Better than sample 7 (Mark resistance on MS better than sample 7) Better than the sample 8 (Mark resistance on MS better than sample 7)</td>
</tr>
<tr>
<td>8.0</td>
<td>Recointability with same system</td>
<td>There should be no lifting, no loss of adhesion and gloss shrinkage.</td>
<td>Passes Passes Passes</td>
</tr>
</tbody>
</table>
Table 4: performance after 72 hrs maturation in air at room temperature of the cured film at 80°C/30 minutes (25 minutes curing and 5 minutes heat up of the panel).

<table>
<thead>
<tr>
<th>SL NO</th>
<th>TEST ITEMS</th>
<th>SPECIFICATION</th>
<th>W/O MODIFIER (Sample 7)</th>
<th>WITH MODIFIER (Sample 8)</th>
<th>WITH MODIFIER AND SILICONE FLOW + ACRYLIC FLOW ADDITIVE (Sample 9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>Gloss at 20°</td>
<td>Minimum 80 units</td>
<td>83 - 85</td>
<td>84 - 85.5</td>
<td>84 - 86</td>
</tr>
<tr>
<td>2.0</td>
<td>Gloss at 60°</td>
<td>Minimum 90 units</td>
<td>92 - 96</td>
<td>93 - 97.5</td>
<td>93 - 97</td>
</tr>
<tr>
<td>3.0</td>
<td>Base Coat</td>
<td>Minimum 18 µm</td>
<td>20 - 23 µm</td>
<td>19 - 24 µm</td>
<td>19 - 24 µm</td>
</tr>
<tr>
<td></td>
<td>Clear Coat</td>
<td>Minimum 30 µm</td>
<td>32 - 34 µm</td>
<td>31 - 33 µm</td>
<td>30 - 35 µm</td>
</tr>
<tr>
<td>4.0</td>
<td>Intercoat Adhesion</td>
<td>To pass as 100/100. No lifting of paint film from any square.</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>5.0</td>
<td>Scratch Hardness</td>
<td>To pass !500 grm</td>
<td>Passes 1500 grm</td>
<td>Passes 2000 grm</td>
<td>Passes 2000 grm</td>
</tr>
<tr>
<td>6.0</td>
<td>Pencil Hardness</td>
<td>Tested on ABS Panel</td>
<td>To pass F</td>
<td>Passes F</td>
<td>Passes H. Slight mark was observed with 2H.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tested on MS Panel</td>
<td>To Pass H</td>
<td>Passes H</td>
<td>Passes 2H. Slight mark was observed with 3H.</td>
</tr>
<tr>
<td>7.0</td>
<td>Nail Hardness</td>
<td>Checked on coating applied on both panel ABS and MS.</td>
<td>There should be no mark after moving the nail gently over the coating.</td>
<td>Better than sample 7 (Mark resistance on MS better than sample 7)</td>
<td>Better than the sample 8 (Mark resistance on MS better than sample 7 and 8)</td>
</tr>
<tr>
<td>8.0</td>
<td>Recoatability with same system</td>
<td>There should be no lifting, no loss of adhesion and gloss shrinkage.</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>------</td>
<td>--------------------------------</td>
<td>------------------------------------------------------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>9.0</td>
<td>Acid Resistance</td>
<td>To Pass N/10 H₂SO₄ X 24 hrs X RT.</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>10.0</td>
<td>Alkali Resistance</td>
<td>To Pass N/10 NaOH X 24 hrs X RT.</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>11.0</td>
<td>Water Resistance Properties</td>
<td>To Pass 96 hrs, w/o any blistering, pin hole and loss of adhesion.</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>12.0</td>
<td>Gasoline Resistance</td>
<td>To Pass 2 hrs, w/o any blistering, pin hole and loss of adhesion</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>13.0</td>
<td>Impact Resistance</td>
<td>To Pass X 21b X 20 cm X ½&quot; dia weight.</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>14.0</td>
<td>Flexibility by conical mandrel.</td>
<td>To pass 20 mm dia. (To be checked on MS panel).</td>
<td>Passes</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>15.0</td>
<td>Accelerated Weathering Test</td>
<td>To pass 500 hrs QUV w/o any loss of film properties. Gloss retention &gt;= 90%</td>
<td>Passes (90%)</td>
<td>Passes (93%)</td>
<td>Passes (92%)</td>
</tr>
</tbody>
</table>

