

# Resins modification by functionalization with alkoxy silanes to be used in organic-inorganic hybrid coatings

Tania TROMBETTA\*, Massimo BEGGIORA\*, Cristiano TUNICE\*,  
Stefano TURRI\*\*, Francesca PICCININI\*\*

\*N. Benasedo, Via Asiago 332, Caronno Pertusella (VA), Italy

\*\*Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano,  
Piazza Leonardo da Vinci 32, 20133 Milan (Italy)

**Key-words:** Alkoxy silane modified resin, organofunctional alkoxy silanes, sol-gel process, hybrid coating, TEOS

## ABSTRACT

Organic-Inorganic hybrids systems have been widely studied in the last recent years because of the attractive properties that exhibit in many applications. Products already exist for corrosion protection for metal coatings, scratch resistance for OEM clear-coat, chemical resistance and easy-to-clean coatings. In general, silica or alumina nano-particles are used as additives in these formulations with high impact on cost. Sol-gel process is an elegant and low cost way of developing the nano-particle inorganic phase in coatings. In this work we will present waterborne and solvent borne resins prototypes containing alkoxy silane groups to build the inorganic phase bonded to the polymer. Organic-Inorganic hybrids coatings obtained from resins modified alkoxy silanes and coating from traditional 2K formulation were compared.

## Introduction

Organic coatings are formulations that contain many different chemical substances. The components can be divided in binders, volatile components, pigments and additives. Each component has specific task and play important role in the final coating that has either protective or aesthetical function. In most cases binders are the coating continuous phase. They bind together pigments and additives.

Many essential characteristics are determined by substrate and coating interfaces as adhesion. The adhesion property of a paint film is key to ensure durable protective function also in severe conditions, such as humidity, heat and mechanical stress.

In coating field, resins modified with silanes are used to obtain outstanding adhesion characteristics or room temperature curable formulations. The silanol group is able to form durable interaction between the substrate, organic or inorganic, and the film via a covalent bond formation. On the same time, trialkoxy silanes groups allow cross-linked polymer network formation. [1][2][3][4][5][6]

Resins modified with silanes coupling agents are also used to develop hybrid organic -inorganic systems via sol-gel process.

Low temperature curing coatings in traditional field can be obtained via 2K formulations. The 2K process involve polyisocyanate either for solvent borne resins or waterborne one. In the 2K system the polyol solution is mixed with polyisocyanate just before use and applied on the substrate. The coating then cures by solvent evaporation and chemical crosslink by urethane bond formation. The cure can be tailored by using polyols with different molecular weight, hydroxyl groups content and by selecting the hardness of polyisocyanate and polyol, according to their glass transition (T<sub>g</sub>). In general, the faster the cure the shorter the pot life.

For solvent system, pot life is higher than waterborne but high VOC is involved. For waterborne system, pot life is still one of the main issue to be optimise due to the competitive reaction of isocyanate with water.

Another type of room temperature coating is traditional solvent free UV curable formulations. They are one component system that cure by photoinitiated polymerization of acrylic monomers and oligomers. These formulations do not contain solvents and its cure is very fast . The main problem of this system is that high reactivity oligomers are difficult to be prepared. Resins used in UV curable systems are, in general, formulations of oligomers with relatively high molecular weight and high viscosity.

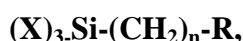
To be applied, oligomers must be formulated with low molecular weight acrylate monomers in order to reduce viscosity and improve crosslink density, but low molecular weight acrylates frequently are associate with skin irritation and other toxicological issue. Another limitation of UV curable coating is associated with the shrinkage during curing process that lead to poor adhesion and absence of cure in dark zone.

Resins modified with alkoxysilanes can also be cured at room temperature. They can be formulated with silicon alkoxide as tetraethyl orthosilicate (TEOS) to develop hybrid organic-inorganic systems via sol-gel process, with a very rich inorganic portion. The sol-gel processing methods were first used for decorative and constructional materials. In the last century many new applications were empirically developed. Nowadays new generation of advanced materials, not accessible using other methods, are obtained by this technology involving mild, low energy conditions due to improved scientific bases and availability of new characterization techniques.

