Reactive Silanes in Cationic UV Jet-inks

Alexander Grant, SunJet, Bath, England UK

Abstract

Cationic UV jet-inks offer many desirable features. This includes, strong adhesion to a range of media, fast cure response in air and low residual odour. Despite this, there remains the need for greater formulation diversity, mainly due to limited raw material supply and viscosity restrictions. For example, the creation of very hard, scratch and chemical resistant films, whilst maintaining a low ink viscosity, is somewhat challenging.

Silane chemistry has been used in the coatings industry for many years to provide hard films with high heat and solvent resistance. A large number of these reactive silanes are low enough in viscosity to be attractive to the jet-ink formulator. But due to a cumbersome reaction process, involving heat, hydrolysis and condensation, the inclusion of such materials has been limited.

This paper looks at how silane chemistry may be incorporated into cationic UV jet-inks. Through photo-initiation, the silane curing mechanism is simplified to a one-step process. By doing so, formulation latitude is increased and improvements to film properties are made.

Cationic jet-inks – background

Although not yet as wide-spread as free-radical UV jet-inks, this type of chemistry is well known for its ability to perform well in many printing applications.[1] The formulations often contain epoxide, and co-monomers such as oxetanes, together with proton releasing photo-initiators. The curing mechanism is influenced by heat and humidity and may show a strong post-cure response, as film properties develop with time. Characteristics such as good adhesion with low shrinkage, rapid cure in air and low residual odour may be obtained with such compositions. However, compared with free-radical raw materials, there is a somewhat limited selection. Additionally, many of these materials are highly viscous and either not readily available or significantly more costly than free-radical. A particularly demanding aspect is the creation of very hard, scratch and chemical resistant films.

Traditional silane chemistry

The combination of inorganic silicas with organic materials has been known for many years.[2] Films prepared this way give a midway point between organic coatings and vitreous enamel in terms of application performance. These hard, heat and solvent resistant films find usage as coatings for DVD's, light bulbs and optical glasses, amongst many others.

The curing mechanism (**Figure 1**) involves a multi-step process of hydrolysis and condensation followed by a high temperature cure (typically 160-350 °C) for some time. In addition, pot-life is generally poor, being highly sensitive to temperature and moisture, making this technology difficult for ink-jet printing, despite offering useful end properties.

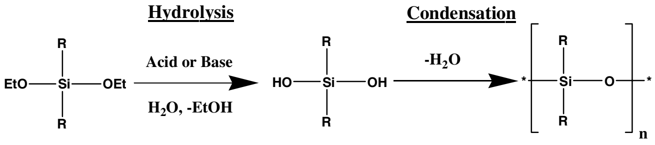

Figure 1: The sol-gel process

Combined approach – cationic UV with reactive silane chemistry

Prior art has described alkoxy silane chemistries that may be activated by use of a cationic photo-initiator to form an organic-inorganic network.[3]

The mechanism in **Figure 2** summarises the creation of such a composite. This occurs through protonation of the alkoxysilane, in this case, with SunChemical's Meerkat photo-initiator, followed by hydrolysis and condensation. In broad terms, the system cures at a speed typical for a UV curable jet-ink and, beneficially, no heating step is required.

