

UV/EB Brochure

November 2018



Summary

Since their introduction in the 1970's UV/EB curing coatings and inks have outperformed coatings and inks market growth consistently to now become an overall accepted high growth and sustainable technology in the industry. Reason for this high growth is the excellent environmental and safety profile, the high performance that can be achieved and the overall favorable cost of UV/EB curing technology. Although penetration of UV/EB technology in some segments is over 50%, the overall penetration in coatings and inks is still only about 5%, meaning there is still plenty of scope for continued high growth of the technology in years to come. There is a lot of development in raw materials, formulations as well as UV/EB curing equipment that enables the technology to be used in more market segments continuously. This paper will give an overview of UV/EB curing technology as well as a look at recent developments and future potential.

UV/EB curing

In UV curing technology multifunctional resins are polymerized or cross-linked by exposure to UV light. The UV light triggers a UV photo initiator in the formulation to generate polymerization initiating species which very rapidly converts the liquid UV resins to a fully cross-linked coating. In EB (electron beam) curing the same multifunctional resins can be used but no photo initiator is needed. The electrons initiate the polymerization and the end result is also a highly cross-linked coating.

So compared to other (traditional) coating technology where heat is used to remove the solvent or water and to optionally trigger cross-linking reactions, in UV cure no heat is used, just UV light and as a result UV curing is more energy efficient than traditional technology.



Additional advantage of UV curing is the fast cure speed. Where traditional drying of solvents or cross-linking of powder coatings can take minutes to hours at high temperature, UV coatings will cure in seconds or less at room temperature.

This fast cure allows for very short and small lines, and produced goods can immediately proceed to the next coating step or to assembly. Because UV lines have a small footprint existing traditional coating or printing lines can usually be easily converted to UV lines.

For many different applications high performance coatings and inks can be produced with UV/EB curing technology. In part this is due to the nature of UV/EB curing, where liquid materials are polymerized and cross-linked after application to the substrate, giving excellent opportunity for interaction with the substrate before cure. And additionally the broad range of different resin types (epoxy, polyester, urethane, acrylics) which are used in UV open the opportunity to formulate to a broad range of final coating properties.

UV/EB technology

There are two main curing technologies used in practice. First is free radical cure of mainly acrylic resins but also some vinyl and unsaturated polyesters are cured this way. The reaction is started by a UV initiator (producing a radical under UV light). The radical initiates polymerization of the acrylic double bonds to form a crosslinked polymeric network. The second is cationic cure, these are mainly epoxide or other cyclic ether ring opening curing reactions triggered by a UV cationic photo initiator (producing a super acid under UV light). In EB cure there is no photo initiator, the electron beam creates radicals direct in the coated film that start the polymerization reaction. The vast majority of applications use acrylic functional resins cured with a UV photo initiator.

UV/EB Resin types:

Acrylic (and vinyl) UV Resins can be generally split in oligomers and monomers (or diluents). The monomers are low viscous materials, most commonly esters of acrylic acid and simple multifunctional or monofunctional polyols. Examples of such polyols are trimethylol propane (TMP to give TMPTA), tripropyleneglycol (TPG to give TPGDA) or 2

phenoxy ethanol (2-PE is acrylated to give 2-PEA). The monomers are generally low volitality and non flammable materials and also have low odour. Monomers generally can have from 1 upto as many as 6 UV curable groups, and the amount of functional groups will determine the properties the monomer will bring to the UV formulation. This is illustrated in figure 2.



The monomers are mainly used for:

Figure 2, effect of monomer functionality on formulation performance.

- Viscosity and Rheology control of the formulation (diluting power)
- Control of the reactivity of the system (higher functionality cures faster)
- Increase crosslink density (enhance hardness and chemical resistance)
- Improve adhesion (penetrate the substrate)

Disadvantage of monomers:

high shrink on polymerization (can cause adhesion issues)

Oligomers are higher molecular weight and higher viscosity UV curing materials and can be made up of several different backbone building technologies to give for example, polyester acrylates, epoxy acrylates, urethane acrylates and acrylic acrylates.

