

# Study of accelerated degradation of pigmented UV-cured print inks

## ABSTRACT

*Print inks have assumed an important role on finished materials, such as plastic packages, which can have a long lifetime when disposed as municipal waste. By this way, it is important to evaluate the influence of physical parameters on the degradation of short lifetime substrates covered by pigmented print inks cured by UV radiation.*

## KEY WORDS

UV technology; pigmented print inks; thermal degradation; oxidation

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## Introduction

The contemporaneous society has paid special attention to packages constituted of plastic materials. By this way, manufacturers are examining processes which are environmentally friendly, cost effective, and energy efficient. As mentioned by some authors (Onusseit et al, 2010; Drobny, 2010; Salleh et al, 2010; Bauer et al, 2009), one such technology that has become more popular and more economically feasible around the world is ultraviolet (UV) and electron beam (EB) curing technology. In this technology, conversion of liquid compositions to solid films is designed to occur when radiation interacts with matter, where either high-energy electron penetrates or photons cause only surface effects. Consequently, this will lead to formation of a polymeric network with high molecular weight.

Sallet et al. (2010) say that EB cured coatings are usually uniformly cured due to the full-depth penetration of the accelerated electrons. This renders the EB cured coatings to be hard but brittle. Meanwhile, its UV counterparts tend to be less “cured” due to the photoinitiators which absorb more of the UV radiation being at the surface, resulting in the surface having the highest radical concentration. By this way, both techniques are indicated for curing varnishes, inks, adhesives and coatings.

Another important factor described by Takahashi et al. (2010) is that UV radiation needs the incorporation of photoinitiators which are then capable to induce polymerization. As reported by Bardi and Machado (2012), a higher degree of curing to take place as a result of enhanced molecular mobility, resulting in a more homogeneous crosslinked network, as well as decreased material cure shrinkage after gelation,

and improved substrate adhesion due to lower stress inside the cured film. Additionally, UV equipments are more accessible and less costly than EB ones, which is a leading factor on industry and market nowadays.

Although it is widely known that radiation curing do not emit volatile organic compounds (VOC), once compositions are solvent-less (Drobny, 2010; Bauer et al, 2009; Calvo et al, 2012; Eldred, 2008), the high degree of crosslinking of the cured films makes the products to last longer when discharged at the environment, sometimes even increasing the lifetime of plastic substrates (Wilke, 2008). By this way, Chen et al. (2011) say that the coatings industry has to be transformed into a “greener” industry by incorporating more alternative renewable raw materials and “greener” technologies into their formulations, once legislation on different countries requires that plastic materials be both degradable as well as biodegradable after their discharge at the environment.

Mechanisms about degradation processes for UV/EB cured inks have been proposed by some authors (Bénard et al, 2008; Chen et al, 2010). Bénard et al. (2008) reviewed some results of photodegradation phenomena of resins cured under UV and EB radiations and suggested that, among the many possible candidates, extrinsic chromophores chemical groups formed during processing and curing of samples are the most probable ones to initiate the oxidation of the polymeric matrix. It was observed that radicals are produced via absorption of chromophoric species present in the film and, as the residual acrylates are consumed, there is a concomitant densification of the network through crosslinking reactions. At the end of the process, it is noted that oxygen permeability remains more or less constant and oxidation kinetics becomes almost linear.

Another experiment was performed by Chen et al. (Chen et al, 2010) through synthesizing soy-based thiols and enes to be cured by UV radiation. It was observed their incorporation to acrylate resin has caused an increasing on the photopolymerization conversion and coating film properties, such as solvent resistance, modulus and elongation, glass transition temperature and thermal degradation temperature.

As discussed by Magagula et al. (2009), photodegradation processes can aid rapid disintegration of polymers into a powdery residue with a much-reduced visual impact, especially when prodegradant additives are used to enhance their oxo-biodegradation. The central element responsible for the pro-oxidative ability usually belongs to the first transition metal series such as manganese, iron and cobalt as stearates, all of which have the capability to exist in both +2 and +3 oxidation states [(Roy et al, 2009). In this context, transition metal carboxylates are particularly suitable in which

cobalt-, iron-, manganese and cerium-based products have been commercialized (Magagula et al, 2009).