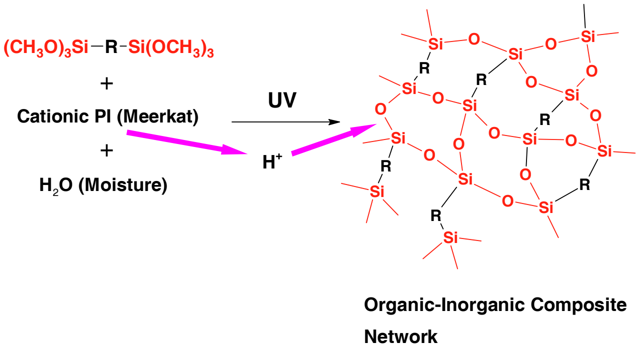

Figure 2: Photo-initiated formation of organic-inorganic network

This one-step approach greatly simplifies the formation of a organo-silane film in an ink or coating application. Whilst this basic concept is of interest in some applications, as the resultant films may be hard and scratch resistant, they do not offer sufficient formulation flexibility to be useful in a broad range of markets. To circumvent this, our study has focused on combining reactive silane chemistry with cationic monomers, photo-initiators and pigments. In essence, the silane component is used at additive levels in a "hybrid" type formulation. Because of this approach, a good balance in properties is expected between 100% conventional cationic UV curable and 100% alkoxy silane compositions.

This paper reports the results of testing such inks in terms of adhesion, hardness and chemical resistance. Additionally, the wetting properties of the inks are described with and without surfactant as well as their storage stability (pot-life).

Experimental

Stability (pot-life): defined herein by <10% change in viscosity measurement after storage for 1 week or greater at 50 ^{o}C. Viscosity: Brookfield DV-II. Spindle 18. Turbiscan: 50^{o}C for 24 hours.

Curing: UV Fusion rig equipped with an "H" bulb. 12 micron draw downs were made on Lenetta card and the minimum cure dosage required to form a non-tacky, hardened film noted.

Chemical resistance: Number of methylethyl ketone (MEK) cotton bud rubs needed to damage the ink film.

Hardness: Pencil hardness test.

Adhesion: Cross hatch adhesion following ISO 2409 procedure.

Contact angle: Fibrodat

Surface energy: Camtel Tensiometer.

Dynamic surface tension: Kruss bubble pressure tensiometer.

Table 1: Cationic UV jet-ink formulations*

	#1 Cationic std	#2 Silane 1	#3 Silane2	#4 Silane3
Epoxide	29	26.00	0.00	28
Co-monomers	56.00	49.00	21.00	10
Functionalised alkoxy silane	**0.0**	**10.0**	**21.0**	**47.0**
Hydrocarbon alkoxy silane	**0.0**	**0.0**	**43.0**	**0.0**
Photo-initiator	3.0	3.0	3.0	3
Cyan pigment dispersion	12	12	12	12

** A total of eight inks were made. The four formulations shown in **Table 1** are surfactant-free; surfactant-containing versions (not shown) have the letter "s" appended to the number. The surfactant used here is a polysiloxane type.*

Film properties

12 micron thick films of ink were applied to untreated glass and UV cured. Adhesion, hardness and methylethyl ketone (MEK) resistance tests were performed initially and overnight. Due to the well known positive effect of heating in cationic curing formulation, results were also collected after one hour storage at 150^{o}C.[4]

In all cases, adhesion to glass was noted to be excellent, with no film removal when tested.

MEK resistance

MEK resistance varied according to ink composition (**Table 2**). The silane-free cationic inks performed poorly in the tests, even when heated after curing, although a slight improvement was noted. Given that typical cationic formulations show a significant post-cure response, this suggests that the initial results were not due to insufficient polymerisation. Instead, the chemical rather than physical nature of the film is accountable for this observation.

Incorporation of alkoxysilane gave a marked improvement in initial performance with no further change upon storage, even at a 10% addition level. However, at very high silane content (#3 and #3s), initial results were surprisingly poor, indicating insufficient reaction had occurred. Leaving the film overnight helped the film develop and good solvent resistance was noted. This suggested there is a strong post-cure effect at certain silane concentrations. Considering that moderately high levels of silane (#4 & #4s) gave similar performance to this, implies it could be the presence of hydrocarbon alkoxysilane contributing to the slow development of film properties.

Table 2: MEK rubs on cured ink film

Ink	Initial	Over night	1 hour 150 ^{o}C
#1	0	3	4
#1s	0	2	6
#2	>50	>50	>50
#2s	>50	>50	>50
#3	4	>50	>50
#3s	4	>50	>50
#4	>50	>50	>50
#4s	>50	>50	>50

Film hardness

Film hardness and the ability to mark the ink film were noted (**Table 3**). The silane-free inks are initially soft and easily marked but show improvement over-night. This suggests the initial film is not fully cured but when it does it improves in hardness. This effect is more pronounced than with the MEK resistance results.