Low temperature curing coatings obtained by sol-gel process using resins modified alkoxysilane groups must deal also with a negative aspect that is high reactivity of alkoxysilane group in presence of water. As observed for moisture curing system (MC), the high reactivity leads to short shelf life. This process, like traditional UV curable coating, faces with dimensional change; the shrinkage leads to stress cracking during drying.

Alkoxysilanes groups can be introduced in a resin by reaction of organofunctional alkoxysilanes, as represented in the figure 1:

Figure 1: Organofunctional alkoxysilane.



where R is organofunctional group,  $(CH_2)_n$  is the spacer between the organic function and the silicon atom and X is the hydrolysable groups.

Introduction of organofunctional alkoxysilane, also called silane coupling agent, into a polymer can be done by reaction of organofunctional group of alkoxy silane with the already polymerized resin or by co-polymerization.

Covalent bond formation with polymer already formed is the simplest way of introducing alkoxysilane groups in the polymer network. This way is used mainly to obtain thermoplastic type polymers. In general, for this modality, alkoxy silane groups are introduced in low concentration.

For modification of polymers already formed, the chemical structure must have proper reactive site to bond with the organofunctional group of silane coupling agent. For example, side carboxylic acid groups in polyacrylates, anionic waterborne polyurethanes, waterborne polyesters and waterborne alkyds can react with epoxy functional alkoxysilanes. Double bonds in alkyds and unsaturated polyesters can react with mercapto functional alkoxysilanes. Introduction of alkoxysilane groups can be also done via reaction with end groups of low molecular weight polycondensation polymers such as polyester, polycarbonates, polyamide. Polyester with end group carboxyl or hydroxyl can be derivatized by using epoxy and isocyanate silanes respectively. For polycarbonates OH ended, derivatization can be done with isocyanate organofunctional silane. Polyamide derivatization can be done with epoxy functional silane either for amine or carboxyl terminal functionalities.

Another way of introducing alkoxy silane groups into the polymer backbone is by co-polymerization of appropriate monomers, for example 3-methacryloxypropyl trimethoxysilane in free radical polymerization. [7]

Polyurethane resins can be modified with amine or diamine organofunctional alkoxy silane or by using isocyanate organofunctional silane.

In many cases the introduction of organofunctional alkoxy silanes is limited by reaction conditions, due to undesirable hydrolysis and condensation of alkoxy groups during the synthesis process, that can lead to polymer gelation.

As mentioned before organic inorganic hybrid coatings and composite materials can be developed by using sol-gel process. The sol-gel process involve reaction that improve comprehensive performances as increasing cross-link density, adhesion and anti corrosive properties. The sol-gel process can be described according to the following steps: hydrolysis, condensation, gelation, ageing, drying and densification [8] [9]

### *Hydrolysis*

In this step, the alkoxy group is hydrolysed by water as reported in the figure 2.

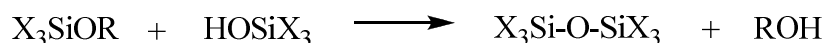
Figure 2: hydrolysis of alkoxy group by water



### *Condensation*

The hydrated silica, silanol groups interact in a condensation reaction forming Si-O-Si bonds as reported in figure 3.

Figure 3: condensation of silanol group.



The hydrolysis and polycondensation reactions initiate at many different sites in the same time. When a determined number of Si-O-Si bonds are formed, they form a sol (colloidal particles dispersed in the liquid)

*Gelation:* The colloidal particles and condensed silica link together to become a three-dimensional network. In this step is observed an abrupt increment of viscosity.

*Ageing:* formation of further cross-link, associated shrinkage of the gel.

*Drying:* evaporation of water, alcohol and other volatiles compounds from the interconnected pore network.

*Densification:* thermal treatment leading to collapse of the open structure and formation of a dense ceramic.

This technology has many advantages as low temperature process, easy to obtain metal doping due to the compatibility between organic metallic precursors, mild chemical conditions of pH for hydrolysis and condensation steps, transparency, porosity, functional surface and hardness.

Sol-gel process do not present only advantages, one drawback of this process is that precursors are moisture sensitive as observed in the first step. The alkoxy groups hydrolysis, following a

condensation step. This phenomenon is a limiting point for large scale production and long term store.

