Ann-Sofie Johansson

ULTRAVIOLET (UV) CURABLE INKS AND COATINGS

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Johansson, Ann-Sofie
Satakunnan ammattikorkeakoulu, Satakunta University of Applied Sciences
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Supervisor 1: Kuusivaara, Juha; Technical Manager, Huntsman Pigments Oy
Supervisor 2: Hannelius, Timo; Senior Lecturer, SAMK
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The purpose of this thesis was to widen the knowledge of ultraviolet (UV) curable inks and coatings for Huntsman Pigments Oy, a leading manufacturer of high quality white pigments and functional additives and the sponsor of this thesis.

This thesis was meant to be a literature work and the gathered information would contribute to the knowledge foundation for Huntsman Pigments Oy to conduct further research in the subject. The aim is that the information would help lead to improvements in laboratory work, product development as well as in customer service.

The methods used to achieve information included searching for information in databases, libraries, on the internet as well as contacting suppliers of UV resin.

UV-curing is a method where ultraviolet radiation is used in order to cure inks and coatings. The change in state from liquid (wet) to solid (dry) is nearly instant as UV-curable material is being passed through an UV curing system, without releasing volatile organic compounds (VOC's) into the atmosphere, compared to traditional curing methods. The technology is therefore considered "green", as it confines to environmental restrictions. The rapid curing allows for high production speed and allows for immediate handling of the cured goods and savings in form of low energy consumption and reduced space requirements of UV unit as no drying ovens are needed.

UV curing was introduced in the 1960's and has increased its popularity the past 20 years, making it the fastest growing technology in the inks and coatings industry, continuously gaining market share with an annual growth of approximately 10%.

ACRONYMS USED IN THIS THESIS

cm²   Square Centimetres

EB   Electron Beam

HAP   Hazardous Air Pollutants

keV   Kilo Electron Volts

kV   Kilo Volts

MDI   Methylene Diphenyl Diisocyanate

µm   Micrometres

mPa·s   Viscosity (mill pascal-second)

nm   Nanometres

UPE   Unsaturated Polyester

VOC   Volatile Organic Compounds

UV   Ultraviolet

2D   Two-dimensional

3D   Three-dimensional

CONTENTS

1 INTRODUCTION

Ultra violet (UV) curing is a technology with an annual growth rate of approximately 10% and continue to increase its' popularity due to the advantages that it offers.

UV curing is a polymerization reaction that includes a light sensitive molecule called photoinitiator, an essential ingredient in UV-curable formulations of inks and coatings. Upon exposure to a certain wavelength, photoinitiators absorb UV radiation and becomes activated and generates active species. These active species initiate the curing and can be a radical, cation or anion. The majority of UV-curable formulations include radical producing photoinitiators.

The major benefit of UV-curable formulations includes the ability of changing phase from liquid into solid in a fraction of a second under exposure of UV radiation, without releasing harmful volatile organic compounds (VOC's), which makes the technology environmentally friendly and improves the work safety. Another important benefit with UV systems includes increased productivity due to the instant curing, allowing for immediate processing and shipping of the cured goods. UV systems also require less space than conventional curing systems as UV lamps replace thermal ovens. Since no power draining ovens are needed, less energy is consumed which leads to costs savings. UV curing is ideal for applications on heat sensitive substrates as the curing is carried out at room temperature.

UV-curable formulation consists of oligomeric resins, reactive diluents, photoinitiators and additives. It is important to understand the chemical structures of the raw materials used in order to predict properties of the liquid formulation as well as the cured film.

The purpose with this thesis was to widen the knowledge on UV-curable inks and coatings and in particular free radical UV curing, for Huntsman Pigments Oy. The idea was that the gathered information would contribute to their own research and development in the subject, which would lead to improvements in laboratory work, product development as well as in customer service for customers using Huntsman Pigment's titanium dioxide grades.

2 HUNTSMAN CORPORATION

Huntsman Corporation was founded in the 1970's by current Executive Chairman, Jon M. Huntsman. The business originally focused on developing innovative products in the field of plastics packaging and later expanding to petrochemicals. (Website of Jon M. Huntsman School of Business Utah State University 2014)

Huntsman has acquired over 30 acquisitions since it was founded and is currently a publicly traded (NYSE-listed) company and a global leading producer of chemical products to a wide range of industries worldwide including: chemicals, plastics, paints and coatings, automotive, textiles, construction, technology, agriculture, health care, detergent, furniture, appliances and packaging.

Huntsman operates in over 30 countries with more than 100 manufacture- and R&D facilities, employing approximately 15.000 associates. Huntsman's revenues reached over $13 billion in 2014. The acquisition of Rockwood's Performance Additives and Titanium Dioxide businesses makes Huntsman Corporation the largest colour- and white pigments company worldwide.

Huntsman's five business divisions include:

- Advanced materials

 Synthetic and advanced polymer products

- Performance products

Intermediate chemistries and technologies

- Pigments

Titanium dioxide- and colour pigments, functional additives and chemicals for timber- and water treatment

- Polyurethanes

Polyurethanes (MDI-based)

- Textile effects

Chemical- and dye products

Peter R. Huntsman is the President, CEO and Director of Huntsman Corporation. (Website of Huntsman Corporation 2015)

2.1 Huntsman Pigments Oy

Huntsman Pigments Oy is located in Pori, Finland. Huntsman Pigments Oy is a leading manufacturer of high quality titanium dioxide (TiO_2) pigments for a wide range of applications including cosmetics, paints, varnishes and printing inks for packaging applications. The plant uses the sulphate route to produce titanium dioxide.

The plant employs approximately 550 people and has an annual production capacity of 130.000 tons of titanium dioxide, making it one of the largest pigment facilities to use the sulphate process. Nearly 95% of the production is exported. (Website of Sachtleben 2015)

2.2 Titanium Dioxide

2.2.1 Source and Ores

Titanium dioxide (TiO_2) is the ultimate white pigment used to impart whiteness and opacity to a wide range of products including paints, plastics, paper, inks, cosmetics, foodstuffs and pharmaceuticals.

Titanium dioxide is a widespread element that exists in nature only together with other elements and is the ninth most common element in the earth's crust, consisting of 0.6% titanium by weight. However, few titanium dioxide containing deposits are concentrated enough, as well as accessible, in order to be financially extractable.

Important titanium dioxide ores in industry include ilmenite, anatase and mineral rutile. Ilmenite ore is the most widespread and abundant of the raw materials containing titanium dioxide.

Ilmenite is a black sand or rock with the chemical formula $FeTiO_3$ or $FeO \cdot TiO_2$, which contain impurities, primarily iron. Theoretical titanium dioxide content of ilmenite is 52.65%. The titanium dioxide concentration of the ore may vary depending on its origin. Ilmenite used in pigment manufacturing contain between 45-60% titanium dioxide (McKay 1994, 60-70; Kemira Pigments 1999, 9).

Naturally occurring anatase and rutile contain higher concentration of titanium dioxide but are unsuitable for utilization as white pigment due to discolouration from impurities. Anatase and rutile have different physical properties but their chemical formula is the same. Naturally occurring antase forms octahedrons while rutile forms prismatic crystals. The third crystalline form is brookite, which forms orthorhombic crystals, but is of no commercial importance. Fewer deposits of rutile and anatase have been identified than of ilmenite (Kemira Pigments 1999, 10).

Rutile has a brown to reddish black colour and contain impurities, mostly iron compounds. The titanium dioxide content is about 95%.

There are two important types of enriched ores, in addition to the naturally occurring ones:

- Titanium slag: the residue left after iron extraction from ilmenite, or mixed deposits (ilmenite-hematite/magnetite).
- Beneficiated ilmenite: treatment of the natural ore which increases its titanium dioxide concentration.

Ilmenite and titanium slag are most commonly used in the sulphate process. Beneficiated ilmenite and rutile are used in the chloride process.

The pigments produced can be either anatase- or rutile-structured and both types can be surface treated in order to impart properties for specific end uses. Both rutile and anatase can be produced by the sulphate route. It is uneconomical to produce anatase by the chloride route, which is exclusively used for production of rutile pigments (McKay 1994, 70-71).

2.2.2 Applications

According to the report entitled "Titanium Dioxide Market for Paints & Coatings, Plastic, Paper, and Other Applications - Global and China Industry Analysis, Size, Share, Growth, Trends and Forecast, 2015 - 2023", the global titanium dioxide market was valued at US $12.18 billion in 2014 and is expecting to grow to US $16.79 billion by 2023. (Website of Transparency Market Research 2015)

Titanium dioxide have been in use for approximately 90 years in a vast range of industrial and consumer applications including coatings, paints, adhesives, paper, plastics, rubber, printing inks, coated fabrics and textiles, catalyst systems, ceramics, floor coverings, roofing materials, pharmaceuticals, cosmetics, water treatment agents, automotive products and food colourant (E171). Titanium dioxide is used to give opacity and whiteness in paints, inks, textiles, plastics, paper, toothpaste (Sosaciu 2008, 118; Website of Titanium Dioxide Manufacturers Association 2014).

Titanium dioxide pigments are able to scatter light and re-radiates more than 99% of incident light and can therefore be used as UV absorbers in sunscreen products. (Website of Sachtleben 2015)

2.2.3 Pigment Properties

Titanium dioxide is a white powder which can be characterized by its brightness and high refractive index (n≈2.4). It is a very stable material, resistant to light, variations in pH and oxidation. It is insoluble in organic solvents and water (Sosaciu 2008, 118).

Titanium dioxide is stable, non-toxic insoluble and heat resistant. It is resistant to reaction with other substances. Of all known white pigments, titanium dioxide is the most stable and is commonly regarded as a safe substance due to its inertness and non-toxicity. Titanium dioxide is approved for being used in contact with food and is used in food packaging and some grades are used as colorant in food.

Most commercial titanium dioxide pigments are coated on the surface with substances. This alters the properties of the particle that behave differently than the (core) titanium dioxide particle.

The crystal type of titanium dioxide (anatase, rutile) is the most important physical characteristic and second is the particle size. Ideally titanium dioxide pigments should consist of nearly spherical crystals in the size range between 0.15-0.25 micrometres (μm). These crystals scatter light very effectively and has good hiding power capabilities for the end use product, however, pigment grades for different applications require their own specific crystal size (Kemira Pigments 1999, 18-19). The specified properties of titanium dioxide pigment are monitored and controlled during manufacturing in order to suit specific applications.

Table 1. Properties of Titanium Dioxide Pigments (Kemira Pigments 1999, 17)

Particle size and distribution
Crystal size and distribution
Crystal structure (anatase, rutile)
Outer shape of crystals (spherical, angular, axis, ratio)
Color (brightness)
Color tone
Tint reducing power (tinting strength, optical efficiency, ability to lighten up a black/coloured mixture, L*)
Tint tone (undertone, b*)
Hiding power (opacity)
Dispersibility
Effect on surface gloss in application
Absorption and adsorption properties
Heat resistance
Light resistance
Weather resistance
Chemical purity
Abrasion characteristics
Dusting characteristics
Flow ability

Table 2. Physical Properties of Anatase and Rutile

	Anatase	Rutile
Density (g/cm^3)	3.9	4.2
Hardness (Mohs scale)	5.5-6	6-7
Refractive Index:		
Air	2.5	2.75
Water	1.9	2.1
Oil	1.7	1.85
Specific heat (kJ/°C·kg)	0.7	0.7
Dielectric constant	48	114
Melting point (°C)	*converts to rutile at 700-800*	1885

As can be seen in table 2, rutile has higher refractive index than anatase and higher number of hardness on Moh's scale, making it harder than anatase (Kemira Pigments 1999, 12).

Titanium dioxide has excellent optical capabilities due to that it is colourless and pure white in powder form with a high refractive index. The titanium dioxide crystals scatter (reflect back) light extremely well and can scatter almost all visible light of any wavelength. To reach the best optical properties of titanium dioxide, the crystals must be of the right size, highly pure with perfect structure.

Due to titanium dioxide's high refractive index, it has higher hiding power, opacity and tint reducing power than other white pigments. Tint reducing power (optical efficiency) is the ability of the pigment to lighten up a mixture that is black or colored (Kemira Pigments 1999, 29).
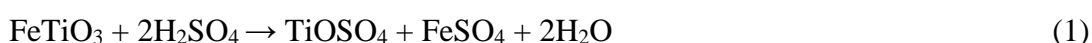
2.2.4 Processing

Titanium dioxide pigments are produced by two chemical processes, either the sulphate or the chloride process. In the the chloride process, titanium dioxide is produced by reacting titanium ores with chlorine gas. In the sulphate process
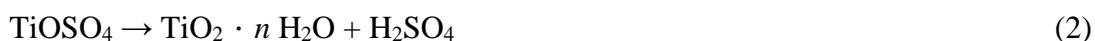
titanium ores are reacted with sulphuric acid. In the European production, 70% comes from the sulphate process and the rest 30% from the chloride process.