Example 4: Testing on 1K Coating system- Various samples of the 1K coating composition were prepared to determine and compare the effect of the modifier of the present invention and the polydialkylsiloxane-polyether based additive on various properties of the resulting coating composition. Preparation of various samples of coating composition is illustrated below:
Sample 10: 10 grams of Acrylic Polyol Resin, Melamine Formaldehyde Resin was
spray coated on a metal plate pretreated with isopropanol and base coated with blazing
silver having a thickness of 23 micron. After a flash off time of 8 minutes the coated metal
plate was baked at 130 °C for 25 minutes.

Sample 11: About 92 grams of Acrylic Polyol Resin, Melamine Formaldehyde
Resin along with 8.5 grams of modifier (sol) along with 0.068 grams of BYK 333 was
mixed thoroughly and kept for 5 minutes. A metal plate was pretreated with 2-propanol
and base coat with blazing silver was applied with thickness of 20 micron. Then clear I K
lacquer as prepared above was applied on it to obtain thickness of 22 microns. After a
flash off time of 8 minutes the coated metal plate was baked at 130 °C for 25 minutes.

The two samples prepared above were tested for determining the surface hardness. Table 4
illustrates the Findings of the tests.

Table 5: Comparison of performance Of Thermosetting Acrylic (TSA) Clear
Lacquer with and without modifier of the present invention

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>TEST ITEMS</th>
<th>SPECIFICATIONS</th>
<th>SAMPLE W/O MODIFIER (Sample 10)</th>
<th>SAMPLE WITH MODIFIER (Sample 11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>LIQUID PAINT CHARACTERISTICS : -</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>Composition</td>
<td>Blend of Thermosetting Acrylic Polyol Resin, Melamine Formaldehyde Resin and Nano additive.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>Supply Viscosity by Fc4 at 30°C.</td>
<td>60 - 70 sees</td>
<td>70 sees.</td>
<td>70 sees.</td>
</tr>
<tr>
<td>4.0</td>
<td>Specific Gravity.</td>
<td>0.98±0.02</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>5.0</td>
<td>% Solid Content</td>
<td>45±2 %</td>
<td>46.79%</td>
<td>46.79%</td>
</tr>
<tr>
<td></td>
<td>Application</td>
<td>Viscosity by Fc4 at RT</td>
<td>20±2 sees</td>
<td>19 sees</td>
</tr>
<tr>
<td>---</td>
<td>-------------</td>
<td>------------------------</td>
<td>------------</td>
<td>---------</td>
</tr>
<tr>
<td>7.0</td>
<td>Recommended Thinner</td>
<td>Mixture of Aromatic hydrocarbon solvents.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>% thinner intake by V/V</td>
<td>40 - 60%</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>9.0</td>
<td>Application Method</td>
<td>Conventional air assisted spraying.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>Flash off Time</td>
<td>8-10 minutes (before baking)</td>
<td>8 minutes.</td>
<td>8 minutes.</td>
</tr>
<tr>
<td>11.0</td>
<td>Baking Schedule</td>
<td>140°C for 25 minutes</td>
<td>140°C/25 min</td>
<td>140°C/25 min</td>
</tr>
</tbody>
</table>