## Results and Discussion

In this work we will present solvent borne and waterborne resins containing alkoxy silane groups that were synthesised to be used in sol-gel process to obtain organic-inorganic hybrid coating. Resins were formulated with tetraethyl orthosilicate (TEOS) to obtain the inorganic phase in the hybrid system.

For the solvent system, coatings obtained via sol-gel process were compared with traditional 2K formulation. The polyol resin used in the 2K formulation was Isoben 6 that is the precursor of alkoxy silane modified resin, Isosil 6.

For comparison it was also studied a hybrid organic-inorganic system using a non modified resin. Sol-gel formulation was prepared by using a hydroxylated polyester base polyurethane resin, Idroben 7051 and TEOS as source of silica. The hybrid organic-inorganic coating from Idroben 7051 was compared with the coating obtained with the same resin in a 2K formulation.

We also prepared a cationic waterborne urethane oligomer containing alkoxy silane groups and used it to develop organic-inorganic coating using sol-gel process.

### Sol-gel process

In the so-gel process the first step is hydrolysis of alkoxy groups. Hydrolysis can be carried out either by using acid or base catalysis. [10]. For the solvent resin we used acid catalysis. For the waterborne resins, one cationic and one anionic, we were forced to use acid and base catalysis respectively.

As hydrolysis rate is affected by the type of alkoxy groups, we selected organo functional alkoxy silanes containing methyl or ethyl groups. Larger alkoxy groups lead to higher steric hindrance and slow reaction rate. As industrial applications require fast process the selection of small groups goes in the right direction.

Co-solvent also plays a important role in sol-gel formulation. For example hydrophobic resins modified with alkoxy silane groups in formulation with TEOS are immiscible with water. To promote hydrolysis, alkoxy groups require molecular contact with water. To speed up hydrolysis rate reaction mixture must be homogeneous. In our formulation we used ethanol as co-solvent in the minimum amount to get the best compromise of high reaction rate and VOC level.

Also the amount of water in formulation will affect the reaction rate. For the solvent borne resin, the amount of water used in the hydrolysis phase of process affects the homogeneity of formulation; the more water is used the more co-solvent is necessary. Moreover stoichiometric ratio for TEOS hydrolysis is four, as reported in figure 1. If we consider that hydrolysis and condensation steps can occur simultaneously and water is produced in the condensation step, the amount of water necessary to be added for a complete hydrolysis is lower than four.

For the waterborne resins, the solvent is water. To have the polymer dispersed in water we used monomers that were salified before polymer dispersion in water by using acid or base for the cationic and anionic resins respectively. The salification step is a key point because the hydrolysed silanol groups can condensate leading to unstable products. pH controlling and high amount of water can influence products stability. As condensation step in the sol-gel process leads to formation of water, high amount of water can help slow down condensation reaction.

The next process steps, gelation, ageing and drying proceeded at room temperature or 100°C. Densification step at high temperature was not the intent of our work.

### Solvent resin

The solvent resin was obtained by reaction of a branched hydroxylated polyester, Isoben 6, with alkoxy silane containing isocyanate group. This polyester is a commercial resin used in 2K

formulations. The characteristics of Isoben 6 are reported in the table 1. Isoben 6 has hydroxyl number of 150 mg KOH/g, it allows to introduce a high concentration of alkoxy silane groups.

Table 1: Characteristics of Isoben 6.

Molecular Weight (calculated)	1500
Dry content	70% Butyl acetate
Viscosity Brookfield @ 25°C	4000 – 5000 cPs
Colour	3 maximum
Acid value (mg KOH/g)	< 20
Hydroxyl value (mg KOH/g)	150

*Synthesis of Isosil 6 - Alkoxy silane derivatization of Isoben 6*

Isoben 6 was reacted with 3-isocyanatepropyltriethoxysilane, Silquest A-link 25 silane, supplied by GE Advanced Materials. Hydroxyl groups of Isoben 6 (90%) was blocked with Silquest A-Link 25 silane. The reaction was maintained at 65 - 75°C until NCO content drops to zero. The reaction was carried out in absence of tin catalyst to avoid catalysis of Si-OH coupling reaction due to potential presence of unwanted moisture during synthesis process. The characteristics of Isosil 6 are reported in the table 2.

Table 2: Characteristics of Isosil 6.