The titanium dioxide production produce waste including solid waste, strong- and weak acid waste, neutralised waste, treatment waste and dust. (Website of European Commission 2015)

The overall chemistry of the sulphate process:

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O \tag{1}$$

$$\overset{(OH-)}{TiOSO_4 \rightarrow TiO_2 \cdot n\, H_2O + H_2SO_4} \tag{2}$$

$$\overset{(heat)}{TiO_2 \cdot n\, H_2O \rightarrow TiO_2 + n\, H_2O} \tag{3}$$

The ore is dried and ground and treated with sulphuric acid (H_2SO_4) with a concentration between 85-92%, which depends on the composition of the ore. The ground ore and sulphuric acid mixture is agitated by compressed air, and hot steam is blown in. At approximately 160°C, an exothermic reaction starts, converting the mixture to a porous cake that may contain ferric, ferrous and titanium sulphates. The cake is extracted with dilute acid or water. If ferric iron is present in the solution it will be reduced to ferrous through addition of scrap iron. The liquor will then be clarified by sedimentation in order to remove insoluble residues such as silica, zircon and residual unreacted ore. An agent is added for flocculation of colloidal materials in order to ensure good clarification. A lot of the iron is removed by cooling to 10°C crystallizing out ferrous sulphate. This step can be neglected in case the original ore has a low iron content, such as titanium slag. Sludge traces is removed by filtration, making the solution concentrated.

The next step of the process is hydrolysis: forming a precipitate of hydrous titanium oxide. This is a critical step and no ferric iron should be present and conditions need to be controlled to allow the precipitate to easily be filtered and washed. Crystals of the right size and type should be produced during calcination process. Precipitation is

obtained by prolonged boiling. At this stage or later in the calcination, nuclei can be added. The added nuclei type determines if rutile or anatase is produced during calcination.

The precipitate is then filtered and washed with water. The acid filtrate is recovered and recycled. Traces of iron is removed by leaching. The next step is calcination which takes place in internally fired and inclined rotary kilns through which the pulp moves under gravity. The pulp is dried and water and sulphur trioxide are driven off. Crystal growth (and conversion to rutile if relevant) takes place at the end of the kiln. The temperature is monitored depending of the type of the pigment being produced, approximately in the range of 1000°C. The pigment is fed into a cooler after calcination. It must cool slowly as to prevent formation of trivalent titanium which could affect the final colour. The unrefined pigment can be dry milled to break down aggregates and be packaged for sale as untreated pigment. Most pigments continue the process by wet milling and treatment (coating) of the particles with inorganic oxides before final milling and packaging (McKay 1994, 71-73).

2.2.5 Advantages of Titanium Dioxide Pigments

- Light scattering capabilities

Titanium dioxide pigments possess excellent light-scattering properties and is used in a wide range of applications requiring white opacity and brightness.

- UV radiation absorption capabilities

Titanium dioxide can absorb UV light and if used in paint or coating system, this ensure lastingness (minimizing degradation of the system; embrittlement, fading and cracking) and protects the substrate. The UV absorption effect ensure the lastingness of the paint. Surface treatments provide efficient absorption of UV energy and allowing for dispersion in different media in applications like sunscreens and light stabilization for wood coatings.

- Energy savings

By using light coloured paints for interior applications, the impression of openness and "space" increases. Light coloured paints also emit energy "luminosity", which reduce the energy needed to light the interior of buildings, compared to darker colours.

The use of titanium dioxide in coloured surfaces in exterior applications leads to energy savings such as in warm/tropical areas, due to the coolness achieved by titanium dioxide because to its light reflectance capability (high refractive index). This also reduces the need for air-conditioning.

- Nanomaterial

As nanomaterial (ultrafine), titanium dioxide provides UV light absorption while appearing transparent and can be used as a DeNOx catalyst support in exhaust gas systems in trucks, cars and power plants, reducing the environmental impact.

- Environmental benefits

Untreated titanium dioxide can be utilized for decomposing environmental pollutants by photocatalysis. (Website of Titanium Dioxide Manufacturers Association 2014)

3 RADIATION CURING

3.1 Market and Forecast

According to a study entitled "The Global Radiation-Cured Products Industry 2012-2017" by consulting firm Kusumgar, Nerlfi & Growney, Inc., specializing in market research and business analysis for polymer and chemical industries, the global consumption of radiation-cured products including inks, coatings and adhesives was valued at approximately $4.94 billion in 2012. According to the consulting company, the growth of the technology is increasing its popularity due to performance, productivity and environmental benefits compared to more traditional technologies.

- Coatings Industry

The largest outlet for radiation-cured products was the coatings industry, representing 58% of the total value in 2012.

The leading end uses of coatings were wood and overprints with nearly 75% of the total coatings volume, and 60% of the coatings value.

Plastics applications such as vinyl flooring, consumer electronic housing, CDs, automotive headlamp lenses and housings accounted for 24% of the coatings value. The fourth largest end uses in coatings were optical fibres and cables. Together the four end uses represent 93% of the value.

- Inks Industry

The ink industry represented 35% of the total radiation-cured products value in 2012 with a volume consumption of 18%. Offset process accounted for nearly 43% of the ink value. The most rapid growing radiation cured ink process is inkjet, which is projected to more than double its volume by 2017. Inkjet accounted for 3% of the volume and 11% of the inks value in 2012.

- Adhesives Industry

The adhesives industry accounted for 7% of the total value of radiation-cured products in 2012, and 4% of the volume.

The large volume for adhesives applications included pressure sensitive, packaging- and DVD lamination. Adhesives for product assembly for medical, electronic and other applications are higher priced than other end uses and accounted for one half of the adhesives value.

The leading raw materials in radiation-cured products consumption were acrylate oligomers and monomers with 74% of the material volume.

Polyurethane dispersions were 4% of the volume.

Photoinitiators represented 8% of the total value.

Other resins used in radiation cured products included:

- Unsaturated polyesters (wood coatings)
- Cycloaliphatic epoxies (for cationic curing)
- Additives
- Fillers
- Pigments
- Styrene (Website of Kusumgar, Nerlfi and Growney 2015)

Table 3. Global Consumption of Radiation-Cured Products Including Inks, Coatings and Adhesives, by Industry and Region, in Millions of Dollars in 2012 and Projections for 2017.

INDUSTRY/REGION	2012	2017
	$	$
Coatings	**2862**	**3875**
Europe	871	1047
Americas	847	1045
Asia-Pacific	1145	1784
Inks	**1728**	**2298**
Europe	587	709
Americas	655	840
Asia-Pacific	486	750
Adhesives	**353**	**464**
Europe	87	104
Americas	124	145
Asia-Pacific	143	214
Rounded Total	4943	6638

As shown in table 3, the coatings industry was the largest outlet for radiation-cured products, accounting for approximately 58% of the total value in 2012.

The ink industry represented approximately 35%, and the adhesives industry 7%. All three industries are projected to grow by 2017. (Website of Kusumgar, Nerlfi and Growney 2014)
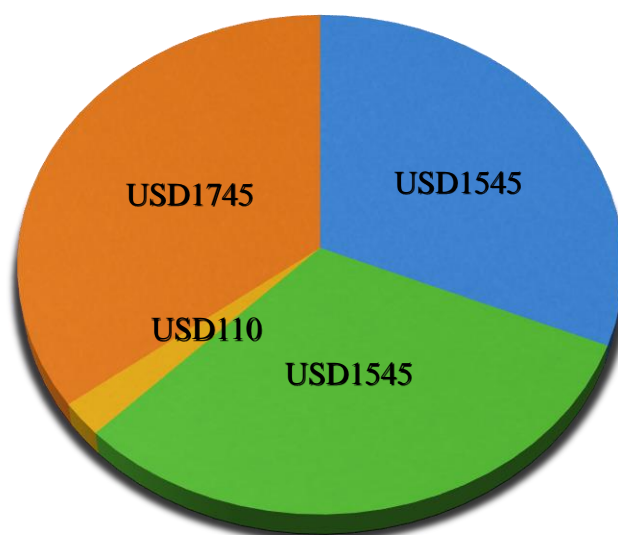
Total: $4.945 Billion

Figure 1. Radiation-Cured Product Consumption by Region in 2012 (Website of European Coatings 2014)

The Asia-Pacific region leads in consumption of radiation-cured products with approximately 35% of the global total value in 2012. This is the most rapid growing region with an annual growth rate of 10% and its share of the volume is forecast to increase from 40% in 2012 to 47% in 2017.

North America and Europe each represented 35% of the total value in 2012. Europe accounted for 31% of the global volume and North America 26%. Both of the regions are projected to grow with an annual rate of 3-4%. (Website of European Coatings 2015)

3.2 Introduction

Radiation curing is polymerization of a chemical system, i.e. the change from liquid state into solid, initiated by incident radiation. The curing process is rapid, occurring in a fraction of a second. Objects can be manufactured, decorated and protected by using this technology. (Fouassier & Rabek 1993, 2.)

Radiation curing include methods using ultraviolet (UV) energy or high energy electrons (EB) to cure coatings, inks or films as opposed to thermal, evaporative or oxidative (air drying) methods (Idacavage 2012). The technology distinguishes itself by the immediate cure, allowing for a dry and cured film in a fraction of a second and absence of volatile organic compounds (VOC's). Cured surfaces can be processed instantly and there is no need for time and energy consuming drying tunnels in the application lines. This in turn leads to avoidance of waiting times, decrease of energy consumption and increase of productivity. (Glöckner, Jung, Struck & Studer 2008, 12-13.)

Which technology that is more suitable for certain applications depends on the specified requirements. The main difference between the two technologies is absence of photoinitiator in EB-curable formulations, as the high energy level of the EB radiation initiates polymerization directly (except in EB cationic curing where an initiator is needed). While EB irradiation is able to initiate polymerization directly, UV light on its own is unable of producing reactive groups but instead require the help of "photoinitiator" which is a light sensitive molecule that initiate the polymerization. (Glöckner, Jung, Struck & Studer 2008, 11, 14.)

Another difference between the methods is the kind of radiation. UV curing require radiation with wavelength between 180nm (UV-C) up to 380nm (near visible light) (Glöckner, Jung, Struck & Studer 2008, 14). The energy range in EB curing is between 90-250 keV. (Website of Dymax Oligomers & Coatings 2015)

EB curing require oxygen to be excluded (inertization) in order to allow for proper cure, meaning that curing surfaces needs to be covered with nitrogen (N_2), while UV curing takes place under atmospheric conditions. UV curing is significantly more widely used than EB curing. Approximately 90% of the radiation curing market in Europe is represented by using UV-light. (Glöckner, Jung, Struck & Studer 2008, 14, 17.)

Table 4. Properties of Conventional and Radiation-Curable Inks and Coatings

	Conventional coating	**Radiation curing coating**
Physical drying	Yes	No
Volatile solvents	Yes	No
Chemical crosslinking	Yes (depends on the binder)	Yes
Drying times	Minutes-days	Fraction of seconds

As shown in table 4, some properties of conventional and radiation-curable coatings and inks are compared to one another. It is evident that radiation curing offers advantages such as instant cure and absence of harmful solvents (VOC's) emissions to the atmosphere. (Glöckner, Jung, Struck & Studer 2008, 12.)

3.3 History

Radiation curing, also known as UV/EB curing, is the most rapidly growing technology in the inks and coatings industry. (Glöckner, Jung, Struck & Studer 2008, 5.) Utilization of the technology dates back to ancient Egypt 4.000 years ago when a type of UV-curable coating that cured when exposed to solar radiation was used in preparation of mummies, and an asphalt-based oil coating as a sealant for ships. The scientific interest in developing radiation-curable systems started out in the 1940's. (U.S Environmental Protection Agency 2001, 2).

The first commercial application of radiation curing technology was introduced in the early 1960's, with the use of an unsaturated polyester (UPE) UV-curable ink resin. Systems based on acrylic unsaturation became industrially applied in the beginning of the 1970's. They are more reactive than UPE which is also the reason why they have increased in growth and applications since. The first industrial application of EB curing occurred in the early 1970's.

The first applications of radiation-curable systems were limited to flat sheets, primarily in wood products and printing. Three-dimensional (3D) curing of UV/EB materials became possible with advancement in plant engineering and curing equipment (e.g. rotating conveyors, numerous UV-sources). Moreover, improvements in poly-

mer science have brought a wide range of UV/EB curable materials with features required by the end-user.

The driving forces behind the development of radiation curing technology was the threat of energy shortages during the 1960's (energy crisis of 1974), as well as increased environmental concerns regarding VOC emissions from conventional curing methods. However, the main interest in radiation curing technology were the unique advantages that it offered, such as high productivity and improved performance (Fouassier & Rabek 1993, 9-10; U.S Environmental Protection Agency 2001, 2).

3.4 Main Advantages

The main radiation curing advantages include:

- Improved productivity and energy savings
- Curing occurs in a fraction of second as less than 1s of exposure is needed, allowing for high cure speed when compared to conventional curing methods which leads to increased production. Since the curing process is very rapid, products are instantly ready for handling/testing/shipment.
- Lower costs per cured part due to transformation to 100% solids and high cure speed.

- Sensitive substrates
- The process is ideal for applications on heat sensitive substrates as the curing is carried out at room temperature.

- Environmental concerns
- Usually compositions are solvent-free (VOC's) eliminating risk of flammability and release of emissions.

- User friendly
- UV lamps can be installed on existing production lines.

- Space friendly
- Reduced space requirements for equipment (Idacavage 2012, 6; Glöckner, Jung, Struck & Studer 2008, 17; Website of Radtech 2015).

3.5 Electron Beam (EB) Curing

Electron beam curing is a non-thermal process taking place in room temperature using high energy electrons to initiate polymerization. The process is considered environmentally friendly and green with practically no emissions of volatile organic compounds (VOC's) or Hazardous Air Pollutants (HAP's), as the EB-curable formulations usually are solvent free and converted to 100% solids.