Epoxy acrylates are the most common used UV/EB oligomers.

Advantages of Epoxy acrylates are that they are fast curing, hard, very good chemical resistant, high gloss and relatively low cost. Disadvantage is that they are yellowing (poor outdoor performance) and very high viscosity. Epoxy acrylates are used in all kinds of applications, from primers to topcoats in coatings for all types of substrates and in almost all types of printing inks.



Figure 3, example of an epoxy acrylate

Urethane acrylates are a very versatile class of UV materials with the ability to achieve a very wide range of performances. A general strong property of urethane acrylates is their toughness. Urethanes can be from very soft and flexible to extremely hard and scratch resistant, from moderate chemical resistance to excellent chemical resistance for high functional hard urethane acrylates. There are aromatic (figure 4) and aliphatic urethane acrylates. The aliphatic types are very low yellowing and can have excellent outdoor durability, but as disadvantage are the most expensive types. Urethane acrylates are generally used in applications where high performance is needed, like plastic coatings, wood topcoats, special primers on difficult substrates and high performance inks and adhesives.



Figure 4 example of an aromatic urethane acrylate

Polyester acrylates have a very broad raw material base which allows for a wide variety of backbone structures and functionalities. Polyester acrylates can have low to very high functionality and can have very hydrophilic to extremely hydrophobic backbones. Polyester acrylates also exist in a wide range of viscosities, from very low (close to monomer viscosity) to very high viscosity. Typical properties of polyester acrylates include; good pigment wetting and dispersing, good water balance for lithographic printing, good adhesion and generally relative low viscosity compared to epoxy or urethanes. Disadvantage of polyester acrylates are the lower molecular weight byproducts that can be formed in some types.



Figure 5, example of a polyester acrylate

Besides these 3 main types there are acrylated acrylics and some other specialty materials that are used in UV/EB cure. Acrylated acrylics depending on the functionality can have good adhesion to many substrates and also usually acrylics have good outdoor durability.

UV/EB formulations are usually made up from oligomers and monomers about 1-1 ratio depending on the required application viscosity and then contain 1-10% of photo initiator (in case of UV cure) and 1-3% of additives to promote flow, leveling, cratering, slip or other properties. Of course the coatings or inks can be pigmented as well or contain fillers. In pigmented coatings or inks with UV cure the photo initiators and lamps may need to be chosen correctly to not overlap too much with the absorption spectrum of the pigments. There are 3 main types of UV lamps, standard mercury lamps (main peak 240nm), Iron doped mercury lamps (broad emission 240-400nm) and gallium doped mercury lamps (main peak 350-400nm), and more recently LED lamps (single peak 360-400nm) are added to the selection. The emission spectra of these lamps are different, so depending on the absorption of the pigment the best lamp can be chosen. Also many different types of photo initiators exist, also with different absorption spectra, which can be chosen to match with the lamps and not overlap with the pigment absorption.

In pigmented films it is important to consider the layer thickness because if the layer is too thick and UV light cannot penetrate to the bottom of the film, no cure will take place With EB there are no issues to cure pigmented films or even multiple layers of pigmented films at once.

UV/EB history

The first patent on UV technology appeared in 1946 focusing on the use of unsaturated polyester resins for use in UV inks. The real first commercial use of UV only started about 15 years later in the early 1960's when UV was used for screen inks. In the early 1970's the first EB units appear in the market for use in multilayer pigmented inks applications. Only from the early 1990's UV/EB became more widely used in printing inks, wood coatings, plastic coatings and electronics. Initially UV/EB developed fast in these segments where flat substrates were used and high performance and fast throughput were key requirements. In these early years UV technology enjoyed a 30% year on year growth as many people started to discover and enjoy the excellent performance that could be achieved with this technology. In this period the technology developed fast as well. Besides the initial unsaturated polyesters, also urethane and epoxy UV resins were developed and the UV/EB active groups broadened to include vinylethers and acrylates. Polyester technology developed to include the multifunctional acrylates of smaller polyols, now known as UV monomers or reactive diluents. When the technology became more mature and volumes increase the growth rate remained high at about 10% in the 2000's. Besides the broadening of the resin portfolio also the amount of photo initiators and additives for UV/EB grew steadily opening up more and more potential applications where UV/EB could be used and ever increasing the performance of the final coatings. Also the development of UV light sources and UV curing equipment has contributed a lot to recent expansion of the technology to more and more segments, as today UV is used in many flat and 3D applications. With newer doped mercury lamps and new line setups (with robotics as option) parts of many shapes and size can be cured well. UV is even used in decorative and on site applications now where cure is done with mobile equipment. The introduction of UV-LED's has even further increased flexibility in design of curing equipment and will in future further expand possible applications for the technology. Also in EB the equipment has changed a lot to controlled power and smaller units that can be installed on many types of existing lines.