Additionally, it is known that the catalytic effect is stronger for pro-oxidants based on metal combinations capable of yielding two metal ions of similar stability and with oxidation number differing by one unit only (Pablos et al, 2010). The photodegradation is initiated with the formation of radicals due to the breakup of chemical bonds in the polymer chain. UV radiation in the range of 290 nm to 320 nm is equivalent to the energy required to dissociate C–C and C–H bonds to induce free radicals. The free radicals formed by this cleavage act as initiators for polymer degradation Kumanayaka et al, 2010). This abiotic degradation phase increases the biodegradability of the polymer in soil, wastewater, sludge and compost, such as reported by Roy et al. (2008).

By this way, this paper aims to investigate the behavior of different UV print inks containing cobalt and cerium stearate under accelerated degradation by means of thermo-analytical methodologies.

## Material and Methods

The following materials were applied for the preparation of the UV-curable clear formulation:

1. Bisphenol A epoxy diacrylate resin (EBECRYL® 3720-TP25, Cytec Industries Inc.) diluted 25% by weight with tripropylene glycol diacrylate (TRPGDA, Cytec Industries Inc.);
2. Trimethylolpropane triacrylate (TMPTA, Cytec Industries Inc.);
3. Blend of photoinitiators 4,5/3,5/2,0 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba-Geigy Co.) / 2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propanone (Esacure KIP 150, Lamberti Co.) / 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one (Irgacure 379, Ciba Specialty Chemicals Inc.), respectively;
4. Talc (Nicon® 674, Luzenac America, Inc.);
5. Polydimethylsiloxane (Pure Silicone Fluid 100,000cSt, Clearco Products Co., Inc.);
6. a, b) Polyethylene/polytetrafluoroethylene wax (CeraSPERSE® 164, Shamrock Technology, Inc.).

In order to obtain coloured print inks, pigments have been added to the clear coatings, such as the following: carbon black (Printex® 45 powder, Evonik Degussa GmbH), yellow pigment derived from diarylide m-xylylidide (Irgalite® Yellow LBIW, Ciba Specialty Chemicals Inc.), blue pigment derived from phtalocyanine (Hostaperm Azul B2G 01-BR, Clariant Pigmentos e Aditivos Ltda.) and ruby pigment derived from monoazo calcium salts (Rubide 4B, Hongyan Pigment Chemical

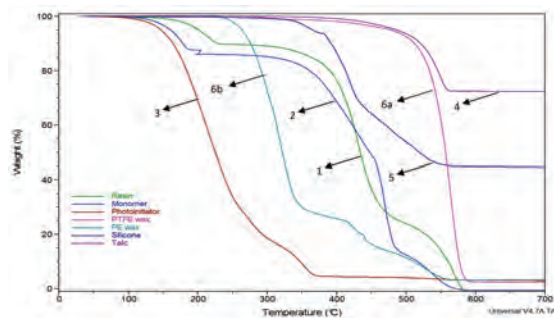
Co., Ltd.). The ratio pigment/clear coating was kept constant (21/79 w/w) in order to investigate only the influence of each pigment under UV curing.

It was also used cobalt stearate (CoSt), supplied as pellets by Strem Chemicals Inc. (Newburyport, MA, USA), and cerium stearate (CeSt), supplied as powder by Strem Chemicals Inc. (Newburyport, MA, USA).

Tests of thermal analysis for cured and uncured print ink samples were performed using simultaneous thermogravimetric analyzer and differential scanning calorimeter SDT Q600 from TA Instruments, New Castle, DE, USA. Around 5 mg pieces thin layer from different parts of the each samples were finely placed into the bottom of a platinum crucible and heated at a constant rate of 10 °C min<sup>-1</sup> from room temperature up to 700 °C under air atmosphere at flow rate of 50 mL min<sup>-1</sup>.