EB curing is suitable for heat-sensitive substrates since the curing is carried out at room temperature, making the technology energy efficient. Applications of EB-curable inks and coatings include the packaging industry, in particular food packaging (Laksin 2010).

EB and UV curing technologies are commonly regarded as competitive although they both offer advantages unachievable by the other, such as the ability of EB to cure thick pigmented segments as EB curing is capable of penetrating through matter, unlike photons of light which are mostly absorbed on the material surface. (Glöckner, Jung, Struck & Studer 2008, 25; Website of Radtech 2015).

The major disadvantages with EB curing technology and main arguments against it are the high investment in equipment and high energy consumption.

The raw materials used for EB curing are almost the same as for UV curing, with the difference that EB curing do not require photoinitiator (free radical polymerization), instead an electron beam (accelerated electrons) is used in curing acrylate-based coatings and inks. Curing is initiated at room temperature and as the irradiation is higher in energy than in UV light there is no need for a radical initiator. EB curing require inert atmosphere to prevent ozone formation. (Arceneaux & Willard, 1.)

When the electrons collide on a coated substrate, some of their energy is transferred to electrons of the double bond. They become excited and initiate the acrylate curing process.

The electron gun (accelerator) comprise of a tungsten cathode which is heated by an electron flow. Under vacuum, electrons are emitted and accelerated by a negative voltage at the anode which generates an electron beam. The electron beam then passes through a titanium foil window that isolates the vacuum chamber from surrounding atmosphere, and under inert (N_2) atmosphere bombards the coated substrate. As electrons hit the surface X-rays can be generated therefore additional lead shielding may be required for safety reasons.
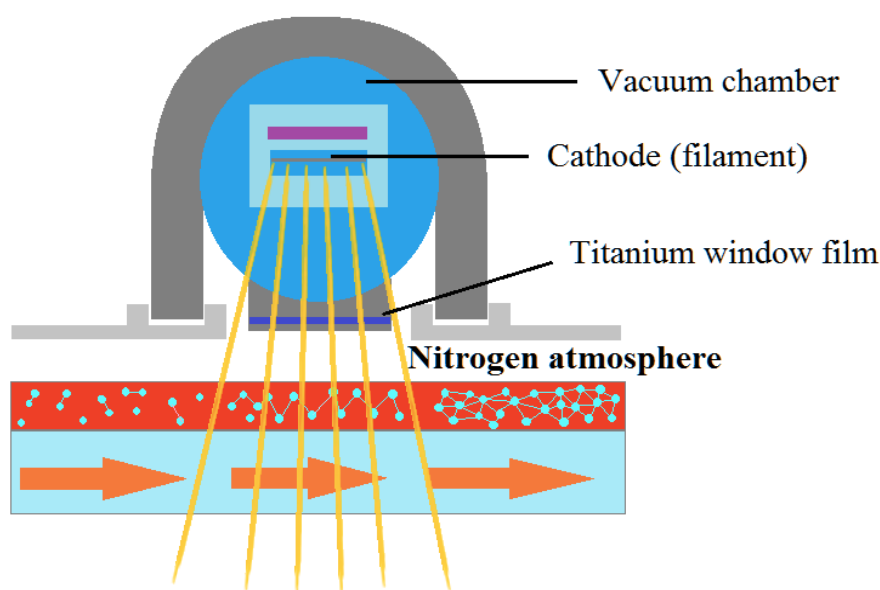
Figure 2. Principle of EB Curing Process

Electrons are accelerated in vacuum from a cathode toward anode, penetrating a thin titanium film which is approximately 0.2mm. The high energy electrons impact with the inks leading to cured pigment layers instantly, i.e. the transformation of short-chained acrylic molecules to long-chained polymers. (Website of Sun Chemical Corporation 2014)

Acceleration voltages needed to transport the electrons are between 70-500kV and the electron energy (keV) depends on this value directly.
If the energy of the electrons is sufficiently high, curing throughout deep layers of thick pigmented films are possible, which are not transparent to UV light. This makes the technology attractive in applications such as printing inks, adhesives and composites. How deep the beam will penetrate through the film, i.e. depth of penetra-

tion, directly depends on the electron energy and density (ρ) of the ink/coating formulation. The unit for depths of penetration is expressed in g/m^2, and typical values range from 20-500 g/m^2. (Glöckner, Jung, Struck & Studer 2008, 26.)

UV technology is by far the most popular method from the usable radiation energy sources of the spectrum while EB technology is the most economical technology for industrial applications with large volumes. Safety requirements of EB technology as well as high investment cost are factors decreasing its popularity (Schwalm 2006, 7).

3.5.1 Cationic Curing

EB curing can also be used in cationic polymerization of epoxies and not only in radical curing applications. The process allows for curing of thick pigmented epoxy or vinyl ether resins and the risk of oxygen inhibition is decreased using cationic curing, which are the reasons the technology is gaining interest.
It is important to use onion salt, which is a common cationic photoinitiator, in cationic curable formulations. The salt produces the required acid for polymerization of the epoxy binder. (Glöckner, Jung, Struck & Studer 2008, 27.)

Table 5. EB Cationic Advantages and Disadvantages (Glöckner, Jung, Struck & Studer 2008, 27)

Advantages	Disadvantages
Uniform polymerization even in thicker films	Radical EB curing is highly oxygen inhibited (installation of inert system necessary)
Rapid hardening at room temperature	Curing on substrates that are only flat 2D
Volatile solvents not required	Complex installation and high equipment cost
Photoinitiator not required (limiting risk of migration of photoinitiator or of photo-by-products)	High energy consumption

4 ULTRAVIOLET (UV) CURING

4.1 Forecast

The UV-curable resin market is expected to reach at 697.2 kilotons by 2018 with an annual growth rate of 7,7%. The world's largest and most rapid growing market of UV-curable resins is Asia-Pacific, consuming more than half of the total global demand in 2012. The main consumers of UV-curable resins in Asia-Pacific area are China and Japan.

In the past few years the global UV-curable resins market has experienced significant growth, which is estimated to continue in the coming years, majorly due to the highly growing Asia-Pacific region with a high growth potential of the Chinese market, and promotion of environment-friendly products (Website of Companies and Markets 2015; Website of Markets and Markets 2015).

4.2 Introduction

UV curing (photoinitiated polymerization, photopolymerization, photocrosslinking) is a polymerization reaction including a functionalized oligomer (binder) which leads to formation of a solid crosslinked film by exposure to UV radiation.

When a light sensitive molecule, photoinitiator, becomes exposed to a certain wavelength it absorbs UV-radiation from the light and undergoes chemical modifications and becomes activated generating active species that initiate the curing process. (Glöckner, Jung, Struck & Studer 2008, 17.)

UV curing can be classified to two main categories that also require different types of photoinitiators to be used.

1. Free Radical

Photoinitiator absorbs UV light generating free radicals. The radicals react with double bonds which leads to polymerizations and chain reaction.

2. Cationic

Cations are produced. Photoinitiator absorbs UV light generating a Lewis acid, which react with epoxy groups resulting in polymerization.

A third type of crosslinking mechanism that can be initiated by light is polyaddition (or polycondensation), where an acid or base is used to produce active species (Glöckner, Jung, Struck & Studer 2008, 17-19; Idacavage 2012).

4.3 Free Radical Curing

UV-cured products for commercial applications are mainly produced by free radical UV curing. Radical photoinitiators represents over 90% of commercially used initiators. Available in smaller amounts are the cationic photoinitiators, mostly sulfonium salts and iodonium salts. One major advantage with radical UV curing method is the curing speed (fraction of a second) which is the reason behind its growth and popularity as it allows for increased productivity and keeping energy costs down.

4.3.1 Process

There are three steps involved in free radical UV curing: initiation, propagation and termination.

- Initiation

Initiation is triggered by light. As shown in Figure 3a, the curing process is initiated by UV-light which activates the photoinitiator to produce free radicals. This step is called "phytolysis". The generated radicals add to double bond of monomers or oligomers, forming a carbon-centered radical (Figure 3b). For the initiation to work, the photoinitiator must be capable of absorbing light emitted by the UV lamp, meaning the absorption spectrum of the photoinitiator must overlap with the emission spectrum of the UV lamp. If the photoinitiator is unable of fulfilling this condition, the film remains liquid as no curing reaction is initiated.

a) Phytolysis

UV light

Photoinitiator $\longrightarrow$ R$^\bullet$ **(radicals)** (4)

b) Curing initiation

(5)
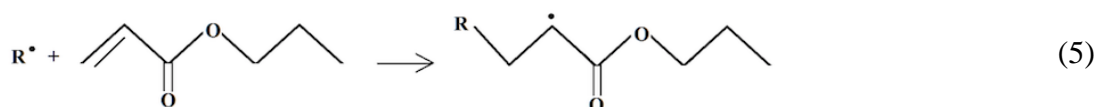
Figure 3. Initiation (Glöckner, Jung, Struck & Studer 2008, 19; Schwalm 2006, 23, 114)

- Propagation

Liquid oligomers and monomers are converted into a solid polymer network. The radicals formed in initiation continue to propagate by a free radical mechanism. The propagation rate depends on the initiation rate and the oligomer reactivity but as viscosity increases the polymerization slows down. Increase of viscosity reduces the chain mobility which affects the polymerization kinetics.

Increase of temperature normally does not affect the propagation rate (system reactivity).

- Termination

In the termination step, most of the growing radicals become deactivated. (Glöckner, Jung, Struck & Studer 2008, 19-21.)

Photoinitiator   UV-light

PHYTOLYSIS

Initiating species   Telechelic oligomer+reactive diluent

INITIATION
PROPAGATION

Growing polymer chain

TERMINATION

Crosslinked network = cured coating
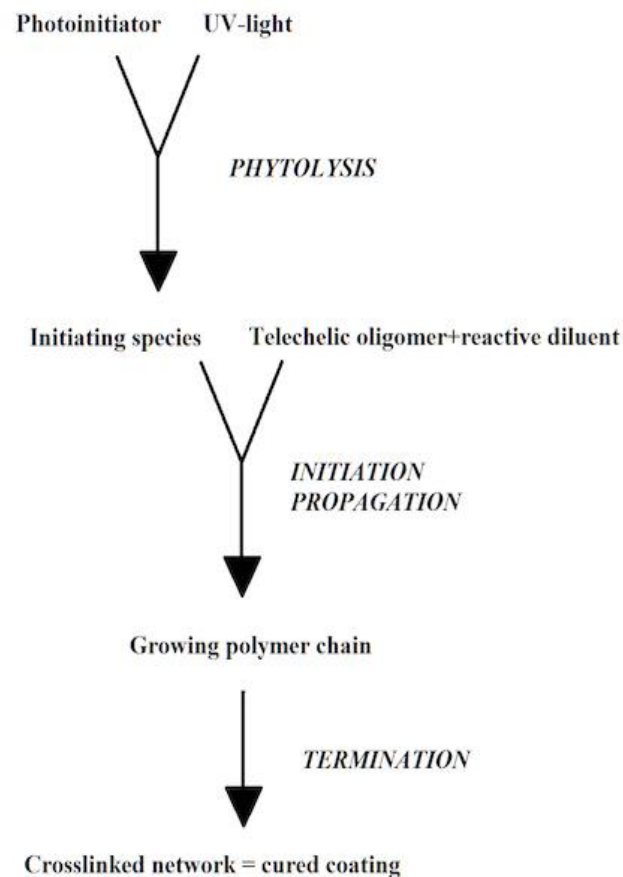
Figure 4. Principle of UV Curing Process (Glöckner, Jung, Struck & Studer 2008, 19)

4.3.2 Electromagnetic Spectrum

UV curing utilize the energy of photons to form reactive species which trigger the curing mechanism. The energy is obtained from radiation sources in the short wavelength region of the electromagnetic spectrum. The UV region of the electromagnetic spectrum mostly used in UV technology include: UV-A, UV-B and UV-C.

Commercial photoinitiator absorption is usually from 230nm (UV-C) up to between 380-400nm (UV-A). Common UV lamps include medium pressure mercury lamps, emitting between 220-580nm. (Glöckner, Jung, Struck & Studer 2008, 19-20.)
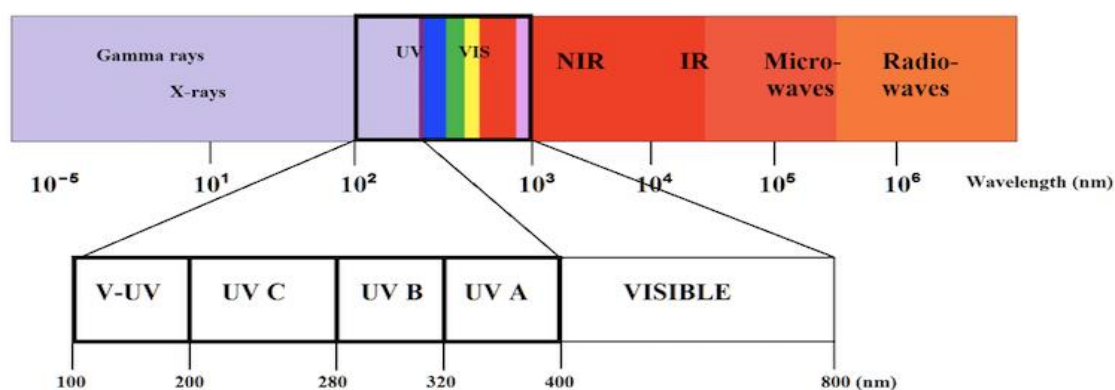
Figure 5. Electromagnetic Energy Spectrum (Schwalm 2006, 7)

Equation for energy content of a photon:

$$E = h\nu = hc/\lambda \qquad (6)$$

ν = frequency

λ = wavelength (nm)

From the equation is can be seen that the shorter the wavelength the higher energy of a photon (Schwalm 2006, 7).