All the silane-containing inks follow the same pattern, giving very hard but markable films initially that then further improve with heating. The silane inks in particular seem to benefit from a post-heating step in this test.

Table 3: Hardness properties of cured ink films

Ink	Initial	Over night	1 hour 150 °C
#1	soft, easily marked	harder but markable	no change
#1s	soft, easily marked	harder but markable	no change
#2	very hard, slight mark	no change	very hard, no mark
#2s	very hard, slight mark	no change	very hard, no mark
#3	very hard, slight mark	no change	very hard, no mark
#3s	very hard, slight mark	no change	very hard, no mark
#4	very hard, slight mark	no change	very hard, no mark
#4s	very hard, slight mark	no change	very hard, no mark

In terms of silane concentration, only the MEK rub test showed a difference across the inks and appears to be sensitive to silane chemistry. Beneficially, as little as 10% was sufficient for strong performance.

In all three tests, it was not possible to distinguish the role of surfactant and therefore it has no significant impact on these film properties. However, our further studies focused on its influence on wetting properties.

Wetting properties

Given the wide usage of polysiloxane based surfactants in coating and ink formulations to improve fluid spread, it is of interest to see how these behave when incorporated in a reactive silane formulation. Considering the hard nature of such films, one might expect that these materials would preferentially migrate to the surface and be the major influence on film properties such as surface energy, and contact angle. Additionally, their low viscosity and molecular weight could influence their movement to the ink-air interface. To address this, dynamic surface tension, advancing contact angles and surface energy measurements were performed with the inks with and without polysiloxane surfactant.

Dynamic surface tension

Inks #1-#4 and their surfactant based versions, #1s-#4s, had their dynamic surface tension measured over a 5000ms time scale. **Figure 3** shows the data collected.

Looking at an arbitrary surface age of 1000ms, some broad trends are apparent.

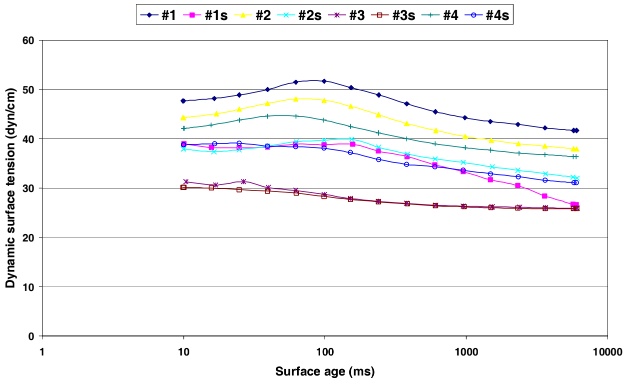

Figure 3: Dynamic surface tension plots

As perhaps expected, surfactant-containing inks all show lower values than surfactant-free, indicating the surfactant is the faster moving species. The exception to this is the high silane containing inks #3 and #3s. In this case, surfactant does not reduce surface tension and alkoxy silane preferentially migrates to the air-ink interface.

To explain this, it is useful to look at the difference in surface tension, between surfactant-free and surfactant-containing inks at the same point in time, across the series (**Table 4**). The results show that as the reactive silane concentration increases, the difference between the two ink types decreases. This suggests that alkoxysilane has a stronger preference to be at the ink-air interface than polysiloxane, depending on concentration. At very high silane content, such as in #3 and #3s, the silane completely masks the effect of the surfactant.

This knowledge allows the formulator to fine tune surface tension values, not only through surfactant selection, but by the level of reactive silane. Additionally, it appears that the hydrocarbon silane has a stronger influence on dynamic surface tension than the functionalized one. Therefore, selection of silane chemistry is also important from a wetting perspective.