**B. BAKED FILM PROPERTIES**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0</td>
<td>To pass</td>
<td>H</td>
<td>Passes</td>
<td>H</td>
</tr>
<tr>
<td>13.0</td>
<td>Pencil Hardness</td>
<td>To pass 2000 gm.</td>
<td>Passes 2000 gm</td>
<td>Passes 3000 gm</td>
</tr>
<tr>
<td>14.0</td>
<td>Scratch Hardness</td>
<td>To pass 20 mm cylindrical mandrel</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>15.0</td>
<td>Flexibility</td>
<td>To pass 2mmX2mmX100 square (there should be no peel off from any square)</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>16.0</td>
<td>Adhesion</td>
<td>System should pass 96 hrs. There should be no blacking</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>17.0</td>
<td>Salt Spray resistance</td>
<td></td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>18.0</td>
<td>Acid resistance</td>
<td>To pass (N/10 H₂SO₄X 24 hrs), Spot test at 20°C</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>------</td>
<td>-----------------</td>
<td>-----------------------------------------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>19.0</td>
<td>Alkali Resistance</td>
<td>To pass (N/10 NaOH X 24 hrs), Spot test at 20°C</td>
<td>Passes</td>
<td>Passes</td>
</tr>
<tr>
<td>20.0</td>
<td>Mar proof Property (Nail Hardness)</td>
<td>There should be no mark by scratching with nail.</td>
<td>Satisfactory</td>
<td>Excellent</td>
</tr>
<tr>
<td>21.0</td>
<td>Gloss at 20°</td>
<td>Minimum 85</td>
<td>86 - 89</td>
<td>89 - 90</td>
</tr>
<tr>
<td>22.0</td>
<td>Dry film thickness</td>
<td><strong>Base Coat</strong></td>
<td><strong>Clear Coat</strong></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>SUBSTRATE and SUBSTRATE CLEANING</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.0</td>
<td>Substrate Type</td>
<td>Metal Sheet Plate Type (MSPT)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>System</td>
<td>MSPT → Application of TSA base coat Blazing Silver → Flash off 5 minutes → Application of TSA Clear Lacquer → Flash off 5 minutes → Baking at 140°C for 25 minutes.</td>
<td></td>
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**INDUSTRIAL APPLICABILITY**

The above disclosed modifier can be used in various polyurethane, acrylic/melamine 2K or 1K coating compositions. This can be also used in UV or thermally curable resin system to obtain remarkable surface properties. Addition of modifier results in obtaining coating compositions having desired surface properties such as improved anti-scratch, mar resistance, recoatability, high gloss retainability, barrier properties. The coating obtained by using this modifier leads to elimination of haziness and formation of crater in the final coating which is clearly not acceptable for the coating industries.
We Claim:

1. A modifier for a coating composition comprising:

   an inorganic nanoparticle having at least one hydroxyl functional group

   covalently bonded to a crosslinking agent, the crosslinking agent having a general
   formula (I):

   \[ Z[₃₋₄XR, \text{Si}(R)_3]_2 \]  
   \[ (I) \]

   where:

   \( R = \text{OMe, OEt;} \)

   \( R_2 = \text{alkyl substituent having 4 to 7 carbon atoms, polyether, polyester;} \)

   \( Z = \text{polydialkylsiloxane;} \)

   the said crosslinking agent obtained by reacting hydride terminated

   polydialkylsiloxane having a molecular weight equal to or less than 450 Da with a

   reaction product of an alkenol and an isocyanatoalkyl-trialkoxysilane,

   the alkenol having a general formula (II):

   \[ \text{CH}_2=\text{CH(CH}_2)_n\text{OH} \]  
   \[ (II) \]

   where \( n = 2 \) to 5;

   the isocyanatoalkyl-trialkoxysilane having a general formula (III):

   \[ X,R,\text{Si}(R)_3 \]  
   \[ (III) \]

   where:

   \( X,= \text{OCN;} \)

   \( R_1 = (\text{CH}_2)_x , \text{where } x = 1 \text{ to } 4; \)

   \( R = \text{OMe, OEt;} \)

   the crosslinking agent further crosslinked with a polydialkylsiloxane diol having a

   molecular weight equal to or less than 450 Da.

2. A modifier for a coating composition as claimed in claim 1 wherein both the

   polydialkylsiloxane diol and the hydride terminated polydialkylsiloxane have an alkyl

   substituent having 1 to 8 carbon atoms.
3. A modifier for a coating composition as claimed in claim 1 wherein the isocyanatoalkyl-trialkoxysilane is 3-isocyanatopropyl-trimethoxysilane.