4.3.3 Components

The use of acrylate oligomers and monomers and in free radical curing of inks and coatings is the most popular chemistry used in both UV and EB technology. The chemical structure of the oligomers and monomers decide the properties of formulation (before and after curing). It is important to understand the chemical structures of the materials used in order to predict properties such as reactivity, viscosity, chemi-

cal resistance, flexibility, adhesion and weathering as well as cost. (Arceneaux & Willard, 1.)

UV-curable formulation comprises of the following components:

- Oligomer (binders, resin)

Impart basic performance properties including adhesion range and flexibility.

Contain polymerizable groups and comprise the major part of formulation, usually between 50-80% and are therefore responsible for the main properties of the formulation and cured film. Oligomers have low molecular weights as solvents are not present, ensuring that the formulation has low viscosity.

In free radical curing the reactive groups (oligomers) include acrylates, unsaturated polyester/styrene resins and thiol-enes.

- Monomer (reactive diluent)

The main function is providing viscosity to inks or coatings. Monomers are the alternative to solvents and reduce the formulation viscosity. Monomers make up and between 0-50% of formulation and copolymerizes with binder and becomes integrated into the polymer matrix during curing.

- Additives

Includes light stabilizers, levelling agents and pigments, used to impart properties such as colour, durability to final material or facilitate the process.

- Pigments

Imparts the correct colour.

- Photoinitiator

Makes sure that the curing is achieved. Depending on the application, the photoinitiator concentration usually range between 0.5-8 wt%. When exposed to light, radical photoinitiator produce free radicals (Glöckner, Jung, Struck & Studer 2008, 17-19, 30; Idacavage 2012; Website of Xaar plc 2015).
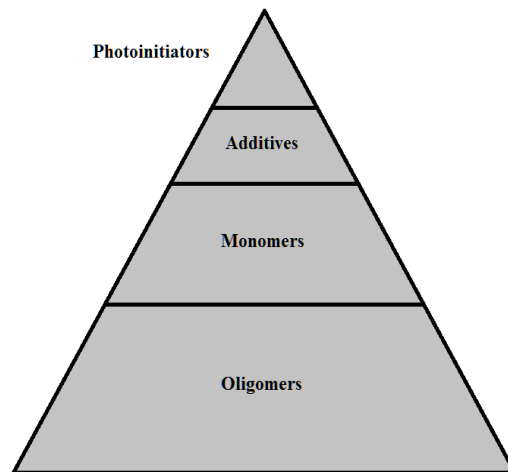
Figure 6. Formulation of UV System (Idacavage 2012)

4.3.4 Oligomers

Free radical curable binders include:

- Acrylate

Acrylate functional oligomers and monomers dominates the UV curing market due to excellent performance regarding cure speed and final properties such as mechanical properties and weathering resistance.

- Unsaturated Polyester/Styrene (UPE) Resins

The second category of binders include low cost unsaturated polyester/styrene resins which used in wood applications despite worse properties over acrylates such as:

- decreased curing speed
- volatility of components (styrene)
- highly oxygen inhibited

- Thiol-ene

The third type of UV-curable systems is Thiol-ene formulations. (Glöckner, Jung, Struck & Studer 2008, 20-21.)

Oligomer types:

- Methacrylates
- Epoxies
- Aliphatic Urethanes
- Aromatic Urethane
- Polyesters
- Acrylics
- Specialty Resin

4.3.5 Monomers

Acrylate monomers serve as diluents for acrylate oligomers to achieve desired ink and coating viscosities for the application. The monomers co-polymerize with the acrylate oligomers forming an integral part of the cured ink or coating as well as influencing the coating performance. Also, the monomer functionality influences the properties of the cured coating. Types of acrylate monomers include mono- di- tri- and multifunctional.

Table 6. Acrylate Monomers Types and Performance (Arceneaux & Willard, 3-4)

Type of Monomer	Performance
Monofunctional	Reduced crosslinking, decreased shrinkage, increased adhesion, great reduction of viscosity, may increase uncured residual material, decrease chemical resistance and reactivity
Difunctional	Good compromise between flexibility, hardness, reduction of viscosity, chemical resistance and reactivity
Trifunctional & higher (multifunctional)	Increased crosslinking, reactivity, hardness, chemical and scratch resistance, not so effective in viscosity reduction

4.3.6 Photoinitiators

Photoinitiators are chemicals that generate radical species when exposed to UV light. Photoinitiators are a crucial part of UV-curable inks and coatings formulation for polymerization reaction to take place. The amount of photoinitator needed in the ink or coating formulation depend on the UV light source, film thickness and the coating/ink properties.

There are two main types of photoinitiators for free radical curing, type I and type II. Type I photoinitiators undergo cleavage upon irradiation and generate two radicals, of which one is reactive and initiate polymerization. Upon irradiation, type II photoinitiators form an excited state and abstract an atom/electron from a donor molecule (synergist) who then acts as an initiating species for the polymerization. (Arceneaux & Willard, 4-5.) More information under heading 7.4.4.

Different photoinitiator absorb UV light at different wavelengths, as different lamps emit energy in different parts of the spectrum. To achieve highest efficiency match λ_{max} (peak absorbance: the wavelength photoinitiator absorb most energy) with UV output of lamp (Idacavage 2012).

4.4 Curing Influencing Parameters

Parameters influencing initiation rate and curing efficiency in free radical UV curing.

- Quantum yield of photoinitiator

Parameter describing the amount of generated initiating species per absorbed photon.

- Increasing photoinitiator concentration

Increasing the concentration of photoinitiator usually promote the curing process.

- High light intensity

Generates relevant number of initiating species simultaneously, improving the curing speed. Increasing the light intensity over a certain limit will not affect the cure speed.

- Oxygen inhibition

Low concentration of photoinitiator and light intensity promotes oxygen inhibition which limits initiation efficiency and polymerization reaction. Solution is to perform curing process under inert atmosphere (N_2). (Glöckner, Jung, Struck & Studer 2008, 20.)

4.5 Advantages and Disadvantages

- Advantages
- Ultra-fast drying (hardening): a fraction of a second in room temperature.
- Low energy consumption, making the technology "green".
- UV equipment is space friendly compared to e.g. ovens for thermal curing.
- Easily controlled reaction: UV light initiates the curing process, and as light is removed polymerization stops.
- Volatile solvents (VOC's) are not needed for adjusting the viscosity, instead reactive diluents (low VOC) used for this purpose are included in the polymer matrix.
- Absent from UV light, formulations do not have a pot life and remain stable for months or longer. (Glöckner, Jung, Struck & Studer 2008, 21.)

- Disadvantages
- Oxygen inhibition
  Oxygen may inhibit free radical UV curing due to: Irradiating conditions (short exposure in low light intensity with small amount of photoinitiator) generating a low amount of radicals, curing of thin layers when oxygen efficiently diffuses into the formulation. These causes leads to tacky surfaces or poor performance of the materials. Curing under inert (N_2) conditions is a solution to the issue.

- Low adhesion on substrates that are non-swelling such as metal and some plastics.
- Curing on flexible surfaces can lead to volume shrinkage of acrylates during polymerization, affecting the film/substrate adhesion.

- Some fillers such as pigments can act as reflectors/light-absorbers preventing light from reaching deeper layers and limiting the cured thickness to max 100 micrometres (μm), using special photoinitiators.
- The film remain liquid in shadowy areas of the substrate in UV curing of three-dimensional substrates. There are some solutions such as special lamps or new UV curing technologies "Plasma Cure" can be a solution when curing in shadow areas. (Glöckner, Jung, Struck & Studer 2008, 22.)

5 UV-CURABLE INKS

5.1 Applications

UV-curable inks first arose in the 1960's and raw materials at this time were quite limited. The inks caused skin rashes with people who worked with them. In the late 1970's and early 1980's, better and less toxic formulations became available due to increased availability of raw materials. UV-inks were also able to adhere, not only to paper but to different plastics. Since then UV-inks have been favoured to solvent-based inks in plastic substrates.

Applications include bottle printing (packaging of liquids), CD/DVD, decal and label, membrane overlays (automobile dashboards, electronic equipment, household appliances) and plastic card printing (Purcell 2012, 5-7).

UV-curable inks are most commonly applied in commercial screen, lithographic (offset) and letterpress/flexographic printing and are popular because of the fast curing, low VOC's, high gloss and good chemical and rub resistance. The use of UV-curable systems in package printing can be divided into two categories: food packaging and non-food packaging. UV-curable inks and coatings in non-food packaging is uncritical unlike in food packaging when the total amount of migratables must be below <60 mg/kg. The photoinitiators or resides of photoinitiators add to the quantity of extractable and need to be carefully selected (Schwalm 2006, 202-203).

UV-curable inks and printing systems can print on almost any kind of substrate and are engineered for indoor applications compared to solvent printing systems that are mostly designed for outdoor applications. This also leads to UV printing systems and inks to print with higher quality due to the shorter viewing distance compared to outdoor prints (Hewlett-Packard Development Company, L.P. 2013, 5).

5.2 Process

Binders (monomers, oligomers) **Pigments** **Photoinitiator** **Free radicals**
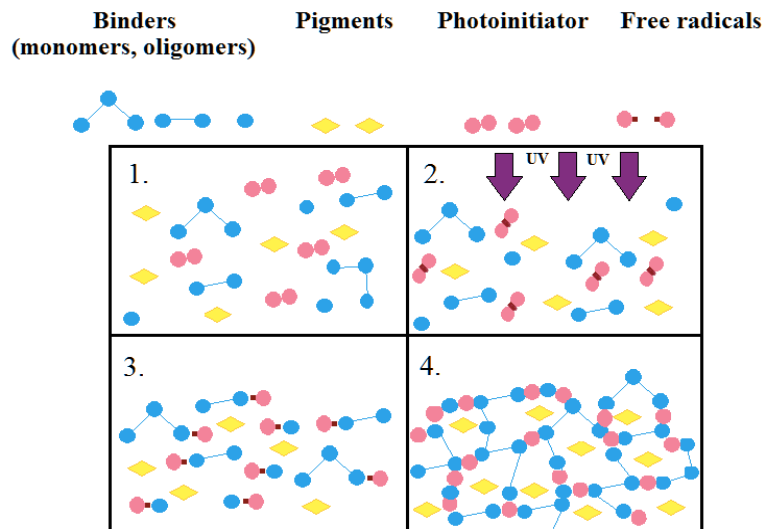
Figure 7. Free Radical UV Curing Ink Process

Step 1. Non polymerized ink liquid.

Step 2. Ink is exposed to UV radiation, which activates photoinitiators present in the ink which is still liquid.

Step 3. Photoinitiators generate free radicals, chain reaction begins (polymerization) and the ink begins to harden.

Step 4. The ink is cured and hardened. At the end of reaction, a solid network is formed integrating the pigment. (Website of Brancher 2015)

5.3 Components and Formulation

Formulations of UV inks comprise of a resin/combination of resins, monomers, photoinitiators, pigments, stabilizers, flow agents and viscosity modifiers (Purcell 2012, 10).

Table 7. Typical UV Printing Ink Formulation (Purcell 2012, 11, 13; Schwalm 2006, 144)

Component	Share	Function
Oligomers (resins)	15-30%	Formation of film, performance properties, back-bone of the ink system.
Monomers (reactive diluent)	30-50%	Formation of film, adjustment of viscosity, liquid part of the ink system dissolving resins and pigments into a viscosity which is printable. Monomers need to complement the selected resins in order to provide necessary properties e.g. hardness and flexibility.
Pigments	5-10%	Formation of colour image Titanium dioxide is used for white inks and carbon black for black inks. Pigments are selected based specifications of the end-use of the ink film, including thermal stability, weather stability, particle size and solubility into the formula.
Photoinitators	1-5%	Photoinitiators absorbs the UV light from the curing unit and initiates the curing.
Stabilizers	0.5-2%	To prevent premature cross-linking (gelling), stabilizers are added to the ink formulation. Stabilizers also provide shelf stability of the ink system.
Flow agents	0.5-1%	Flow agents are added to the ink system in order for the print to appear smoothly, making the ink surface free from defects.
Viscosity modifiers	0.5-3%	Viscosity modifiers are powders that are used to change the viscosity of the

		formulation as ink formulas may need to be runny or heavy, depending on the printing technology.

5.4 Formulation of UV Flexographic Ink

Below are tables of typical formulation of white UV flexographic ink and as well as a starting point formulation.

Table 8. Formulation of White UV Flexographic Ink (Allnex 2014)

Component	Share
Mono/Oligomers	70-75%
Pigments	12-18%
Photoinitiators	7-9%
Additives	1-2%

Table 9. Starting Point Formulation for White Flexographic Ink (Allnex 2014; Website of Flexo Tech 2015)

Ink Preparation	WHITE
EBECRYL®571 / DPGDA (75/25)	39
Florstab UV-1 (Kromachem)	1
Solsperse 32000	1
EBECRYL 7100	15
TPO	3.5
TiO_2	40
EBECRYL 350	0.5

5.5 Advantages

Advantages for printing with UV inks instead of solvent based inks include:

- Low VOC's
- UV-curable inks usually do not usually emit VOC's and can reduce/avoid the need for costly air permits.