UV/EB curing equipment:

Normal UV lamps are mercury lamps and can be doped with iron or gallium to control the emission spectra, lamps typically have output of 80-120W/cm2 and lamps are available in many lengths. In first instance because of the lamp shape UV was mainly used for flat substrates such as wood boards and paper sheets, but with more recent developments and improvements in lamp designs and line setups and the use of mirrors and now many 3D substrates can be cured efficiently. In automotive coatings work was done to expose a full car body to a UV plasma to ensure no shadow areas (unexposed) would exist anymore. Equally in EB the curing equipment has become much smaller, better controlled in power output and more cost efficient as well as easier to operate in recent years. Modern EB units can be installed on existing printing lines nowadays, allowing for cure of multiple pigmented layers and even laminating adhesives between plastic or paper sheets all in one single cure step.

UV/EB Market

The 2008 market for UV Resins globally was 296kT (excluding photo initiators and additives). The Asia Region is the biggest market and also the market with the highest growth (figure 6). The breakdown to market segments (Figure 7) global shows that Graphic arts is especially strong in Europe and Americas, while Electronics is especially strong in Asia. Industrial coatings are a significant market in all 3 regions.

In industrial coatings especially wood coatings and paper coatings are important sub segments. Other sub segments are plastic coatings, resilient flooring, metal coatings, opto electronics and adhesives. In Graphic arts UV/EB is mostly used in Lithographic printing and in flexo printing. Other segments are screen printing, letterpress and ink jet printing.

In electronics UV/EB is used in printed circuit boards as photo resist coatings, in displays both on inside for the electronics as on outside as hard coat. In addition, on the plastics as wear resistant coatings.

UV/EB coatings are among the fastest growing technologies in the coatings market, the main driver for this fast growth is the combination of high performance with acceptable overall coating cost and the excellent sustainable safety and environmental profile of UV/EB coatings.



Figure 6 : UV global market per Region in 2016







Figure 8 : UV annual growth in various applications 2018-2020

Because the technology is still developing fast, both in the field of UV/EB curable resins as well as in the area of UV curing equipment, more and more applications are able to use UV curable coatings,

UV/EB applications

Adhesives

Between the beginnings in the 50s when light-curing adhesives were mainly used in the furniture industry, through the first boom in the field of printing inks in the 70s, up to today's high-tech applications in a wide variety of industries, lies a rapid development which is still in progress. Therefore, adhesives cured by light have become indispensable for many users.

In the family of photoinitiated-curing adhesives, one distinguishes between two basically dissimilar basis materials (acrylates and epoxy resins) and the reaction mechanisms associated with them. In their liquid state, radial-curing acrylates as well as cationically polymerizing epoxies provide a multitude of properties to ensure simple and reliable handling.