Dry content	70% in Butyl Acetate*
Concentration of –Si(OR) <sub>3</sub>	1 eq/kg (on dry content)
Viscosity Brookfield @ 25°C	3500 – 4500 cPs

\*Theoretical value based on starting polyester.

This polyester modified alkoxy silane was used to develop sol-gel hybrid coatings using TEOS to build up the inorganic phase. Due to the high concentration of alkoxy silane in the polymer and branched structure the stability of Isoben 6 modified alkoxy silane in butyl acetate is not very high. To improve product stability, the resin synthesised in butyl acetate was diluted with ethanol in two different concentrations, 65% and 60%. Selection of ethanol is due to the fact that ethanol is the same alcohol of Silquest A-Link 25 alkoxy group and it is a good co-solvent to be used in sol-gel formulation. Resin was kept at 30°C and stability was verified by measuring the viscosity at 25°C. Results are reported in table 3.

Table 3: Stability test on Isoben 6 modified alkoxy silane by viscosity measurements.

Time	Viscosity Brookfield @ 25°C (cPs)		
	No ethanol Dry content (70%)	16,6% ethanol Dry content (65%)	33,3% ethanol Dry content (60%)
T <sub>0</sub>	4500	875	350
1 week	5750	875	350
2 week	11750	1000	375
3 week	20750	1125	375
7 week	gel	1500	375
14 weeks	/	1750	375

As we can observe the resin in butyl acetate has short shelf life. The viscosity increases very fast. After 7 weeks it was observed resin gelation. We observe also the higher concentration of ethanol in the resins more stable it is.

### Hybrid organic inorganic coating via sol - gel process for solvent resin

Formulations were prepared using TEOS at different ratios. Also different alkoxy silane containing organofunctional groups were co-formulate with TEOS.,  $\gamma$ -glycidoxypropyltrimethoxysilane, from experimental tested, gave the best performances. Isosil 6 was target of a complete study by Turri, Piccinini, Levi , Torlaj.

Isosil 6 and TEOS were formulated with water and ethanol as co-solvent. The hydrolysis step was carried out using acid catalysis. Isosil 6 and TEOS 70g and 30g respectively, were solubilised in 50 g ethanol. To this mixture, 0,21 g of HCl 37% pre-diluted in 12,9 g of water was added drop wise under stirring. The mixture was held stirring at 50°C for 1 hour before coating into glass plates. Film obtained was cured in two different temperature: room temperature and 100°C for 1 hour. Formulation had pot life of 1 day.

All films obtained were complete transparent and homogeneous. Chemical resistance and pencil hardness were measured on films cured in both temperature condition. The data are reported in the table 4.

For comparative purpose a standard 2K formulation was prepared as follows: 84,5 g of Isoben 6 pre diluted with 15 g of butyl acetate and additivated with BYK 306 (0,2g ) and BYK 057, (0,1 g) was mixed with a solution of Hartben A75, polyisocyanate 75% in PMA with NCO content of 17%, (38,6 g) dilute with 28,6 g of butyl acetate. Undesirable competitive reactions can influence final film characteristics. Formulation stability was evaluated by measuring formulation viscosity versus time. For the formulation described above viscosity increment is quite high. After 2 hours viscosity was two times the initial value. After 3 hours solvent was added to keep appropriate viscosity value in order applied. Film obtained after three hours from formulation preparation presented either lower hardness or chemical resistance.

Table 4: Characteristics of films obtained from Isosil 6 net resin, hybrid organic inorganic via sol-gel process and Isoben 6 2K formulation.

Resin	Room temperature		100°C	
	1 day	7 days	1 day	7 days
Pencil hardness				
Net Isosil 6	6B	6B	6B	na
Isosil 6: TEOS sol-gel formulation	5B	2B	2B	B
Isoben 6 2K formulation	6B	6B	na	na
Double rubs MEK				
Net Isosil 6	2	2	2	2
Isosil 6: TEOS sol-gel formulation	50	50	100	100
Isoben 6 2K formulation	20	50	na	na

Observing the data of hardness and chemical resistance test on coatings obtained via sol-gel process using the solvent resin, we can say that good improvement was obtained when inorganic phase was developed. Comparing the result we can say that resin modified alkoxy silane can not be used as mono-component system because double rubs MEK is extremely low. If we observe hardness valued obtained for net Isosil 6 and sol-gel formulation even if low concentration of TEOS was used, with a estimated SiO<sub>2</sub> concentration of 13%, we can make out that inorganic phase was formed. The chemical resistance improvement can be attributed to Si-O-Si bonds formation in two competitive ways, intermolecular SiOH self condensation or reaction with SiOH from glass plate substrate. For curing carried out at 100°C is observed a big enhancement in hardness 2B to B. The difference between room temperature and high temperature curing hardness performance for Isosil 6 sol-gel formulation can be attributed to most efficient drying step at 100°C, with loss of water, alcohol and other volatile component. No fracture and crack formation during drying of gels was observed.