- Higher production speed
- UV-inks only require less than a second of exposure of UV light enabling printers to work at high speed compared to solvent printers.

- Reduced drying cost
- No energy draining drying equipment are needed which saves in floor space, capital investment and energy costs.

- Ink consumption reduction
- UV-curable inks have a higher liter price than solvent inks but usually far less ink is required due to their low viscosity and as there is no penetration into the media.

- Reduced waste
- UV inks allows for direct printing on rigid substrates which eliminates for printing of flexible media and then sticking onto the rigid media. Direct rigid printing reduces waste as well as simplifies workflow. Solvent inks are only to be used with flexible media.

- Intense colour
- UV-curable inks are not absorbed into the media and enables a more vibrant intense colour on the surface of the printed media (Hewlett-Packard Development Company, L.P. 2013, 5).

5.6 Challenges

5.6.1 Mercury Vapor Curing Lamps

One major challenge regarding UV curing of inks could be developments of alternatives to the conventional mercury vapour curing lamps, as European Union regulations has classified mercury as a hazardous substance. Therefore, the use of mercury in electrical and electronic equipment should be phased out and be replaced with new technologies, such as UV curing of inks and varnishes with light emitting diodes (LED's). This requires changes in ink formulations although using LED equipment offer ecological benefits over conventional curing systems, as it achieves significant cuts in energy consumption. (Website of Ink Work Magazine 2015)

5.6.2 Yellowing, Absorption and Scattering of Titanium Dioxide

The main problem of using TiO_2 pigment in UV-curable inks is the capability of the pigment to scatter and absorb light, which may lead to little UV light to be used by the photoinitiators. Photoinitiators that have broad absorption spectrums (e.g. thioxanthones) can deal with the limited light available. However, as these photoinitiators absorb light at the blue end of the visible spectrum, they cause a yellowish colour to the coating. The best photoinitiators to use with TiO_2 are the phosphine oxides due to their broad absorption spectra and the ability of photo-bleach (loose colour) upon curing, unlike the thioxanthones. Photo-bleaching promotes through-cure.

Commercially available phosphine oxide photoinitiators:
  - TPO
  - TPO-L (a liquid product)
  - BAPO (Omnirad 380) (IMG Resins 2015)

5.7   Innovations

5.7.1 Self-Curing Acrylate Resins

Photoinitiators with low molecular weight (200-250 Dalton) have been able to migrate to food and improvements have been made to increase safety of UV-curable inks and varnishes with the development of polymeric photoinitiators. The polymeric photoinitiators molecular weights are usually 700 Dalton or more. By increasing the polymeric photoinitiators molecular weight, the risk of migration becomes reduced. Disadvantages of polymeric photoinitiators include poor solubility in acrylates, reduction of ink flow which causes problems with the ink transfer and low reactivity which results in reduced printing speed. (Gevaert, Botreau, Cahen & Heylen 2014.)

Allnex, manufacture of inks for indirect food packaging applications, have introduced a solution to the concern of migration of low molecular weight photoinitiators, highly reactive self-curing acrylate resin for low migration inks and coatings, without the need for additional photoinitiators. The raw materials used in the resins are very pure and of high quality. Upon UV irradiation, the resins generate free radicals without formation of by-products and upon curing, are bound into the matrix of the film, which reduces the risk of migration.

- o EBECRYL® LEO 10101; optimal for overprint varnishes and flexographic inks
- o EBECRYL® LEO 10102; for lithographic (offset) printing (Website of Allnex 2015)

6 INK PRINTING PROCESSES

Below is a description of the printing processes including gravure, flexography/letterpress, screen-printing, lithography (offset) and inkjet.

6.1 Gravure

The image is produced by series areas of pitched cells. These are formed with an etching needle in the top layer of a steel cylinder made of copper. The ink is delivered/transported to the pitches and then transferred to the printing stock. Due to the high cylinder costs, the process is not appealing for general printing purposes, instead it is the ultimate process for fine line printing such as magazines and catalogues, due to the precise control over process dots (Schwalm 2006, 200).

6.2 Flexography/letterpress

Flexography is the major printing method used for printing packaging materials such as folding cartons, plastic bags, paper sacks, milk and beverage cartons, disposable cups and containers, labels, adhesive tapes, envelopes, newspapers and candy- and food wrappers. (Website of Printer's National Environmental Assistance Center 2015)

The printing plates in flexography and letterpress are produced via image-wise exposure of photopolymer plate where the unexposed parts are washed away while the exposed parts become hard relief pattern, although softer pattern are produced in flexographic printing plate. The ink becomes transported from the constructed pattern to the substrate (Schwalm 2006, 201).

Both flexographic and letterpress plates are produced utilizing a relief type plate (plates with raised images). Only the raised images come in contact with the substrate during printing. Flexographic plates are made of flexible material including plastic, rubber or UV sensitive polymer (photopolymer), in order to become attached to a roller or cylinder for ink application. (Website of Printer's National Environmental Assistance Center 2015)

The use UV-inks in flexographic printing applications are increasing steadily and reasons for the growth rate include:

- low viscous
- 100% solids
- exceptional image sharpness
- excellent end-use properties (capability of achieving rub and chemical resistance)

The consistency of UV flexographic inks does not change during processing, unlike solvent-borne inks which can evaporate, or water-based inks where the pH changes.

The disadvantages of using UV flexographic inks include:

- higher operating costs
- skin irritability from the UV ink chemistry
- adhesion problems (some polymeric substrates)
- cost and heating related with the use of UV lamps units

Formulations for UV flexographic inks include epoxy acrylate resins or blends of epoxy and urethane acrylates with the viscosity in the range of 300–500 mPa·s (Schwalm 2006, 203).

6.3 Screen-printing

The process of screen-printing includes an image being produced on a metal screen where the nonprinting pores are blocked with waxes or coatings. With the help of a doctor blade or flexible squeegee, the ink is pressed through the open meshes of the screen. A wide range of substrates can be used such as plastics, paper and textiles, making screen-printing the most versatile of all the printing processes. Screen-printing can print on substrates of any size, shape and thickness, which is a great advantage over the other printing processes. Typical screen-printing products include posters, labels and decals (sticker). Advantages of screen-printing include low cost and fast fabrication of the screen image and achievability of high colour strength and high gloss (Schwalm 2006, 201, 203).

The largest printing application is UV inks for screen printing, which allows for printing on many types of substrates such as paper, textiles, plastics, leather, wood, metals, wood and ceramics. Main applications include labels, signs, book covers, decals and optical disks (CD, DVD). Advantages include high colour strength, high gloss and quick fabrication of the screen image (Schwalm 2006, 203).

6.4 Lithography/offset

Lithography is an "offset" printing technique where the ink is applied to the printing plate to form the "image" and then becomes transferred or "offset" to a rubber blanket. The image on the blanket is then transferred to the substrate that produce the printed product. (Website of Printers' National Environmental Assistance Center 2015)

Lithographic/offset printing uses hydrophilic oxidized aluminum plates. The image areas are hydrophobic and the hydrophilic areas are wetted with water to repel the hydrophobic usually oil-based ink. The ink is then transferred from the plate to a rubber cylinder and then to the substrate.

Advantages include:
- low cost
- high reactivity
- high gloss
- good wetting behavior of the ink (Schwalm 2006, 2003-204)

Offset is the largest printing application although UV offset only have a small share.

6.5 Inkjet

Inkjet technology enable for non-contact printing, where tiny ink droplets are used to facilitate direct printing without contact between the device and the printed surface.

As inkjet technology allows for non-contact printing, all kinds of substrates can be used. The technology consists of a simple structure, which combine the inkjet print

head with the scanning mechanism. This allows for keeping device costs down. Moreover, inkjet printers require no plates, offering savings in printing set up time compared to conventional printing systems requiring fixed printing block or plate.

The technology can be widely used in fields ranging from general purpose to industrial. Applications of inkjet includes printing of textiles, laminates and furniture, glass, ceramic walls, floor tiles, paper and vinyl wall coverings. (Website of Xennia 2015)

UV inkjet inks dries to 100% solids without releasing VOC's or flammable solvents. UV inkjet inks have the capability to adhere to various substrates and have less maintenance and issues caused by ink jetting which result in overall reliability of the inkjet printing system. The inks are more durable and resistant to external wiping and cleaning by solvents used in various graphics and industrial uses. (Website of Radtech 2015)

7 UV-CURABLE COATINGS

7.1 Function and Application

The surface of UV coatings is exposed to both mechanical and chemical stresses, the primary functions of coatings are to provide a protective barrier against scratching, corrosion, stone chipping, UV radiation, abrasion or against chemical attacks such as red wine/coffee on furniture coatings, acid rain and bird excrement on automotive coatings, and to provide desirable appearance such as colour and gloss.

Due to environmental concern of the use of solvents and VOC regulations, the share of conventional solvent-based coatings (containing 50-70% solvents) are significantly declining and more environmentally friendly systems are steadily increasing, in particular water-based, powder and radiation (UV/EB) curable coatings. UV-curable coatings are usually 100% liquids, also referred to 100% solids although the formulation is in liquid form, meaning that it contains no VOC's (solvents/other volatiles). However, small amounts of solvents are used in UV-curable water-based formulations and UV-powder, to reduce the viscosity.

UV-curable coatings are widely used and exist nearly everywhere around us in our daily lives. The UV coatings market is increasing to applications where traditional thermal curing systems have been utilized. UV coatings are commonly used on heat-sensitive substrates, including paper, wood and plastics. Clear coats can e.g. be used for parquets, vinyl flooring, furniture, on plastic substrates, headlight lenses and overprint varnishes (high gloss packaging, posters) and electronic parts. UV coatings are also used on metals (automotive, coil coating), bikes and appliances (washing machines, refrigerator and cars).
Applications include adhesives and protective coatings for CD, DVD, glass fiber wires, in- and outside of beverage cans and on electronic parts.

Table 10. Coating Technologies Advantages and Disadvantages (Schwalm 2006, 1-4)

Coating Type	Advantages	Limitations
High Solids	Excellent properties Ease of handling High comfort factor and familiarity from years working with solvent-based coatings	Contain solvents Long curing time
Waterborne	Low VOC's Wide range of properties chemistries and application techniques	Weak chemical resistance (lack of performance in environment due to humidity sensitivity) Difficulties in drying Foaming
Powder	100% solids Nearly environmentally ideal	Expensive Long curing time Orange peel structure
Radiation curing (UV/EB)	100% solids Reduced: energy consumption, emissions, investment costs and space requirements	Costly raw materials Oxygen inhibition Difficulties of curing in pigmented coatings and shadow areas

7.2 Process

The substrate is first coated and then becomes exposed to intense radiation as it passes UV lamp units, and within a fraction of a second the liquid is transferred into a completely dry and cured solid crosslinked network, ready for immediate processing.

The technology of UV curing is based on photo initiated transformation of a reactive liquid formulation into a solid crosslinked coating film. The initiating species can be an anion, a cation or a radical. The majority of UV-curable coatings include radical producing photoinitiators. This text will focus on radical polymerization.
The main components of radical polymerization include reactive resins, monomeric diluents and photoinitiators.

UV induced radically initiated crosslinking can be divided into three steps: initiation, propagation and termination (Schwalm 2006, 9, 22-24). See heading 4.3.1 for more on the process.
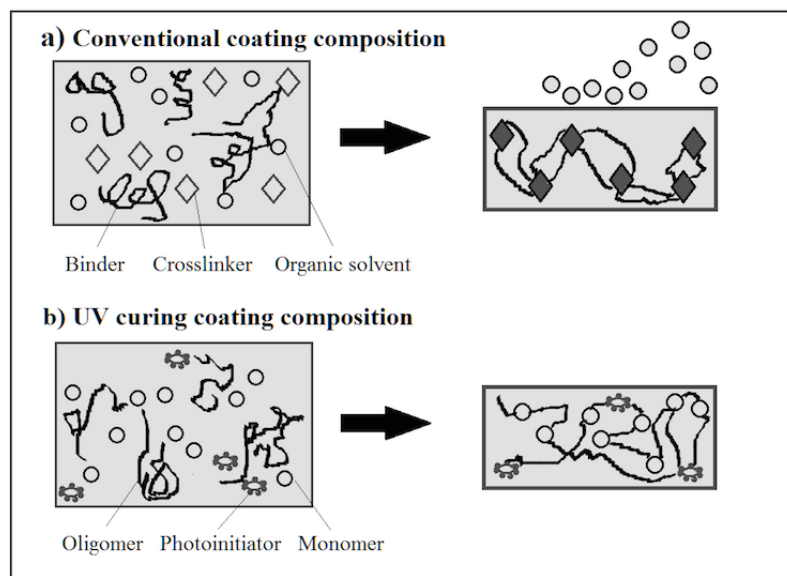

Figure 8. Differences Between Conventional and UV-Curable Coatings

a) Curing of conventional coating. The film emits organic solvents during crosslinking and drying.

b) UV-curable coating crosslinking without emitting organic solvents. (Glöckner, Jung, Struck & Studer 2008, 12.)

7.2.1 Parameters

The application determines the type of substrate and required properties. The required properties determine formulation chemistry which in turn determine the equipment set-up.