4. A modifier for a coating composition as claimed in claim 1 wherein the alkenol is but-3-ene-1-ol.

5. A modifier for a coating composition as claimed in claim 1, wherein the molar ratio of the crosslinking agent and the polydialkylsiloxane diol is in a range of 0.1 to 1.4.

6. A modifier for a coating composition as claimed in claim 1, wherein the inorganic nanoparticle is selected from the group comprising of silica, alumina, titania, zirconia, clay and mixtures thereof.

7. A coating composition comprising a modifier, the modifier comprising:

an inorganic nanoparticle having at least one hydroxyl functional group covalently bonded to a crosslinking agent, the crosslinking agent having a general formula (I):

$$Z[R_{2}XR,Si(R)_{3}]_{2}$$

where:

$R = OMe, OEt$;

$R_{i} = (CH_{2})_{x}$, where $x = 1$ to $4$;

$X = NHCOO$;

$R_{2} = alkyl$ substituent having 4 to 7 carbon atoms, polyether, polyester;

$Z = polydialkylsiloxane$;

the said crosslinking agent obtained by reacting hydride terminated polydialkylsiloxane having a molecular weight equal to or less than 450 Da with a reaction product of an alkenol and an isocyanatoalkyl-trialkoxysilane, the alkenol having a general formula (II):

$$CH_{2}=CH(CH_{2})_{n}OH$$

where $n = 2$ to 5;

the isocyanatoalkyl-trialkoxysilane having a general formula (III):

$$X,R,Si(R)_{3}$$

(III)
where:

Xi= OCN;

$R_1 = (\text{CH}_2)_x$ where $x = 1$ to $4$;

$R =$ OMe, OEt;

designated the crosslinking agent further crosslinked with a polydialkylsiloxane diol having a molecular weight equal to or less than 450 Da.

8. A coating composition as claimed in claim 7 further comprising polyether modified polydialkylsiloxane.

9. A coating composition as claimed in claim 8 wherein the amount of polyether-modified polydialkylsiloxane in the coating composition is 0.02% to 0.5% of total weight.

10. A modifier kit for a coating composition comprising:

- a first component comprising an inorganic nanoparticle having at least one hydroxyl functional group covalently bonded to a crosslinking agent, the crosslinking agent having a general formula (I):

$$Z[R_2XR|Si(R_1)_{12}]$$  \hspace{1cm} (I)

where:

$R =$ OMe, OEt;

$R_1 = (\text{CH}_2)_x$ where $x = 1$ to $4$;

$X =$ NHCOO;

$R_2 =$ alkyl substituent having 4 to 7 carbon atoms, polyether, polyester;

$Z =$ polydialkylsiloxane;

designates the said crosslinking agent obtained by reacting hydride terminated polydialkylsiloxane having a molecular weight equal to or less than 450 Da with a reaction product of an alkenol and an isocyanatoalkyl-trialkoxysilane

the alkenol having a general formula (II):

$$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{OH}$$  \hspace{1cm} (II)

where $n =$ 2 to 5;

designates the isocyanatoalkyl-trialkoxysilane having a general formula (III):
X,R,Si(R)₃, \text{(III)}

where:

X, = OCN;

Rᵢ = (CH₂)ₓ, where x = 1 to 4;

R = OMe, OEt;

the crosslinking agent further crosslinked with a polydialkylsiloxane diol having a molecular weight equal to or less than 450 Da;

- a second component comprising a polyether-modified polydialkylsiloxane;

such that the first component and the second component are to be added to the coating composition to obtain a modified coating composition.
**INTERNATIONAL SEARCH REPORT**

International application No. PCT/IB2015/000022

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According to International Patent Classification (IPC) or to both national classification and IPC

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search Serins used)

Patseer and IPO Internal database.

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☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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Date of the actual completion of the international search: 18-06-2015
Date of mailing of the international search report: 18-06-2015

Name and mailing address of the ISA/Authorized officer:
Indian Patent Office
Plot No. 32, Sector 14, Dwarka, New Delhi-110075
Facsimile No.
Sathish Moorthy
Telephone No. +91-1125300200

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