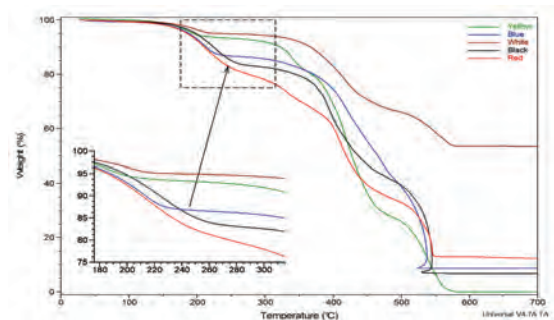
## Results

Figure 1 depicts the non-isothermal thermogravimetric (TG) curves of the print inks components.

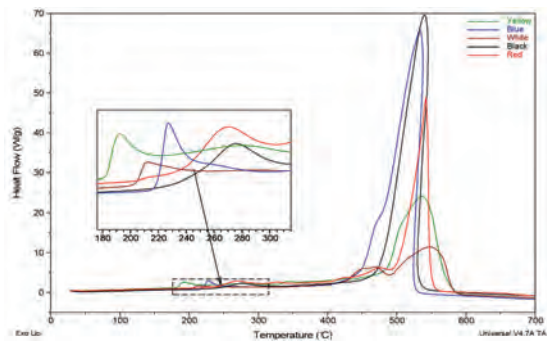


» **Figure 1:** The non-isothermal thermogravimetric (TG) curves of the print inks components

Figure 2 and Figure 3 present the thermal behavior of the studied uncured print ink samples as a function of the temperature.

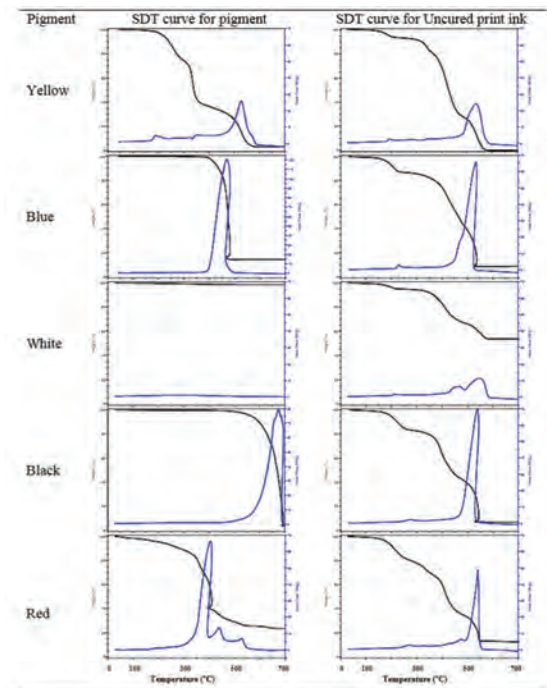


» **Figure 2:** The thermal behavior of the studied uncured print ink samples as a function of the temperature



» **Figure 3:** The thermal behavior of the studied uncured print ink samples as a function of the temperature

In order to achieve more details about this thermal behavior, simultaneous DSC/TG (SDT) curves were obtained for pristine pigments and studied uncured print inks, which are shown on Figure 4.

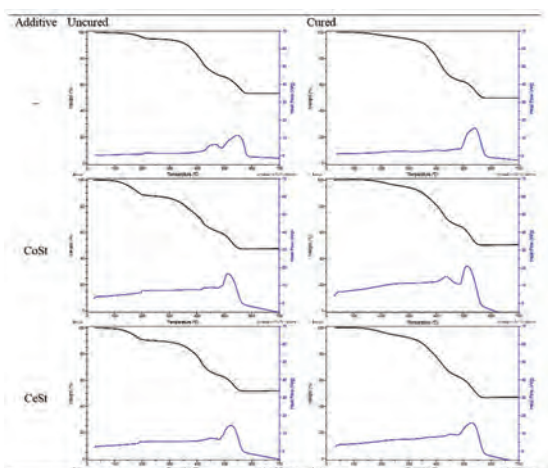


» **Figure 4:** Curves for pristine pigments and studied uncured print inks

Figure 5 presents the thermal degradation behavior from white print ink, thermally cured as function of linear increasing of temperature inside the SDT furnace, and UV-cured at 200 mW cm<sup>-2</sup>, without or with cobalt stearate or cerium stearate.