Examples of use:

- Bonding of miniature loudspeakers in cell phones
- Bonding of automotive cameras
- Dam&Fill chip encapsulation
- Bonding of ONSERT connection elements
- Bonding and sealing of automotive sensors
- Optical bonding: Bonding of touch panel displays of iPhones and iPads
- Aluminum door hinges for glass shower enclosures
- Bonding of electric motors

Advantages of the light-curing adhesives:

- Simple and reliable process thanks to one-component nature (no mixing system)
- Fast curing in just seconds (short cycle times)
- Curing without adding temperature (energy-saving)
- Curing on demand > Precise positioning and fixing of the components to be bonded

- Curing also in shadowed areas
- High reliability
- Outstanding visual appearance
- Excellent adhesion
- Simple transport and storage

Industrial wood finishing

The wood finishing industry is one of the main application areas for UV and EB, with commercial systems used since the 1960s. UV and EB coatings are typically known for high gloss and body, whilst offering excellent adhesion, scratch and abrasion resistance. They are commonly used for high quality coatings in the parquet, wood and furniture industry. The newer Waterborne UV coatings, fit very well into furniture coating lines to substitute solvent-borne systems and reduce/eliminate VOC emissions. In the past, only clear coats and flat substrates could be cured, but today also pigmented coatings and 3D applications are established. Special designed matting agents and additives are available for UV/EB systems.

Applications:

- Parquet
- Furniture
- Door Skins
- Dash Boards
- Decorative Panels

Advantage:

- VOC free
- Economical benefits
- Fast process
- High quality coatings
- Scratch & mar resistance
- •

Consumer electronics

In the consumer electronics market with mobile phones, laptops and game console coatings as some example applications, the use of UV/EB coatings has increased significant over the last decade. Main reason for this growth is the excellent performance that can be achieved with UV/EB coatings, especially very good wear resistance, outdoor durability and resistance against household chemicals and fat for the plastic parts. With an ever increasing demand for high performance and longer lasting parts, combined with the global occurring shift to more environmentally friendly coating technology, UV/EB coatings will have a bright future in consumer electronics as the best technology to deliver this combination.

Also in the manufacture of printed circuit boards and displays in the consumer electronics market a significant amount of UV/EB coatings and inks are used. UV/EB coatings and inks are used because they enable high precision etching, allow for accurate printing on circuit boards and displays and give high performance protective final coatings for long lasting protection.

Most of these applications are applied by spray coatings, and also here many advances have been made in UV/EB formulations to make them better suitable for spraying with zero VOC's. Also the equipment for UV/EB spraying has developed significantly in recent years.

Application areas are:

• As protective coating on plastic parts of electronics (mobile phones, TV, laptop)

- On the printed circuit boards as etch resists
- In the displays of electronic devices
- Display hard coats

Advantages

- Very high wear resistance
- Excellent Chemical resistance
- Operate at room temperature (no parts deformation by heat)
- Excellent adhesion
- Excellent durability

Plastic coatings

A wide variety of plastic products are decorated and coated with UV/EB curable inks and coatings to improve both their appearance and their performance. Surface pretreatment is generally necessary so the ink or coating will adhere to the plastic surface. New waterborne UV coatings offer additional possibilities, such as soft-touch finishes and flexible coatings.

Advantages:

- Cold curing can be used on heat-sensitive substrates
- High processing speed
- In-mold coating
- Improved functionality and performance properties, such as high scratch- and abrasion-resistance.
- Instant curing reduced space requirements for post-curing

Applications:

- Flooring
- Automotive parts
- Mobile phones and high-quality electronics
- Plastic films

Graphic Arts

The use of UV/EB curing technology has been in existence in Graphic Arts Printing and Varnishing applications for over 30 years. The benefits of instant drying and excellent film properties that UV/EB curing give were originally demonstrated in Screen and Offset printing technology. With UV cured Over Print Varnishes the high gloss achieved and excellent product resistance meant that more expensive print finishing techniques such as Laminating were no longer always necessary.

The ability to use the same ink on a wide number of substrates allied to 'stay open' benefits allowed the use of UV/EB to grow steadily throughout the period. The development of Narrow Web presses to produce labels naturally aligned themselves to incorporate the benefits of UV/EB Curing technology. And as Printers realised the 'Cost per Copy' benefits of UVEB Printing continued to grow in Offset applications. The challenge of producing Food Packaging quality systems has been met by using UV/EB technology and this is definitely a growth area for the future. Newer printing technologies such as inkjet are also finding that UV/EB drying offers unique technical advantages. The introduction of UV/EB into these newer applications ensures that UV/EB is the technology for the future.