Comparing also the results of 2K formulation obtained with Isoben 6, polyester polyol precursor of Isosil 6 and the sol-gel formulation, we can conclude that same results can be achieved without using isocyanate for room temperature curing condition. If we consider pot life parameter, Isosil 6 - TEOS sol-gel formulation has higher pot life. One drawback of this formulation is VOC involved.

*Synthesis of waterborne cationic polyurethane oligomer*

We synthesized a waterborne cationic polyurethane oligomer, solvent free. The oligomer was obtained, via acetone process, without catalyst. In this case we synthesized a isocyanic pre-polymer in the first step. In the second step the prepolymer NCO ended was blocked with amino-functional alkoxy silane from Dow corning Z-6011 Silane, 3-Aminopropyltriethoxysilane.

The reaction ratio between NCO: amine group was 1:0,95. Blocking reaction was carried out at 25°C. The oligomer was salified with acetic acid and dispersed in water. After solvent stripping was obtained a hazy water dispersion with the characteristics reported in table 5. After one month the dispersion had the characteristics of starting one.

Table 5: Characteristics of waterborne cationic polyurethane oligomer.

Dry content	38% in water
Viscosity Brookfield @ 25°C	100 - 300 cPs
pH	5,5
Concentration of $-\text{Si}(\text{OR})_3$	0,43 eq/kg
Concentration of $-\text{NR}_3$	0,43 eq/kg

The resin was used to develop a hybrid organic inorganic coating. Different resin-alkoxy silane ratio were tested. Low concentration of TEOS give films with poor hardness and chemical resistance. High TEOS concentration leads to formulation high viscosity and limited pot life, requiring very high dilution. Those formulations show poor wettability. High amount of ethanol is necessary to be added to achieve homogeneous film.

In the table 6 is reported a formulation used in the sol-gel process with good compromise of formulation characteristics and film performances. Also for the water base formulation co-condensation of  $\gamma$ -glycidoxypropyltrimethoxysilane leads to film with better characteristics. pH was corrected using water solution of nitric acid (5,8% w/w) to achieve the value desired.

Table 6: Formulation for waterborne cationic oligourethane resin modified alkoxy silane.

Component	Quantity
Resin 38% in water	65,58 (g)
Silicon alkoxy (TEOS)	18,35 (g)
$\gamma$ -glycidoxypropyltrimethoxysilane (GPS)	2,29 (g)
Ethanol	18,35 (g)
Water solution $\text{HNO}_3$ (5,8% w/w)	13,76 (g)
pH	3,7

\*  $\gamma$ -glycidoxypropyltrimethoxysilane

In table 7 pencil hardness and chemical resistance (double rubs MEK) are reported for film obtained from net resin and the sol-gel formulation, applied after 3 hours from sol formulation. Glass plates were coated with bar coater and the dry films have 8 $\mu$  thickness. Samples were cured at 2 different temperatures: one sample was cured in the oven at 50°C for 1 hour and a second one at 100°C for 1 hour. The hardness value was checked after 1 day and 7 days. All films tested were homogeneous and transparent.

Table 7: Pencil hardness and chemical resistance (double rubs MEK), for film from net waterborne cationic resin and sol-gel formulation:

Resin	Room temperature		50°C		100°C	
	1 day	7 days	1 day	7 days	1 day	7 days
Net resin	6B	6B	6B	6B	6B	6B
Sol-gel	6B	2B	B	F	F	2H
Double rubs MEK						
Net resin	10	20	10	20	20	20
Sol-gel	20	80	50	80	100	100

For the waterborne cationic oligomer the concentration of alkoxy silane groups (0,43 eq/kg) is less than half of Isosil 6. The resin presented good stability even if in aqueous medium alkoxy silanes undergoes hydrolysis and produces reactive silanol groups. Silanols must lose water to condense. As the rate of hydrolysis depends on the concentration and pH of silane solution, high amount of water can be a key parameter to avoid drying, limiting covalent linkages formation.