Table 1 presents the values for the onset degradation temperature measured by tangent method associated to

the second event of the TG curves from thermally-cured and UV-cured white print ink samples.



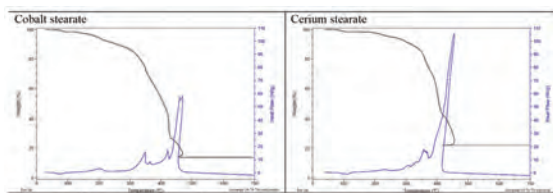
» **Figure 5:** thermal degradation behavior from white print ink, thermally cured as function of linear increasing of temperature inside the SDT furnace, and UV-cured at  $200 \text{ mW cm}^{-2}$ , without or with cobalt stearate or cerium stearate

**Table 1**

Toluene boiling component determination of aluminum-free Tetra Pak packaging

Sample	Onset degradation temperature (°C)
Thermally cross-linked resin	391
Thermally cross-linked monomer	362
Thermally cured white print ink	370
UV cured white print ink	353
Thermally cured white print ink containing CeSt	342
UV cured white print ink containing CeSt	340
Thermally cured white print ink containing CoSt	339
UV cured white print ink containing CoSt	324

According to Figure 5, the presence of CoSt or CeSt has not influenced the thermal curing behavior of the studied print ink, probably due to the thermal decomposition of the metallic stearates, as illustrated in Figure 6.



» **Figure 6:** Curves for pristine pigments and studied uncured print inks

## Discussion

By analyzing Figure 1, it can be seen that some components suffer thermal degradation simply by heat influence, whereas some others undergo chemical reactions before being thermally decomposed. As it can be observed on curve 2, the first step of mass loss occurs at the range of  $150^{\circ}\text{C}$  up to  $200^{\circ}\text{C}$ . Under this temperature, the monomer suffers fast polymerization, exothermic reactions, which induce a deformation on the TG curve around  $200^{\circ}\text{C}$ . The enthalpy of this reaction is high enough to promote the volatilization of a fraction of the sample, inducing a deformation on the TG curve around  $200^{\circ}\text{C}$ . Additionally, it is important to point out that the studied resin has itself diluted on 25% of monomer, according to supplier information. So, the same thermal behavior can be observed on the curve 1 from the epoxy-acrylate resin, as in the supplied form, in the range of  $170^{\circ}\text{C}$  up to  $230^{\circ}\text{C}$ . On the other hand, the product from the thermal curing reaction of the resin is different from the product derived from the thermal curing reaction of the monomer, as it can be observed by the differences between curves 1 and 2 (Figure 1). An addendum has to be made about the mass loss from talc sample (curve 4). According to Sánchez-Soto et al. (1997), this mass loss may be attributed to water release at lower temperatures, after some grinding time. This result is in accordance with particle size diminution and surface area evolution. It is also discussed that a reaggregation process takes place and probably avoid the water elimination by dynamic thermal treatment throughout larger particles, and thus it causes that water diffusion is more hindered.

By analyzing Figure 2, it can be seen that the compositions present different profiles of mass loss which can be clearly attributed to the different origins of the pigments once the ratio clear coating/pigment was left constant for all samples. Additionally, all studied uncured samples present at least three different thermal events:

- in the range of  $150^{\circ}\text{C}$  up to  $290^{\circ}\text{C}$ , which corresponds to volatilization of components, mainly photoinitiator and monomer, during thermal curing reaction, as previously described. This event just occurs because these compositions are proposed to be cured by radiation technology, more specifically UV light, not by heat, which state-of-art says that no volatile components are produced during UV curing reaction.
- from  $310^{\circ}\text{C}$  up to  $450^{\circ}\text{C}$ , corresponding to the thermal degradation of the so-formed cross-linked network by thermal curing, as suggested by Alves et al. (2009) and Kim et al. (2011).
- from  $500^{\circ}\text{C}$  up to  $580^{\circ}\text{C}$  due to the conversion of carbonaceous residue to carbon dioxide.