The function of the coating (e.g. protection against scratches, chemical attacks, deterioration caused by weather conditions) determines the type and property requirements of the coating, and thickness. The coating's chemical formulation must provide the desired properties, such as scratch/chemical resistance, colour effects, hard-

ness, high gloss and flexibility. These chemical components (resins, reactive diluents, photoinitiators, additives) need to be properly selected for the curing process to be effective. It is also important to match the chemistry of the coating with the characteristics of the lamp system for the curing to be economic, an important factor of the coating process, which determine over the kind of coating to be used. Therefore, when calculating the total costs of a coating process it is necessary to consider the whole process design and equipment set-up and not only material costs.

o Example

If a coating contains pigments, a photoinitiator capable of absorbing at longer wavelengths need to be chosen. The lamp system should be chosen capable of emitting in the longer wavelength range. The required coatings properties decide the chemistry. The exposure equipment and photochemistry must then be adjusted in order to achieve the desired coating properties.

Application

The end-product determines: substrate, purpose and performance of the coating, application method, film thickness and process speed

Equipment
-UV energy
-Irradiance
-Spectral wavelength distribution
-IR radiation
-Cure speed (nr of lamps)
-Cure atmosphere (air, inert)

Chemistry
-Formulation determines physical properties
-Selection of components: resins, diluents, PI's and additives
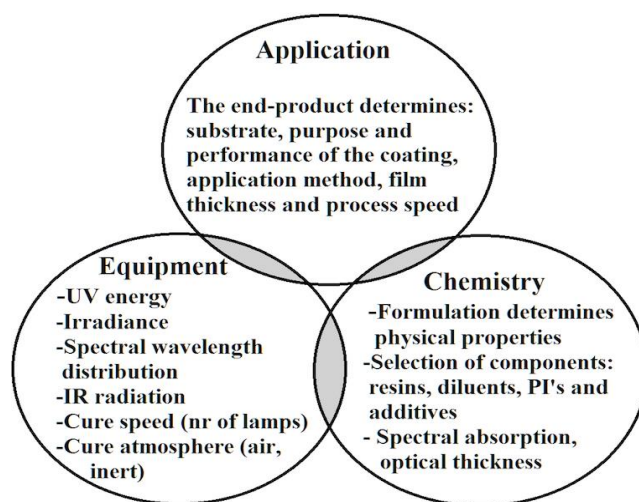- Spectral absorption, optical thickness

Figure 9. Relation Between UV Process Parameters (Schwalm 2006, 21)

The required coating properties determine the chemistry to be used, and the chemistry and the equipment need to be adjusted in order to achieve the target properties in an efficient cure process (Schwalm 2006, 19-21).

7.2.2 Kinetics

Equation for rate of polymerization (r_p):

$$r_p = k_p \,/(2k_t)^{0.5} \, [M_0] \, r_i^{0.5} \tag{7}$$

k_p = rate constant of polymerization

k_t = rate constant of termination

$[M_0]$ = monomer concentration

r_i = initiation rate

Equation for rate of initiation (r_i):

$$r_i = \Phi_i \, I_a \tag{8}$$

r_i = rate of initiation

Φ_i = quantum yield of initiation (Quantum yield of initiation= number of growing chains per photon absorbed)

I_a = irradiance absorbed

Equation for photoinitiatior concentration [PI]:

$$r_i = \Phi_i \, I_0 \, (1 - e^{-2.3[PI]\varepsilon}) \, A/V \tag{9}$$

I_0 = incident irradiance

ε = PI extinction coefficient

l = sample thickness

A = exposed area

V = exposure volume (Schwalm 2006, 22-27)

7.2.3 Coating Application Process

Applying UV coating to the substrate is usually performed in automated processes, including:

1. Roll- and curtain coaters: for flat-panel production with typical viscosity range of <4000 mPa·s.

2. Spray guns (conventional or airless): for three-dimensional/shaped objects with viscosities less than 500 mPa·s.

3. Vacuum coaters

4. Electrostatic (Schwalm 2006, 37)

7.3   Equipment

The equipment in UV curing line for coatings include:

- One/multiple UV lamps, with integrated exhaust removal of ozone/VOC's produced during exposure
- Lamp housings and reflectors (redirects the lights to the curing target area)
- Power supply and electric or electronic control
- Shielding and cooling unit for lamp and substrate
- Conveyor belt, a transportation unit for substrates such as conveyor belt and printer
- Auxiliary parts (Schwalm 2006, 44, 56)

7.3.1 UV Lamps

Important factors of UV-curable lamps include irradiance (W/cm^2), which is the radiant power at the curing surface area from all angles, as well as from the installed

reflectors who redirect the light to the curing area. The arriving irradiation at the surface area is dependent on the distance of the lamp (Schwalm 2006, 30-40).

The second important factor is curing time or curing speed, which is determined by the velocity of the conveyor belt. The curing speed influences the heat applied on the coating surface so the heat evolution of the lamp should be considered since (depending on the substrate and coating system) the emitted IR could be harmful to plastic substrate that may get ruined, or it could be useful in heating the coating and increase the crosslinking conversion.

1. Mercury Lamps

Most commonly used UV lamps include medium pressure mercury (Hg) vapor arc lamps, operating in the range of 1bar and 80W/cm, and low pressure lamps at 10^{-6} bar and 12W/cm emitting in the wavelength of 185 and 254nm. Mercury is used in UV systems since 35% of the radiation is emitted in the UV range.

The mercury is enclosed inside a quartz tube which becomes excited by electrodes (arcs) or microwaves. Due to degradation of the electrodes and fogging on the quartz walls, output of the bulbs is reduced after 1000-2000 h.

1.1 Microwave Powered Mercury Lamps

Microwave powered mercury lamps are of the medium pressure mercury vapor type but are operated by microwaves that excites the mercury to emit the wavelength of the mercury lamp. The operation lifespan is between 5000-8000 h without spectral energy output changes.

2. Excimer Lamps

The main advantage with excimer lamps is they do not warm up the substrate therefore are used in printing applications reducing smell and no warping of the printed product. Excimer lamps emit only at a specific wavelength.

3. Light Emitting Diodes (LED) Based Light Sources

Emit in the UV region and include advantages such as portability, low heat production and low power consumption.

It is important to select photoinitiator based on their absorption with the peak wavelength of the lamp source in order to achieve maximum conversion of light into for-

mation of radicals that start the polymerization. If there are other light absorbing components present in the formulation such as pigments or light stabilizers that compete with the photoinitiator of the light. For this purpose, lamps are used that are able to provide enough energy and absorption at wavelengths outside of the absorption of pigments and light stabilizers. The emission spectrum of the mercury lamp is altered by adding halides of other metals (iron, gallium). Iron contain additional longer wavelength absorption in the range between 350-400nm, which is in the UV-A range. These lamps are used when the additives of the formulation absorb strongly in the UV-C range, such as UV-absorbers and longer wavelength ranges are needed for the photoinitiators. Indium and Gallium are in further spectral wavelength range of 400-450nm and are used in pigmented formulations. These doped (metal halide modified) mercury lamps have electric inputs between 80-200W/cm (Schwalm 2006, 45-47).

7.3.2 Reflectors

Reflectors are used to redirect the emitted light to the right direction, i.e. the targeted curing area (coating surface), since light is emitted in all directions by the UV lamp. Reflectors with a good design may collect and redirect 75% of the radiant energy (Joules, J) onto the coating from the build. Parabolic reflectors can only collect approximately 55%. Since the reflectors mostly consist of aluminium, infrared radiation (IR) which can lead to unwanted heating of the substrate. This have led to development of reflectors able to reflect UV radiation but not IR or visible radiation.

Selection of an appropriate UV lamp type relies on the matching the photoinitiator absorption and lamp spectrum. The effective energy on the surface can also be optimized factors such as reflector design (Schwalm 2006, 48-49).

7.4 Raw Materials (Radical Polymerization)

The raw materials in UV coatings formulations comprise of low molecular weight resins, usually with molecular weights (M) in the range between 300–5000g/mol.

Majority of the resins have too high viscosity and are therefore diluted with reactive diluents to adjust the viscosity. The most commonly used reactive diluents include mono- or multifunctional acrylates.

Photoinitiators make sure the curing reaction is effective. Radically polymerizable photoinitiators generate radicals which add to unsaturated double bonds. These are essential raw materials for UV-curable formulation. In addition, additives are used in the formulations (Schwalm 2006, 94-97).

- Oligomers

Oligomers (also known as pre polymers, resins, binders) are the main components of the formulation and responsible for the main properties of the formulation and cured film. Oligomers have low molecular weights as volatile solvents are not presents in the formulation (compared to binders in conventional systems), leading to low formulation viscosities.

- Monomers

Monomers (reactive solvents, diluents) reduce the viscosity of the formulation and are the alternative of solvents, and become incorporated into the film during exposure of light and impacts on the physical properties of the cured film.

- Additives

Additives are used to improve properties: substrate wetting, leveling, slip and scrap resistance, deaeration and defoaming. (Glöckner, Jung, Struck & Studer 2008, 30.)

- surfactants
- defoamers
- leveling agents
- flexibilizers
- flow regulators
- pigments (printing inks)
- UV stabilizers (HALS and UV absorbers type radical scavengers), or fillers (clay, silica, calcium carbonate).

    The main function of UV absorbers is to protect the coating (both clear coats and underlying coat) from detrimental solar UV radiation which can lead to degradation and discoloration, by absorbing UV light and convert it into heat

which is dissipated through the surface of the coating. Radical scavengers of the Hindered Amine Light Stabilizers (HALS) type prevent oxidative degradation of the top layer. Instead of absorbing radiation, they protect the coating resin from the detrimental effect of free radicals by neutralizing them and hindering chemical degradation. HALS regenerates during the neutralization process and provide long-term protection of the coating.

- nanoparticles

  Obtain increased scratch resistance. (Schwalm 2006, 94-97, 227; Website of Interlux 2015.)

- Photoinitiators

Photoinitiator molecules generate reactive species upon irradiation (UV light) when they reach an excited state which initiates polymerization of oligomer and monomer. (Glöckner, Jung, Struck & Studer 2008, 31.)

The most used resins are radically polymerizable acrylates and unsaturated polyesters. Thiol-ene systems are insensitive against oxygen inhibition, but are only used in some niche applications.

Table 11. Common Characteristics for UV Raw Materials (Schwalm 2006, 126)

Oligomeric resins	Diluents	Photoinitiators
Functionality	Viscosity	Absorbance spectrum
Viscosity	Density	Appearance
Density	Colour	Melting point
Molar mass	Molar mass	Solubility
Colour	Acid value	
Hydroxyl value		
Acid value		

7.4.1 Composition of Formulation

The coating formulation depend on the coating requirements and since the application field is wide, the requirements of the coating properties vary greatly which means that formulations differ in chemistry and composition.

Generally, UV-curable coatings formulations comprise of: 25–90% oligomeric resins, 15–60% reactive diluents, 0.5–8% photoinitiators, 1–5% additives (levelling agents, defoamers, and possibly pigments, fillers and matting agents (Schwalm 2006, 140).

Table 12. Composition of UV-Curable Coating

Typical composition of UV-curable coating and function of components (Schwalm 2006, 9-15, 140).

Component and share (%)	Function
Oligomeric resin **25-90%**	Film formation, basic coating properties
Reactive diluents **15-60%** (Monomers)	Adjusting viscosity (instead of solvents) Film formation (low weight molecular compound incorporated into polymer network)
Photoinitiator **0.5-8%**	Initiation of the curing
Additives **1-50%**	Surfactants, fillers, pigments, UV absorbers, stabilisers, levelling agents, radical scavengers, etc., Tailor the coating formulation after coating property requirements and application

7.4.2 Resin Types

- Acrylates
- Epoxy acrylates
- Polyester acrylates
- Urethane acrylates
- Polyether acrylates
- Acrylated polyacrylates
- Acrylated oils

- Unsaturated Polyesters
- Poly-ENE-Thiol systems

o Features and Function

Epoxy acrylates are highly reactive and the cured coatings have good chemical stability. Main uses include wood coatings, paper coatings and inks.

Applications of urethane acrylates are mostly on plastics such as PVC floor coverings, wooden parquet, screen inks and optical fibers. Good optical properties and non-yellowing behavior is required for these applications, therefore more than 80% of the used urethane acrylates are based on aliphatic isocyanates.

Low functional urethane acrylates have a high flexibility and are usually based on flexible polyester or polyether diols. Higher functional urethane acrylates are used in hard, scratch and chemical resistant coatings. In addition to good mechanical properties, aliphatic type urethane acrylates include good weather stability (no yellowing when exposed to exterior conditions), hence they are the favored class of resins for exterior applications.

Polyester acrylates are mostly used in wood and paper coatings as well as in inks.

Acrylated polyacrylates include good exterior durability, low colour and good chemical resistance (Schwalm 2006, 97-98, 100-101).

o Properties of Resins (Acrylate Oligomers)

- Epoxy acrylates
  - High viscosity
  - High reactivity
  - Good chemical stability
  - Good cost/performance ratio
  - Yellowing tendencies

- Polyester acrylates
  - Good overall performance
  - Wide variety of flexible or hard resin
  - Low/reduced odour

- Low residual monomers
- Well compatible with other resins

- Urethane acrylates
  - Known for toughness and flexibility
  - Non-yellowing properties
  - High weathering resistance
  - High viscosity
  - Expensive

- Polyether acrylates
  - Low viscosity
  - Used as resins and reactive diluent
  - Highly reactive

- Acrylated polyacrylates
  - High exterior durability
  - Wide variety available

The reason why there are so many resin types is that one resin type itself cannot fulfil the requirements of a coating as they are diverse (Schwalm 2006, 102).