Waterborne cationic oligomer shows similar behaviour to solvent resin Isosil 6. Film from net resin give low crosslink extension and substrate adhesion at low temperature as observed for double rubs MEK test results. Significant variation is observed introducing TEOS in formulation. Improvement of chemical resistance and pencil hardness passing from net resin to sol-gel formulation is due to the replacement of soft organic polymeric matrix by hard inorganic siloxane matrix (SiO<sub>2</sub>) 7%. For sol-gel formulation, it can be easily observed an important variation of hardness accompanied by chemical resistance improvement after 7 days of film preparation at room temperature. This improvement can be attributed to a slow cross-linking via trans-pore condensation reactions of pore surface hydroxyl groups. The effect of this process is a stiffening and shrinkage of the sample. This shrink leads to expulsion of liquid from the pores of gel with enhancement of hardness and chemical resistance. In fact after 7 days, at room temperature, film chemical resistance as MEK double rubs and hardness are quite close to those obtained for films cured at 100°C.

#### *Hybrid organic inorganic coating obtained via sol-gel process with non modified resin*

As observed, introduction of alkoxy silane group into a polymer leads to resin stability reduction. To check if high performances can be obtained for unmodified resin in a sol-gel formulation, we selected an anionic, hydroxylated polyurethane, used in 2K formulations for parquet application. This resin has high hydroxyl groups content that can participate with alkoxy silane groups in the condensation process. This resin, Idroben 7051, has also carboxylic pendant groups that in co-formulation with  $\gamma$ -glycidoxypropyltrimethoxysilane can lead to reaction with epoxy groups and bonding covalently the inorganic phase to the polymer structure. The characteristics of Idroben 7051 is reported in the table 8.

Table 8: characteristics of Idroben 7051

Dry content	40% in water
Viscosity Brookfield @ 25°C	125 cPs
pH	7 – 8,5
Concentration of -COOH	0,4 eq/kg
Hydroxyl value (mg KOH/g)	150

Also for this case many different resin: TEOS:  $\gamma$ -glycidoxypropyltrimethoxysilane ratio were tested. We start formulating by mixing the resin with  $\gamma$ -glycidoxypropyltrimethoxysilane (GPS), in which the ratio of epoxy groups where 80% of carboxylic group present in the resin. The  $\gamma$ -glycidoxypropyltrimethoxysilane (GPS) was added drop wise into the resin under stirring. The mixture was kept under stirring for 1 h. The system was held for 24 hours at room temperature. In



this condition, reaction between carboxylic and epoxy groups can take place. The reaction of carboxylic and groups with formation of hydroxy ester lead to a light pH increment. The ratio  $(\text{CH}_3\text{CH}_2)_3\text{N}:\text{COOH}$  increases comparing with the starting resin. In fact, after 24h the pH measured was 8,22. and viscosity 250 cPs versus the starting resin pH of 7,96 and viscosity of 125 cPs. The sol - gel formulation was completed by adding to the previous mixture (part 1) the solution obtained by mixing water, ethanol and TEOS (part 2), see table 9.

Formulation stability was measure observing physical changes in formulation as viscosity increase and by coating the sol-gel formulation at different time from its preparation and measuring film hardness. After 24h of sol preparation viscosity increase of 15% was observed. Small amount of water was added to return into initial viscosity value. Coating obtained from 24 hours formulation gave films with same characteristics of initial formulation. After 72 hours a very high increase of viscosity was observed leading almost to complete jellification

We compared also the performances of hybrid coating obtained from sol-gel process with Idroben 7051 in a 2K standard formulations. For this purpose 50 g of Idroben 7051 was mixed with 16 g Rhodocoat 803. To this mixture 7 g of PMA and 17 g of water were added to reach a solid content of 44,5%. Results are reported in table 10. Formulation stability was evaluated by applying the coating after 1 hour, 2 hours, 3 hours and 4 hours after formulation preparation. For each time film hardness was measured after 7 days. It was observed that after 1 hour hardness start decreasing and it is 5% less than initial value. After 2 hours it is 11% less and after 4 hours it is 20% less.