Concerning the steps of thermal degradation of the studied print inks, the idea of mass loss during thermal curing can be proved if we also analyze Figure 3 on the temperature range of 150-290°C. It can be seen that each composition presents an exothermic peak on this temperature range, resulting from concomitant exothermic thermal curing reaction and endothermic volatilization event, which extension is dependent on the pigment chemical family. Some more detailed discussion about the influence of thermal curing on UV-curable compositions is presented by Ruiz et al. (2002).

SDT analysis presented of Figure 4 allows us to observe that, in fact, thermal degradation is greatly influenced by the pigment incorporated to the clear coating. If we note, for example, that yellow pigment already presents an exothermic peak at the aforementioned temperature range, so it is necessary to subtract this enthalpy in order to obtain the real curing enthalpy. As this is not accurate, we choose to continue our discussion just based on the white print ink, which corresponding pigment has higher thermal stability. So, two pro-degradant additives were incorporated to the white print ink in order to evaluate a possible increasing on the accelerated degradation rate of the samples before/after UV curing. Furthermore, the samples containing pro-degradant agents, which were previously cured by UV light, presented a meaningful reduction (around 30°C) on thermal stability when compared to the stability of thermally-cured and unmodified sample (without pro-degradant agent). It is observed that the thermal stability for the cured white print ink remains roughly the same as the uncured one. As discussed by Wei et al. (2012), the auto-oxidation reactions are initiated by thermal or photochemical energy input. Alternatively, metal oxides and other salts present in pigments can have a notable effect on varnishes and media as they promote light-induced oxidation reaction. These oxidants are usually chemical elements or substances with elements in high oxidation numbers or highly electronegative substances/elements that can gain one or two extra electrons by oxidizing an element or substance.

The most remarkable changes are observed for the onset degradation temperature corresponding to the degradation of the polymeric network (Table 1), as it was previously discussed. If we consider that both components resin and monomer have an average onset degradation temperature around 375°C, we will note that this value is roughly the value for the onset degradation temperature of the thermally-cured white print ink. When this composition is UV-irradiated, it is observed a reduction on this temperature, indicating that the sample is more susceptible to accelerated degradation. The same behavior is observed for formulations containing CoSt and CeSt, but in a highlighted way, indicating the pro-activity of the agents to catalyze the thermal degradation of the UV-cured white print ink studied samples.

## Conclusions

The accelerated degradation by temperature has shown to be able to activate the catalytic ability for chemical bonding rupture of the polymeric components in the studied print inks after UV curing, as it happens when applied to more conservative polymer systems, especially polyolefins. Additionally, the use of additives aimed to accelerate the thermal degradation of polymers has shown to be efficient when coupled with the inks composition substances. This effect is remarkable seen by the reduction on both degradation onset temperature and oxidation onset temperature for the samples containing the pro-degrading additives.