Applications:

- Offset
- Gravure
- Screen
- Flexography

- Inkjet
- Over Print Varnish

UV/EB New developments

Field applied coatings

In the past five or so years, commercial UV curing has moved out of the factory and into the field, with numerous improvements in UV curing equipment and coating pushing the transformation of this technology into the area that one calls Field Applied Decorative Coatings. In these field applied UV curing applications, the substrate to be coated is stationary while the UV curing equipment is moved over the surface or substrate for curing. Applying and curing a UV coating in a factory is a well-controlled process while moving this process to the field introduces many uncontrolled variables, which means that a robust coating and cure process are needed. UV curable field applied decorative coatings are being developed in an effort to address some of the shortcomings of commercially available coating systems on the market. Today, these field applied or on site decorative coatings for wood, vinyl, tile, concrete, composite are all in some phase of commercialization in a wide variety of markets.

Applications of UV/EB technology in this industry:

- Concrete Floor Coating
- Wood Floor Coating
- Vinyl Floor Coating
- Countertops Coating
- Tubs Coating

The benefits of using UV cured field applied coatings as compared to conventional coating technologies for these

different surfaces are numerous and are similar to factory applied UV coatings: increased productivity and performance. In addition, the immediate cure aspect provides cost savings to the end user through immediate use, and added benefits of quality, since the finish will not be damaged once it is cured. The contractor benefits from the reduced coating job completion time, the reduced VOCs and odor, the easier handling of the 1K UV system.

Metal coatings

Although it may be new to the metal coatings industry, UV/EB technology has been around for 40 years in many industrial applications and has demonstrated to be the 'technology of choice' for many of the new challenges to overcome. UV/EB technology is still gaining broader acceptance throughout the European Industry. RadTech members are confident that UV/EB technology will be recognized as one of the leading technologies for VOC reduction and economic developments in the future.





Today, UV/EB technology still has a limited footprint in the metal coatings market. The metal coatings market includes several industries as automotive, protective (e.g. pipes, agricultural and construction equipment), coil, can and consumer electronics. However, some UV/EB metal coating applications are well established and new ones are emerging. UV/EB curing technology does not pretend to immediately replace all the conventional coating systems used in metal coating industry today. However, regardless of whether you are looking for anti-corrosion primer, pigmented base coat, protective or aesthetic topcoat, UV/EB curable coatings are considered to be a feasible and valuable alternative to some of the existing coating technologies.

Applications of UV/EB technology in this industry:

- Automotive Industry: UV coatings on Light Reflectors, seat frames, wiper frames, diesel engine pumps, truck axle
- Protective Industry: Temporary storage and welding UV primer for pipes, Protective and aesthetic topcoat for pipes
- Coil Coating Industry: UV topcoat for household appliance and UV primer and UV or EB topcoat for construction steel and aluminium
- Can Coating Industry: UV Base Rim Coats, UV protective topcoat
- Consumer Electronics: UV topcoat on mobile phone housing

Advantages of UV/EB technology in this industry:

UV/EB curable coatings share the same general attributes as conventional solvent based coatings but also add new capabilities such as improved properties (better surface performance), environmentally-friendly features (reduced VOCs, highest material utilization, reduced waste), lower energy consumption, low temperature drying requirements, fast cure cycles, reduced space requirements and increased productivity. The use of UV/EB curable coatings can simplify production, eliminate solvent extraction steps and consequently reduce the cost (no drying zone). Moreover, UV/EB technology is not subject to any possible carbon tax because it does not produce CO2. Existing coating units can be easy retro-fitted with UV technology given the small footprint. Due to the immediate drying mechanism, UV technology reduces lead time and increases the coating throughput.