Table 9: sol-gel process formulation for Idroben 7051

Component		Quantity
Part 1	Idroben 7051 40% in water	100 (g)
	$\gamma$ -glycidoxypropyltrimethoxysilane (GPS)	5,7(g)
Part 2	Silicon alkoxy (TEOS)	20 (g)
	H <sub>2</sub> O	50 (g)
	Ethanol	50 (g)
pH		8,1

In the table 10 are reported the Persoz pendulum hardness and chemical resistance (double rubs MEK) for film obtained from sol-gel formulation applied after 1 hour of sol formulation. Glass plates were coated with bar coater and the dry films have a thickness of 15 $\mu$ . Two curing temperature were tested: 100°C for 1 hour and room temperature. The hardness value and chemical resistance were measured after 1day, 7 days and 1 month.

Table 10: hardness and chemical resistance for net resin 7051, its sol-gel and 2K formulation

Formulation	Room temperature			100°C		
	1 day	7 days	1 month	1 day	7 days	1 month
Net Idroben 7051	138	211	211	na	na	na
Sol-gel	240	251	337	331	359	365
2K*	293	367	370	/	/	/
Double rubs MEK						
Net Idroben 7051	0	0	0	na	na	na
Idroben 7051 sol-gel	3	4	4	3	4	3
2K*	2	40	50	/	/	/

\*For 2K formulation film thickness 20 $\mu$

Observing the data reported in table 10 for films obtained from formulation containing a resin without alkoxy silane, we can say that great improvement in hardness is observed. We can see also

that hardness change a lot after 1 month for film cured at room temperature, reaching the same value for curing at 100°C. Taking into account the hardness and chemical resistance data we can predict that inorganic phase develops without linkage with polymer. Neither hydroxyl groups from the resin participate from Si-O-Si network nor glycidyl groups from  $\gamma$ -glycidoxypropyltrimethoxysilane (GPS) react with carboxylic from the resin to generate a cross-linked organic-inorganic network.

Also this coating with SiO<sub>2</sub> (14%), are transparent and glossy. Comparing sol-gel and 2K formulations stability with respect to pot life and film performance we can say that the pot life of sol-gel is higher than 2K formulation. Hardness can be obtained by developing SiO<sub>2</sub> phase into the resin by using TEOS but chemical resistance still better for 2K system.

## Conclusion

Introduction of alkoxy silane groups in resins can be done by simple chemical reaction of organofunctional alkoxy silanes with polymers containing reactive functional sites, as carried out in Isoben 6 by functionalizing the hydroxyl groups with isocyanate containing alkoxy silane groups. From the other side alkoxy silane groups can be also introduced in the polymerization step.

High amounts of SiO<sub>2</sub>, in the nano metric scale, can be developed by using sol-gel process. Films are stiff, transparent and glossy. Important characteristics of these films that have still to be tested, are mechanical properties, abrasion resistance and weatherability. Of course the higher the inorganic phase the poorer the flexibility. Much work has still to be carried out; high amount of solvent are present in formulation and pot life still reduced, limiting a large scale industrial application.

Project financial supported by Regione Lombardia

## References

1. T. Trombetta, US Patent 2005/0164010A1, Solvay Solexis, 2005
2. P. C. Gaa, D. E. Dana, US Patent 4582873, PPG Industries, 1986
3. K. C. Frisch, B. H. Edwards, A. Sengupta, L. W. Holland, R. G. Hansen, I. R. Owen, US Patent 5554686, 3M, 1996
4. , H, J Chang, US Patent 3983291, 3M, 1973
5. S. Wada, K. Imoto, K. Honda US Patent 6410626, Daikin Industries, 2002
6. R. A. Halling WO 9523804, E. I. Du Pont de Nemours, 1995.
7. E. P. Plueddemann US Patent 3956353, Dow Corning, 1976)
8. Sol-gel Materials chemistry and Applications, J. D. Wright and N. A. J. M. Sommerdijk, CRC Press, Florida, 2001
9. L. L. Hench, J. K. West, Chem. Rev. 1990, 90, 33 -72
10. Silane Coupling Agents, E. P. Plueddemann, Plenum Press, New York, 1991. chapter 3