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## References

1. Alves, E. F., Oliveira, R. C., Silva, L. H. M. & Colodette, J. L. (2009) Thermal and spectroscopic analyses on the molecular interaction between eucalyptus kraft pulp components and offset printing ink. *Brazilian Archives of Biology and Technology*. [Online] 52 (3) 689-699. Available from: [http://www.scielo.br/scielo.php?pid=S1516-89132009000300021&script=sci\\_arttext](http://www.scielo.br/scielo.php?pid=S1516-89132009000300021&script=sci_arttext) [Accessed 27th July 2013].
2. Bardi, M. A. G. & Machado, L.D.B. (2012) Accompanying of parameters of color, gloss and hardness on polymeric films coated with pigmented inks cured by different radiation doses of ultraviolet light. *Radiation Physics and Chemistry*. [Online] 81 (9) 1332-1335. Available from: <http://www.sciencedirect.com/science/article/pii/S0969806X1100466X> [Accessed 27th July 2013].
3. Bauer, F., Decker, U., Czihal, K., Mehnert, R., Riedel, C., Riemschneider, M., Schubert, R. & Buchmeiser, M. R. (2009) UV curing and matting of acrylate nanocomposite coatings by 172 nm excimer irradiation. *Progress in Organic Coating*. [Online] 64 (4) 474-481. Available from: <http://www.sciencedirect.com/science/article/pii/S0300944008001999> [Accessed 27th July 2013].
4. Bénard, F., Mailhot, B., Mallécol, J. & Gardette, J. L. (2008) Photoageing of an electron beam cured polyurethane acrylate resin. *Polymer Degradation and Stability*. [Online] 93 (6) 1122-1130. Available from: <http://www.sciencedirect.com/science/article/pii/S014139100800075X> [Accessed 27th July 2013].