7.4.3 Monomers

In order to adjust the application viscosity, reactive diluents including monomers and oligomeric acrylates are used.

Monomers like styrene, N-vinyl pyrrolidone and mono-functional esters of acrylic acid, belong to the best diluents however their usage is decreasing due to their high volatility, strong odour, skin irritation and flammability. Their mono-functionality results in a better flexibility (higher molecular weight, crosslink density), monomers with lower volatility and odour have been developed, such as isobornyl acrylate or trimethylol propane formal mono-acrylate.

Vinyl ethers have the advantages over acrylates of high diluting power, which is usually better than acrylates as well as lower toxicity (no labelling, no irritancy). The disadvantage is that vinyl ethers do not homo-polymerize radically, therefor in order to avoid unreacted vinyl ether groups in the coating, the content of the vinyl ether reactive diluents should not exceed about 10% in acrylate system (Schwalm 2006, 111-114).

Table 13. Reactive Diluents Types in UV-Curable Systems (Schwalm 2006, 112)

ACRYLATES

Monofunctional	Difunctional	Multifunctional
Isobornyl acrylate (IBOA)	Tripropylene glycol diacrylate (TPGDA)	Trimethylolpropane triacrylate (TMPTA)
Trimethylolpropane-formal-mono-acrylate henoxyethyl acrylate (POEA)	Dipropylene glycol diacrylate (DPGDA)	Propoxylated glycerole triacrylate
	Hexandiol diacrylate (HDDA)	Pentaerythritol triacrylate (PETIA)
	Neopentylglycol diacrylate (NPGDA)	Pentaerythritol tetraacrylate (PT4A)
		Dipentaerythritol penta/hexa acrylate

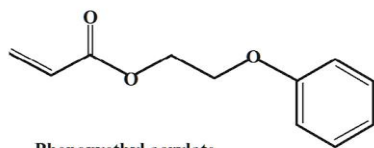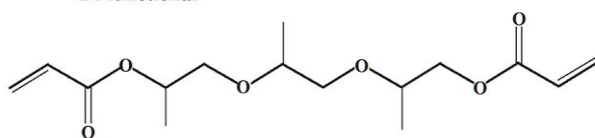| METHACRYLATES	OTHERS
Hydroxypropyl-MA	Styrene
Isobornyl-MA	N-Vinyl caprolactam
Dicyclopentenyl-oxy-ethyl-MA	N-Vinyl pyrrolidone
Hydroxyethyl-MA	N-Vinyl formamid
	Silanes
	Vinyl ethers
	Divinylether of Tripropylenglycol
	Divinylether of cyclohexanedimethanol
	Vinylether capped urethanes

Monofunctional

Phenoxyethyl acrylate

Di-functional

Tripropyleneglycol diacrylate

Multi-functional
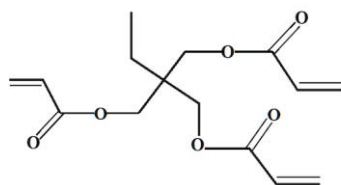
Trimethyolopropan triacrylate

Figure 10. Structure of Some Acrylate Reactive Diluents (Acrylate Monomers) (Schwalm 2006, 113)
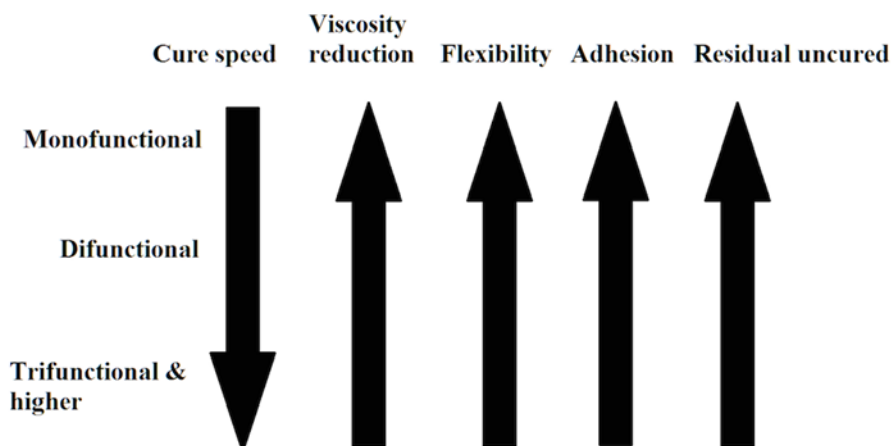
Figure 11. Descriptive Figure Regarding Selection of Acrylate Monomers (Idacavage 2012)

7.4.4 Radical Photoinitiator and Classes

Photoinitiators are molecules that when exposed to light (irradiation) absorb photons and form reactive species in their excited state, which initiate the curing reactions. Radical photoinitiators are by far the most used, representing more than 90% of commercially used initiators (Schwalm 2006, 114).

Short wavelength photoinitiators cure on the surface and longer wavelength photoinitiators cure through deeper thicker layers.

Photoinitiators that are activated by longer wavelengths (absorb UV light in the near visible region over 430nm) are able to penetrate into the deeper layers of the coating. Photoinitiators that absorb in the longer wavelengths are associated with off-white colour, while photoinitators that absorb shorter wavelength provide a clear white colour. Shorter wavelengths around 230nm has higher photon energy but is less penetrating and useful for surface cure.

Selection of photoinitiators or combination of photoinitiators depend on several issues including resin system (unsaturated polyester UPES, epoxy acrylates, urethane acrylates), monomer selection (mono- multifunctional acrylate monomers), lamp

type, desired properties of the coating as well as substrate. (Ciba speciality chemicals Inc., 2)

Most radical photoinitiators include the benzoyl (phenyl–CO–) structure.
Radical photoinitiators should include properties with the most important being:

- Highly absorbent at exposure wavelength
- High yield of formation of initiating species
- Highly reactive radical to the monomer

The most important photoinitiator types include the α-cleavable type (Norrish type I) and the non-cleavable type ("electron transfer-hydrogen abstraction" type II).
The α-cleavage-type are very versatile, exhibiting higher efficiency compared to hydrogen abstraction types and therefor are the most widely used. (Schwalm 2006, 115)
The non-cleavable photoinitiators generate radicals through hydrogen abstraction or electron transfer from a co-initiator (hydrogen donor, amine).

Examples of α-cleavable type photoinitiators (type I):
- Benzoin ethers
- Dialkoxy acetophenones
- Hydroxy alkyl ketones
- Acyl phosphine oxides
- Amino ketones

Examples of non-cleavable type photoinitiators (type II):
- Benzophenones
- Benzyl (1,2 diketones)
- Thioxanthones (Schwalm 2006, 115)

Photoinitiators are usually differentiated according to their absorption profiles (absorption spectra). Typical photoinitiator concentration is the range of 1–5% and commonly 2–3%, in order to overcome the effects of oxygen inhibition. Under inert curing conditions the concentrations of 0.5–1% are enough. The concentration

should not be too high in order to avoid problems of light penetrating the bottom layers which can result in through cure problems.

Photoinitiators should be selected to match the output spectrum of the UV light source. The standard lamps used include medium pressure mercury lamps as they provide high power and emission lines where most of the commercially available photoinitiators absorb (Schwalm 2006, 117).

1. Low Yellowing Photoinitiators

A general problem during photoinitiation is the yellowing and factors contributing include photoinitiators, resins, stabilizers and exposure conditions. Also, the structures of the photoinitiator and photoproducts can cause yellowing. Design of non-yellowing photoinitiators included systems that generate non-absorbing (non-yellowing) photoproducts. The best non-yellowing type of photoinitiator is 1-Hydroxy-cyclohexyl-phenyl-ketone.

One method is based on the photobleaching, by using acyl phosphine oxides, which are yellowish as such but that turns colorless after curing (Schwalm 2006, 118-119).

2. Photoinitiators for Pigmented, UV-Stabilized Coatings and Through Cure (Thicker Coatings)

Photoinitiators of the acyl phosphine oxide type can absorb longer wavelengths (>300 nm) and can be used in pigmented and UV absorber containing films, providing through cure in thicker coatings. The usual concentration of this type of photoinitiators is between 0.5–1% and are often used in combination with hydroxyketone type photoinitiators which provide surface cure while phosphine oxides provide through cure.

3. Low Emission Photoinitiators (Novel Photoinitiators)

A huge concern in the packaging industry is migration of compounds into food, i.e. set-off from components printed on the outside of the packaging material.

If not formulated and processed correctly compounds such as reactive oligomers and photoinitiators may migrate. (Website of European Coatings 2015)

Novel photoinitiators have been developed to prevent odour and migration and are based on a difunctional hydroxyketone (Schwalm 2006, 119).

7.4.5 Additives

The additives used are the same as in classical solvent-based formulations and often tailor made based on requirements of the coating. Additives are needed as the basic components of UV-curable formulations (resins, diluents, photoinitiators) are not enough to produce a satisfactory coating. The quality of the coating is determined by wetting of surface (substrate) or pigments, usually with the help of the solvent, and removal of air, hence additives are used.

Surface active additives:

- Additives for substrate wetting

Reduce tension of coating system. Low molecular weight silicones, hydrocarbon organics or fluorinated surfactants are used in UV-curable systems.

- Additives for surface control

Improve flow, levelling and slip and scratch resistance. Higher molecular weights silicones with polymerizable groups are used as these compounds tend to move to surface improving the slip and scratch resistance.

- Additives for de-aeration

Replace surfactants and stabilize the bubbles by raising and bursting them at the surface. Benzoine is used as de-aeration additive in powder coatings (Schwalm 2006, 125-126).

7.5 Selection of Raw Materials for Exterior Applications

For interior applications, the selection of the raw materials is determined by application segment, required properties and application method without overall general restrictions. However, in UV curing of exterior applications and pigmented systems it is very important to carefully select raw materials and exposure equipment. Pigments absorb in the UV region so the lamp and photoinitiators need to be adjusted to allow for through-curing.

It is important to choose the right raw materials to meet the specific coating requirements. The resins are largely responsible for the basic properties of the coating but selection of reactive diluent, photoinitiators (solubility, absorption) and additives (UV protection) are important as well.

Photoinitiators need to be formulated with complimentary light stabilizers. Using light stabilizers leads to reduced yellowing behavior as well as resulting in greater coatings durability. There is a higher demand on the raw materials for UV-curable exterior applications (tendency of yellowing, climatic conditions, sunlight exposure).

The first step is selecting resins for exterior UV-curable systems that:

- do not consist of chemical structures that can be destroyed by UV light
- tendency under typical weathering conditions to yellowing or cracking

In exterior applications, aromatic systems have a stronger tendency to yellowing and photochemical degradation as they absorb stronger in the UV region. However, the least suitable resins for coatings with regards to thermal stresses are amine modified acrylates, as they have stronger tendency to yellowing than other resins. Acrylates of polyether, polyester and epoxy discolour slightly while urethane acrylate has the best temperature colour fastness (shows the least discolouration) (Schwalm 2006, 133, 150).

In UV coatings for exterior applications sunlight also plays a role as they will be subjected to sunlight radiation (photochemical yellowing). The most durable of all the UV resins which display good colour fastness is the urethane acrylates (Schwalm 2006, 131-135).

A combination of photoinitiators are usually used: standard hydroxyalkyl ketone (HAK) for surface cure and an acylphosphine oxide (APO) type for through-cure.
The exposure lamp should be capable of emitting at longer wavelength, such as gallium or ferric added mercury lamps. The resins must be resistant to weather conditions (oxidative and hydrolytically stable). Suitable resin includes: aliphatic urethane acrylates (UA) or acrylated polyacrylates (APA) in combination with acrylate diluents of hydrocarbon type such as hexane-diol-di-acrylate and decane-diol di acrylate.

The coating need to contain UV absorbers and radical scavengers (HALS type, hindered amine light stabilizer), in order to protect the substrate and coating against discolouration and degradation.

Urethane acrylates are the best raw materials for UV curing for exterior applications (Schwalm 2006, 150,173).

7.6 Disadvantages and Solution of UV System

Three main disadvantages of radically induced UV curing include oxygen inhibition, which retards the curing reaction at the surface and contribute to yellowing (initial yellowing). The third main drawback is related to lack of radical formation in areas (shadow areas) where the light does not penetrate and where curing does not occur (Schwalm, R. 2006, 179).

7.6.1 Oxygen Inhibition

The UV process takes places in atmospheric air conditions. The polymerization reaction may be delayed, or even halted, by the oxygen present in the ambient air. The production of radicals (formed by photoinitiator) is inhibited as the oxygen reacts with the radicals forming peroxide species (RO_2), and hydro-peroxides (RO_2H). This leads to reaction termination i.e. reduction of polymerization, improperly cured surfaces due to incomplete surface network formation, and remaining acrylate bonds.

In presence of air, oxygen reacts with the photoinitiator or propagating radical forming a peroxy-radical, which acts as an inhibitor and retards the acrylate polymerization reaction until all oxygen is consumed. Polymerization in thin films becomes retarded and in thicker films the result is tacky surfaces due to very low acrylate conversions. The layer thickness of the inhibition is dependent on the oxygen diffusion into the coating and diffusivity of oxygen into the coating depends on factors such as the type and polarity of the materials used and the viscosity.

    o   Methods Reducing Oxygen Inhibition

It is possible to overcome the harmful effects of oxygen inhibition. The methods include high irradiance, selection of efficient photoinitiators as well as using high photoinitiator concentrations, selection of highly reactive formulations and addition of additives such as amines or waxes.