Table 4: Dynamic surface tension values at 1000ms

	#1	#2	#3	#4
	Cationic std	Silane 1	Silane2	Silane3
Total silane content	0	10.00	64.00	47
(a) DST 1000ms	44.30	40.50	26.30	36.6
(b) DST 1000ms (with surfactant)	33.3	35.2	26.2	33.6
Delta DST (a)-(b)	11.0	5.3	0.1	3.0

Surface energy

Achieving an appropriate level of surface energy in the cured film of ink is important to obtain good print quality.

For instance, should the cured film show a surface energy below the surface tension of the ink, it would be difficult for subsequent drops of ink to spread well. In general, the following condition should be satisfied to attain effective ink wetting[5]:-

$$\theta_{\text{ink}} < \theta_{\text{substrate}} \qquad (1)$$

Where θ_{ink} and $\theta_{\text{substrate}}$ are ink and media surface energies respectively.

To test this, surface energy measurements were performed using cured films of ink on polyester. Using a variety of model fluids, dynamic advancing contact angles were measured. By using the Fowkes equation **(2)** below it was possible to evaluate polar and dispersive values for surface energy.[5, 6]

$$\gamma_L \cdot (1 + \cos\theta) = 2\sqrt{\gamma_S{}^d \cdot \gamma_L{}^d} \qquad (2)$$

Here γ_L is the surface energy of the fluid, θ is the advancing contact angle of the liquid on the solid, $\gamma_S{}^d$ is the dispersive component of the solid surface energy and $\gamma_L{}^d$ is the dispersive component of the liquid surface energy.

Figure 4 shows that surface energy values vary between 17 mN/m and 34 mN/m across the series of cured inks, allowing good formulation adjustments. In turn, this should facilitate control of ink wetting. The non-silane based inks (#1 & #1s) show the highest total values and an approximately even split between polar and dispersive components. When silane is present, there is a tendency for the polar component to diminish, and the total surface energy to decrease.

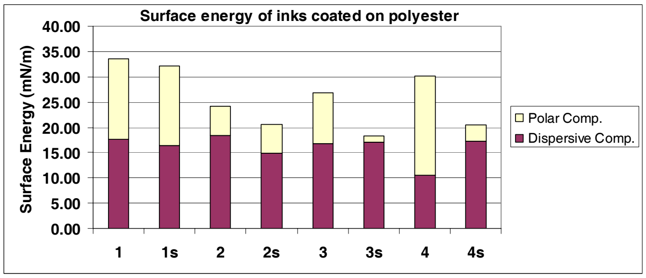

Figure 4: Surface energy of inks coated & cured on polyester

Surfactant lowers the surface energy in all cases and has a profound effect on the dispersive energy noted in #3s and #4s. These both contain high silane levels. It should be noted that the trend observed with the DST measurements related to the liquid-air interface does not hold in the case of the cured film. For example, the results show that the high silane containing ink (#4) gave the lowest surface tension but had similar surface energy to formulations with lower silane concentration.

Given the surface tension data presented in **Table 4** and the general wetting equation **(2)**, the inks would not be expected to spread well on a cured film of themselves. However, the results suggest this could be addressed through surfactant and/or silane modification.

Equilibrium advancing contact angle

A Fibrodat was used to apply droplets of water onto the cured surface of the inks, to gather contact angle data. High contact angle is indicative of little fluid spread and suggests low film surface energy. The results are shown in **Table 5**.

In sample #1, the ink spread is rapid and undetectable by the instrument, implying the surface energy of the cured ink film is greater than the surface tension of water. Given the latter has a typical value of 72.0 dyn/cm and the surface energy value shown in **Figure 4** for the ink, this is clearly not the reason.

In all other cases, as surfactant-free is compared with surfactant-containing, contact angle increases in the presence of surfactant, indicating the surface energy of the cured ink decreases. This correlates well with the findings shown in **Figure 4**.

Additionally, the formulations containing reactive silane show higher contact angle values than silane-free. When surfactant is combined with a high silane concentration, the largest water contact angles are found.