5. Calvo, W. A. P., Duarte, C. L., Machado, L. D. B., Manzoli, J. E., Geraldo, A. B. C., Kodama, Y., Silva, L. G. A., Pino, E. S., Somessari, E. S. R., Silveira, C. G. & Rela, P.R. (2012) Electron beam accelerators—trends in radiation processing technology for industrial and environmental applications in Latin America and the Caribbean. *Radiation Physics and Chemistry*. [Online] 81 (8) 1276-1281. Available from: <http://www.sciencedirect.com/science/article/pii/S0969806X12000795> [Accessed 27th July 2013].
6. Chen, Z., Chisholm, B. J., Patani, R., Wu, J. F., Fernando, S., Jogodzinski, K. & Webster, D. C. (2010) Soy-based UV-curable thiol-ene coatings. *Journal of Coatings Technology and Research*. [Online] 7 (5) 603-613. Available from: <http://link.springer.com/article/10.1007/s11998-010-9241-x> [Accessed 27th July 2013].
7. Chen, Z., Wu, J. F., Fernando, S. & Jagodzinski, K. (2011) Soy-based, high biorenewable content UV curable coatings. *Progress in Organic Coatings*. [Online] 71 (1) 98-109. Available from: <http://www.sciencedirect.com/science/article/pii/S0300944011000075> [Accessed 27th July 2013].
8. Drobny, J. G. (2010) *Radiation Technology for Polymers*. Boca Raton, CRC Press.
9. Eldred, N. R. (2008) Printing inks. In: Eldred, N. R. (ed.) *Package Printing*. Pittsburgh, USA, PIA/GATFP, pp. 229-259.
10. Kim, Y. D., Cho, J. H., Park, C. R., Choi, J.-H., Yoon, C. & Kim, J. P. (2011) Synthesis, application and investigation of structure-thermal stability relationships of thermally stable water-soluble azo naphthalene dyes for LCD red color filters. *Dyes and Pigments*. [Online] 89 (1) 1-8. Available from: <http://www.sciencedirect.com/science/article/pii/S0143720810001580> [Accessed 27th July 2013].
11. Kumanayaka, T. O., Parthasarathy, R. & Jollands, M. (2010) Accelerating effect of montmorillonite on oxidative degradation of polyethylene nanocomposites. *Polymer Degradation and Stability*. [Online] 95 (4) 672-676. Available from <http://www.sciencedirect.com/science/article/pii/S01413910090003863> [Accessed 27th July 2013].
12. Magagula, B., Nhlapo, N. & Focke, W. W. (2009) Mn2Al-LDH- and Co2Al-LDH-stearate as photodegradants for LDPE film. *Polymer Degradation and Stability*. [Online] 94 (6) 947-954. Available from: <http://www.sciencedirect.com/science/article/pii/S014139100900086X> [Accessed 27th July 2013].
13. Onusseit, H., Wefringhaus, R., Dreezen, G., Wichelhaus, J., Schall, J., Thiele L. & van Halteren A. (2010) Adhesives, 1. General, In: Elvers, B. (Ed.), *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany, Wiley-VCH Verlag GmbH & Co., pp. 439-481.
14. Pablos, J. L., Abrusci, C., Marín, I., Lopéz-Marín, J., Catalina, F., Espí, E. & Corrales, T. (2010) Photodegradation of polyethylenes: comparative effect of Fe and Ca-stearates as pro-oxidant additives. *Polymer Degradation and Stability*. [Online] 95 (10) 2057-2064. Available from: <http://www.sciencedirect.com/science/article/pii/S0141391010002776> [Accessed 27th July 2013].
15. Roy, P. K., Titus, S., Surekha, P., Tulsi, E., Deshmukh, C. & Rajagopal, C. (2008) Degradation of abiotically aged LDPE films containing pro-oxidant by bacterial consortium. *Polymer Degradation and Stability*. [Online] 93 (10) 1917-1922. Available from: <http://www.sciencedirect.com/science/article/pii/S0141391008002012> [Accessed 27th July 2013].
16. Roy, P. K., Surekha, P., Raman, R. & Rajagopal, C. (2009) Investigating the role of metal oxidation state on the degradation behaviour of LDPE. *Polymer Degradation and Stability*. [Online] 94 (7) 1033-1039. Available from: <http://www.sciencedirect.com/science/article/pii/S0141391009001499> [Accessed 27th July 2013].
17. Ruiz, C. S. B., Machado, L. D. B., Vanin, J. A. & Volponi, J. E. (2002) Cure degree estimation of photocurable coatings by DSC and differential photocalorimetry. *Journal of Thermal Analysis and Calorimetry*. [Online] 67 (2) 335-341. Available from <http://www.akademai.com/content/3n0x-7lv6al5g11h6/> [Accessed 27th July 2013].
18. Salleh, N. G. N., Yhaya, M. F., Hassan, A., Bakar, A. A. & Mokhtar, M. (2010) Effect of UV/EB radiation dosages on the properties of nanocomposite coatings. *Radiation Physics and Chemistry*. [Online] 80 (2) 136-141. Available from: <http://www.sciencedirect.com/science/article/pii/S0969806X10003105> [Accessed 26th July 2013].
19. Sánchez-Soto, P. J., Wiewióra, A., Avilés, M. A., Justo, A., Pérez-Maqueda, L. A., Pérez-Rodríguez, J. L. & Bylina, P. (1997) Talc from Puebla de Lillo, Spain. II. Effect of dry grinding on particle size and shape. *Applied Clay Science*. [Online] 12 (4) 297-312. Available from: <http://www.sciencedirect.com/science/article/pii/S0169131797000136> [Accessed 27th July 2013].
20. Takahashi, T., Takasawa, Y., Gowa, T., Okubo, S., Sasaki, T., Miura, T., Oshima, A., Tagawa, S. & Washio, M. (2010) Study on UV/EB nanoimprint lithography using nano-/micro-fabricated crosslinked PTFE mold. *Journal of Photopolymer Science and Technology*. [Online] 23 (1) 69-74. Available from: [https://www.jstage.jst.go.jp/article/photopolymer/23/1/23\\_1\\_69/\\_article](https://www.jstage.jst.go.jp/article/photopolymer/23/1/23_1_69/_article) [Accessed 27th July 2013].
21. Wilke, G. (2008) Coatings for plastic parts. In: Streitberger, H.-J. & Dössel, K.-F. (eds.) *Automotive Paints and Coatings*. Weinheim, Germany, Wiley-VCH Verlag GmbH & Co., pp. 307-350.
22. Wei, S., Pintus, V. & Schreiner, M. (2012) Photochemical degradation study of polyvinyl acetate paints used in artworks by Py-GC/MS. *Journal of Analytical and Applied Pyrolysis*. [Online] 97 158-163. Available from: <http://www.sciencedirect.com/science/article/pii/S0165237012000964> [Accessed 27th July 2013].