The harmful effects of oxygen diffusivity into the coating can also be decreased when:

- Decreasing the concentration of oxygen in the atmosphere
- Increasing the viscosity of formulation
- Decreasing sample temperature

Inhibition of oxygen in acrylate based formulations depend on the concentration and type of the photoinitiators used, formulation reactivity and irradiance.
The methods which reduces the inhibition effect of oxygen include both physical and chemical methods.

    1.   Physical Methods

    1.1 Increased UV-radiation (high irradiance)
By using high irradiance and the amount of free radical's increases and halts the inhibition effect as the radical species consume the oxygen, which produces a non-tacky surface. Increased irradiance (W/m^2) increases the conversion of double bonds. However, increased UV radiation do not only increase amount of radical species but also to energy consumption and reduction of UV lamp's lifespan, leading to higher manufacturing costs.

    1.2 Inert curing atmosphere
A more expensive way of overcoming the harmful effects of oxygen is by inerting (N_2) the exposure atmosphere by inert gases such as nitrogen, carbon dioxide and argon. There are some advantages of using carbon dioxide over nitrogen such as good availability and price efficiency, possibility of being maintained in a container without great loss (as carbon dioxide is heavier than air).

1.3 Physical barriers (protective films, wax)

These methods include preventing entrance of oxygen by using floating waxes as a barrier. Also, by covering the coated substrate with a transparent protective foil inerting can be achieved.

2. Chemical Methods

2.1 Addition of amines

The effects of oxygen inhibition can be overcome by adding amines into the formulation as additives or as bound to acrylates due to amines excellent oxygen scavenging properties. They also include some disadvantages such as coating yellowing, plasticizing effect which restricts the usage, and poor weather stability.

2.2 High photoinitiator concentration

Oxygen readily reacts with photoinitiator or radicals, therefore by increasing the concentration, radicals consume the oxygen and prevent diffusion in the deeper layers (Schwalm 2006, 183).

An increased amount of photoinitiators (excess) in the UV formulation may also lead to yellowing and release of odour (Website of Air Liquide 2014; Website of ChemQuest 2015; Website of GEW UV 2015; Schwalm 2006, 180-184).

2.3 Acrylate monomer structure

Oxygen inhibition can be reduced by effective monomer structures including labile hydrogen atoms with amines, or to increase viscosity.

The type and structure of resins and diluents are selected by application requirements and if they allow using ethylene or propylene glycol, oxygen inhibition can be reduced (Schwalm 2006, 183).

2.4 High reactivity of resins

The cure speed is determined by the monomer and oligomer reactivity, which in turn determine the reaction time of oxygen penetrating into the sample. If the viscosity is low, photo polymerization does not occur as the diffusion of oxygen is high even though the resin reactivity is high.

2.5 Viscosity of formulation

The viscosity of the UV-curable formulation determines the rate of oxygen diffusion into the film.

2.6 Oxygen scavenging of a dye sensitizer

Not a widely used method as the coating becomes discoloured by the dye (Schwalm, 2006, 184).

7.6.2 Shadow Areas

Shadow areas may occur in car bodies and car doors consisting of hollow regions that will remain uncured due to difficulties of the UV radiation to reach these places.

Approaches to overcome difficulties in curing of three-dimensional objects include:

- Light tunnels with lamps for the objects to be illuminated from all sides
- Placing lamps on robots
- Curing under inert atmosphere by using reflective aluminium walls (Laro-lux®) (Schwalm 2006, 185)

1. Using dual curing systems

   1.1 UV and thermal curing

   UV and thermal curing is a dual cure system that include UV radiation with thermal curing, using two types of functional groups: commonly UV-curable acrylate double bonds and thermally curable groups such as polyol and isocyanate.

   1.2 UV and oxidative drying

2. UV plasma curing

UV plasma curing is based on the concept of inert curing, where three dimensional object are cured in an evacuated plasma chamber (Schwalm 2006, 186).

7.6.3 Initial Yellowing

Initial photo-yellowing develops in the coating immediately after exposure to UV/EB radiation and is somewhat reversible as some of it bleaches and diminishes few hours after exposure. Initial photo-yellowing is different from yellowing from ageing and weathering. The degree of initial photo-yellowing is not associated with long term yellowing. The storage conditions after curing play a role in the bleaching rate, the higher storage temperature the faster bleaching rate.

There may also be a relation between the photoinitiator concentration (or the concentration of radicals) and initial photo-yellowing. It is likely that the yellowing is caused by radicals that have become trapped in the polymer matrix, having long lifetimes (decay) of hours to months. Reducing the amount of radical species reduces the photo-yellowing.

The photoinitiator benzophenone develops significant discolouration if exposed to sunlight but has low levels of initial yellowing.

Yellowing due to ageing is increased if amines are used (co-initiator). Amines can be used to increase the reactivity of the system or as hydrogen donors but with the right photoinitiator the initial photo-yellowing may be reduced. The initial photo-yellowing is increased with Norrish Type I photoinitiators in presence of amines.

Initial photo-yellowing can be influenced by stabilizers, amines and the atmosphere although the resin and photoinitiator play a larger role.

The raw materials and curing conditions need to be investigated for the specific application to reduce the photo-yellowing effect (Schwalm 2006, 186-193).

7.7   Recent Developments in UV Curing

7.7.1 Dual-Curable Coatings (UV and Thermal)

This is a method that combines UV curing with thermal curing, to cure shadow areas or if improved adhesion is desirable. UV curing offers high scratch resistance while thermal curing offers curing of shadow areas (Schwalm 2006, 218).

7.7.2 Nanocoatings (Nanocomposites)

UV-curable coatings containing inorganic parts (usually below 100nm in size) together with organic in order to combine properties which cannot be achieved with single materials, such as good barrier properties, high hardness and scratch resistance of inorganic materials and high flexibility, high toughness and easy process ability of organics.
Different nanoparticles types include: SiO_2, TiO_2, Al_2O_3, $CaCO_3$ (Schwalm 2006, 223, 226).

7.7.3 Inert UV Curing with Tanning Lamps (Larolux®)

The Larolux® process is a method in overcoming the effects of oxygen inhibition. Carbon dioxide is used to inert containers (which contain the UV lamps), either in gas form or as dry ice which evaporates carbon dioxide. The gas consumption is less than with nitrogen.
The process allows for reduced material costs in the form of less amounts of photoinitiator, and inexpensive equipment. When the oxygen atmosphere is reduced, and there is no need for high intensity lamps as lower radiation intensities are sufficient for curing. Also, it is possible to increase the distance between the lamp and substrate, or using UV lamps with lower power, to achieve lower radiation intensities.
The reflecting walls reduces the shadow areas (Schwalm 2006, 244-246).

7.7.4 UV Plasma Curing

Another method in overcoming difficulties with curing in shadow areas (3D) is UV curing in a plasma reactor where the curing takes place under inert conditions.

The coated substrates are placed in a vacuum chamber (pressure under 0.1mbar) containing inert gases such as nitrogen, helium or argon. The plasma of the chamber is ignited by a microwave (800-900W) and emits electromagnetic radiation in the UV range. The UV-curable coating is completely crosslinked after approximately 90 seconds. The shadow areas are not avoided in the chamber due to the direction of the emissions that are reflected or diffracted and are distributed over the total volume. Plasma curing requires less space compared to conventional drying ovens (thermal curing oven) (Schwalm 2006, 246-249).

7.7.5 Self-Healing Coatings

The chemistry of polyurethane coatings offers self-healing properties, and hence are suitable and used in the automotive industry as scratch resistant paintwork as well as in office furniture.

Polyurethanes are excellent for coatings since they offer strength and elasticity. Fixed covalent bonds offers resistance and hardness, while reversible hydrogen bonds offer elastic strength. A polyurethane coating that is crosslinked has a "polymer memory", which is an advantage in scratches. As scratches occurs, polymer chains are displaced physically. The covalent bonds are not affected, however, the hydrogen bonds are disconnected. Input of heat triggers the memory effect (car in the sun), putting the tensed system in motion. When the polymers relax, the hydrogen bonds are repositioning themselves to their original shape/formation, causing the scratch to disappear. (Website of Bayer Coatings 2015)
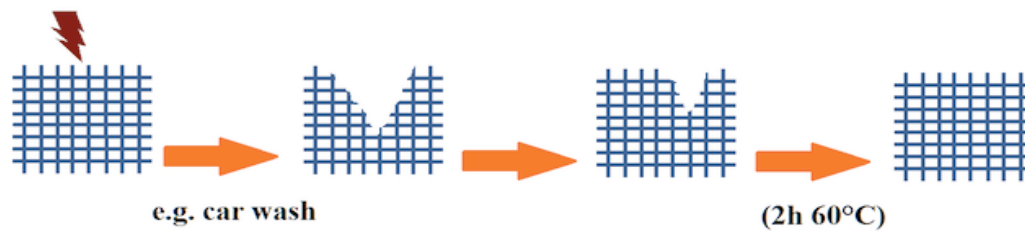
Figure 12. Illustration of The Self-Healing Coatings Memory Effect (Website of Bayer Coatings 2015)

7.7.6 UV-Powder Coatings

Advantages of UV-powder coatings include good recyclability of overspray, solvent free system, low temperature cure excellent flow characteristics and properties. UV-powders can be used on heat sensitive substrate such as wood and plastic as UV-powders only require temperatures between 90-120°C to be melted (Schwalm 2006, 214). UV-powder coatings need low melting temperatures as well as low viscosity (to provide good flow). Applications of UV-powder coatings include medium density fibreboard (MDF) and PVC flooring. (Glöckner, Jung, Struck & Studer 2008, 81.)

7.8 Advantages and Disadvantages of UV Coatings

The main advantages and disadvantages are listed below.

- Economic Advantages
- Savings in energy (rapid curing at room temperature, cold cure)
- Material savings
- Space savings
- Fast production speed
- Capability of processing post cure products immediately

- Ecological Advantages
- Solvent free formulations (usually), meaning reduced VOC's
- Waste reduction (easy recycling)
- Savings in energy

- Performance related advantages
- Low substrate heating
- High product durability
- Application versatility
- High scratch- and chemical resistance (chemical/mechanical resistance)
- Great abrasion, stain and solvent resistance
- Superior/exceptional surface toughness

- Disadvantages
- Higher material costs (alkyds, polyesters, epoxies) compared to conventional/traditional coatings
- Limited availability of 3D curing equipment
- UV curing not be possible in presence of UV exterior durability stabilizers,
- Oxygen inhibition (leaves a tacky surface, oxygen reacts with peroxide species)
- Moisture sensitivity (cationic curing system)
- Difficult to cure of thick pigmented coatings (thicknesses $>5\mu m$) (Schwalm 2006, 11, 14-16)

8 SUMMARY AND CONCLUSIONS

UV curing is a rapidly growing technology mainly due to achievement of environmental compliance with little or no VOC's, which improves work safety, eliminates/reduce the need for costly air permits and leads to increased productivity as the rapid curing enable immediate handling and processing of the cured goods. This contributes to shorter time to market. Other benefits include low temperature curing which enables curing of heat-sensitive substrates, reduced energy consumption which leads to savings, decreased space requirements of UV systems as well as improved product quality. The technology is widely used by industries including automotive, electronics, graphic arts and decorating of metal, glass, wood and plastics.

One concern of using UV curing is in regards to food packaging, with the risk of migration of ink components into the foodstuff, which could be prevented if using appropriate inks and coatings designed for these type of sensitive applications.

UV lamps emit in different part of the spectrum and it is important to match the photoinitiator absorption with the peak wavelength of the UV lamp source, in order to obtain maximum conversion of light energy into formation of radicals. UV-curable lamps include mercury, excimer and LED's. Developments of alternatives to the conventional mercury vapour lamp may be one challenge in UV curing as European Union regulations has classified mercury as a hazardous substance. UV curing with light emitting diodes (LED's) requires changes in ink formulations although using LED equipment offer ecological benefits as it reduces energy consumption.

There are three main disadvantages of radically induced UV curing; oxygen inhibition, initial yellowing and lack of formation of radicals in shadow areas, where curing does not occur as light is unable to penetrate. Methods used to overcome oxygen inhibition include high irradiance, selection of efficient photoinitiators and using high photoinitiator concentration, selection of highly reactive formulations and addition of additives such as amines or waxes, as well as decreasing the concentration of oxygen in the atmosphere.

The type of raw materials used in UV curing depends on several variables including application as well as UV system set up. UV formulations comprise of oligomeric resins, monomers (reactive diluents), small amount of light sensitive photoinitiators and additives, that become exposed to UV light (180-380nm) upon which inks and coatings instantly harden.

The use of acrylate oligomers and monomers and in free radical curing of inks and coatings is the most popular chemistry used in both UV and EB technology. The chemical structure of the oligomers and monomers decide the properties of formulation both before and after curing. It is important to understand the chemical structures of the raw materials used in order to predict properties such as reactivity, viscosity, chemical resistance, flexibility, adhesion and weathering as well as cost.

The share of conventional solvent-based curing methods is declining and more environmentally friendly systems such as UV curing are increasing. UV curing is expected to continue its' growth in the coming years mainly due to the highly growing Asia-Pacific region and the Chinese market's growth potential and promotion environment-friendly products.

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