3D printings

3-D Printing or additive manufacturing (AM) is a general term used to describe a process where thin layers of material are printed on top of one another to form a physical, threedimensional part. It is important to distinguish the differences between 3-D printers and rapid prototyping machines in the realm of 3-D Printing since these terms are widely used interchangeably. 3-D printers are smaller, simple versions of rapid prototyping machines at lower cost and less capability. Rapid prototyping is an accepted manufacturing method used by automotive and aircraft industries for many years on a larger scale, whereas 3-D printers are mainly used in office or home environments. According to a report published in IDTechEx by Dr. Wendy Kneissl, "the market for photopolymers will comprise the largest portion of the market over the coming 10 years". Stereolithography, which uses layers of photopolymers and UV light to cure objects, is the most popular rapid prototyping technology, capturing almost half of the share in rapid technology. It offers the highest quality of all commercially available systems. According to a global study done by BIS Research, "Photopolymers accounted for the highest market revenue among all materials used in the 3-D printing market (metals, metal alloys, plastics, photopolymers, ceramic, nylon, paper, and wax)".

The global 3-D printing market is predicted to grow from \$2.5 billion in 2013 to \$16.2 billion by 2018, according to Canalys, one of the research firms studying 3-D Printing and its impact. This steady increase is attributed to shorter timelines for marketing and distribution. This will be driven by companies like Shapeways and Sculpteo who handle design and distribution so products can be purchased and delivered anywhere in the world. The ability to ship and print the designs helps push printing on demand.



UV/EB future outlook

Because of the ever ongoing rapid development in raw materials such as resins, photo initiators and additives suitable for use in UV/EB curing as well as the equally impressing improvements in curing equipment UV/EB technology not only has grown rapidly over the past 30 years but will continue to do so in the future. Because of this high level of innovation in UV/EB more and more applications become possible and new market segments open up to the technology. UV/EB is one of the winning technologies in the market because of its excellent environmental and safety profile, and its ability to deliver very high performance coatings and ink systems at low overall application costs. So we can only conclude that UV/EB will have a bright future and continued high growth.

UV/EB Questions and Answers

Q: Is UV/EB suitable for 3D shaped substrates?

A: Yes it is. Because traditional mercury UV lamps are flat the initial penetration of UV technology was mainly on flat substrates like wood panels, paper coatings and printing inks. Because of a lot of development in lamp and curing equipment technology nowadays 3D substrates like for example car bumpers, car wheel rims or cellphones can be coated and cured with UV light. The lamps are smaller and set up in angles and the parts are rotated to get light exposure everywhere on the coated part. With UV LED it is even possible to have very flexible lamp designs to cure 3D parts better. In the automotive industry experiments have been done to bring full coated parts (car bodies) inside a vacuum chamber where subsequently a UV plasma is generated. In this way you actually bring the part inside the lamp and there are no unexposed (or shadow) areas left anymore at all.

Q: Are UV/EB materials safe to use?

A: UV/EB materials are much less toxic than solvent borne coatings. UV/EB materials have very low systematic toxicity, are not reproductive toxins and generally are not carcinogenic or mutagenic materials. UV/EB materials are not flammable and have very high or no flashpoint, so easy to use and store. UV/EB materials contain no or very little VOC's and UV/EB materials are not absorb through skin like solvents are. For safe handling of any chemical good industrial hygiene practices, knowledge of safe handling procedures as described in the MSDS and worker training are important. When these principles are followed, experience has shown that UV/EB curing materials are safe.

Q: Is it possible to use UV/EB in pigmented coats?

A: UV/EB is widely used in printing inks so there is broad experience with the use of UV/EB in pigmented systems.

With EB pigmented coatings of any thickness can be cured easiliy.

With UV it depends on the type of pigments, the used photo initiators and thickness of the coatings. Pigments will block the UV light from penetrating into the coating, so for very thick coatings the UV light may not reach the bottom of the coating and hence this will then not properly cure. UV absorption of each pigment is different so if UV doped lamps with various emission spectra are used and this is combined with the right selection of photo initiator (PI should absorb in different spectral range than the pigment and this range should be aligned with emission range of the lamp then good cure of pigmented coatings is till possible.

For thick pigmented coatings also so called dual cure technology has been developed, here UV is combined with another (usually thermal) cure technology to ensure also good cure at the bottom of the thick pigmented coating.