Table 5: Contact angle of water on cured ink film

Time (s)	Contact Angle (°)							
	#1	#1s	#2	#2s	#3	#3s	#4	#4s
0.2	N/A	61.8	71.1	74.1	67.2	80	66.3	81.9
0.6	N/A	61.3	70.9	73.4	67	79.3	65.9	80.9
1	N/A	61.9	71.2	73.4	67	79.5	65.8	81.3

In summary, both surfactant and silane chemistry and concentration have a strong influence on surface energy, dynamic surface tension and therefore how the inks are likely to spread on media and cured films of themselves. This broad effect means it is possible to fine tune the composition to meet end-user requirements.

Pot-life

The Turbiscan was used to monitor stability of a representative alkoxysilane ink, using #3 for this purpose. The sample was held over-night at 50°C and readings taken every 30 minutes (see **Figure 5**).

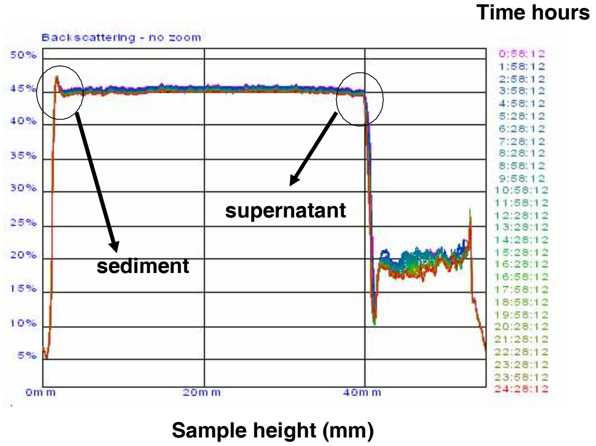

Figure 5: Turbiscan trace for silane containing ink #3

Very little settlement or sedimentation was noted at the bottom (left hand side) and top of the sample (right hand side), respectively. Some change in backscatter was noted in the bulk of the sample but this is in line with similar non-silane containing inks, and as such considered satisfactory.

Viscosity stability after 1 week storage at 60 °C was measured and the results shown in **Table 6**.

Table 6: Viscosity stability of cationic formulations over 1 week at 60°C

	#1	#2	#3	#4
	Cationic std	**Silane 1**	**Silane2**	**Silane3**
Initial viscosity	**9.84**	**9.35**	**1.89**	**6.18**
Viscosity after 1 week 60C	**10.7**	**9.78**	**1.98**	**6.3**

It can be seen that silane addition has no detrimental effect on the ink stability from viscosity and Turbiscan measurements. This clearly indicates that alkoxysilane chemistry is compatible with "conventional" cationic raw materials and as such stable hybrid formulations may be made.

Conclusions

Inclusion of alkoxysilane chemistry in cationic UV curable formulations, provides hard, scratch and chemical resistant films with good adhesion. The pot-life of such formulations is satisfactory in terms of viscosity stability and particle dynamics.

The compositions are readily cured in a one-step UV curing process, which can be further improved upon with heating, depending on application.

In terms of ink wetting, both surfactant and silane move rapidly to the air-ink interface according to DST, contact angle and surface energy measurements. The resultant low surface energy films are dependent on the concentration and chemical nature of the reactive silanes.

Taking all these findings into consideration, usage of reactive silane chemistry in combination with cationic UV jet-inks offers wide formulation and application latitude. In turn, the benefits of silane chemistry may be tailored towards a broad range of market demands.

Acknowledgements

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Author biography

Alexander Grant is currently Research Manager at SunJet in Bath, UK. This followed his position of Scientist at SunChemical in NJ, USA, working on ink-jet for computer-to-plate and packaging applications. Before this he worked as Polymer Scientist with National Starch, developing emulsions for paints and coatings. He has a PhD from Cambridge University in the synthesis of liquid crystalline polymers and holds several patents in jet-ink formulations.