Progress in Radiation Curing MARKETING AND TECHNOLOGY

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Over the past 30 years, radiation curing has achieved great progress in both market growth and technology. In 2000, the worldwide radiation curing market of coatings, inks, photoresists, adhesives, and others was estimated at over 158,000 tons with an average growth rate of over nine percent. This paper gives a short overview of the present market and technology, and discusses market trends and technological development for radiation curable products.

Radiation curing including ultraviolet (UV) and electron beam (EB) curing technology has been greatly developed since the 1970s. Increasingly used in various sectors of applications, mainly in the coating industry, graphic arts, and microelectronics, this technology is replacing conventional thermally cured solvent-based coatings, inks, and adhesives. The worldwide annual growth rate is between 8-12% in recent years. This is due to their distinct advantages, such as fast cure speed, room temperature operation, VOC minimization, and high-quality end products. The increasing use of curable materials for coatings, inks, and adhesives provides an incentive for the development of new varieties of oligomers, multifunctional comonomers, and photoinitiators. The total volume of radiation curable products in 2000 was estimated at over 158,000 tons, of which Asia and Europe each shared 35% and America shared 30%, while the total volume of radiation curable products in these regions was 109,000 tons five years ago.[1]

This paper gives a short overview of the present market and technology, and discusses market trends and technological development for radiation curable products.

ASIA[1]

With the current rapid economic development and strict environmental regulation control, there is a new surge of interest in the radiation curing technology market in Asia. Even under the negative influence of the Asian financial crisis, the market for radiation curing has been greatly expanded in recent years. The strong growth in radiation curing currently is predominant in UV curing technology in this area. Applications of EB-curing technology are still very few today, except for Japan. However, as the price of low energy accelerator further decreases, this technology is going to be very promising in the future markets.

The industry growth rates for UV/EB radiation curable materials in 2000 in different regions are given in *Table* 1. It can be seen that the growth rate of the market in China remains the highest.

Although a significant number of radiation curable products, including both raw materials and finished products are imported, locally manufactured products are rapidly expanding. The trends of imported goods are given in *Table* 2. It can be seen that China has the biggest decrease from 49% to 18%.

The total production values of the radiation cure resins and the formulated products in Asia in 2000 are given in *Table* 3. Japan has the biggest market, exceeding total value of other Asian countries for UV/EB curing systems. Injection molding applications, wood coatings, graphics, and electronics are gaining increased interest in Asia. The printing ink manufacturers in Taipei are expanding

Table 1—Market Growth Rates in Asia (%)

Japan	7	Malaysia	13
Korea	9	Singapore	9
China	22	Indonesia	8
Taipei, Taiwan	7	Australia	7
Philippines	10	New Zealand	8
Thailand	12	India	7

Table 2—Trends For Imported Goods in Asia

	Imported Goods (%)	Five-Year Trend of Imported Goods(%)
Japan	5	5
Korea	18	10
China	49	18
Taipei, Taiwan	10	8
Rest of Asia	75	70

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Table 3—Market Values of the Radiation Cure Resins and the Formulated Products in Asia in 2000 (x 10^6 US$)

	Value of Radiation Cure Resins	Value of Formulated Products
Japan	157.8	271.0
Korea	26.5	46.4
China	27.2	49.1
Taipei, Taiwan	50.0	77.1
Rest of Asia	17.6	33.4

Table 4—Application Areas for UV Curable Coatings and Inks in 2000

Application	Volume (Ton)
Coatings	
Wood & bamboo	4,938
Poly(vinyl chloride)	2,451
Overprints for paper	2,229
Plastic	688
Automotive part	680
Metal	235
Inks	
Offset	225
Flexographic	62
Screen	613
Optical Disk	160

Table 5—Production Values of Radiation Industry in China

	Consumption (U.S.$ mil)		
Products	1998	1999	2000
Monomers + Oligomers	3.07	4.28	19.33
Photoinitiators	4.16	27.00	47.44
UV coatings	24.58	35.74	49.61
UV inks	8.67	12.28	23.33
UV lamps	0.48	1.08	3.37
UV lines	0.36	0.84	2.36
Others	2.41	3.28	4.70
Total	43.73	84.51	150.15

Table 6—Markets for Comonomers and Oligomers

	Market, Tons		Growth	
Materials	1998	2000	%	Major Uses
Reactive diluents	11,000	13,200	25	Coatings, OP Varnishes, Optics
Mono-acrylates	1,200	1,700	42	Coatings, OP Varnishes
Di-acrylates	3,600	4,100	14	Printing Inks, Hard
Multi-acrylates	5,200	6,200	19	Coatings, Resists
Methacrylates	600	600	0	Dry Films
Others	400	600	50	Epoxides, oxetanes, Sytrene, etc.
Oligomers	13,200			
Epoxy acrylates	3,600			Solder resists, Coatings for bldg.
Urethane acrylates	3,500			Optical fiber coatings
Polyester acrylates	2,500			Wood coatings
Other acrylates	600			
Unsat. polyester	600			Wood coatings (70%)
Photoinitiators	1,140			

Table 7—Industrial Applications of Radiation Curable Products in Japan (1999)

Application	Volume (Ton)	Share (%)
Coating	13,750	37.3
Inks & OPV	7,940	21.5
Photolithography	14,728	39.9
Adhesives	238	0.6
Others	250	0.7

their market share at the deficit of Europe importers, mainly by offering inks.

China[2,3]

RadTech China, founded in 1993, is the professional organization of the Chinese radcure sector. It began with 60 members and now has over 200 members. An average growth rate of over 25% per year for UV curable materials is expected to continue in the next few years. Coatings and inks remain the largest application areas. The main markets for UV curing resins are printing inks, coatings for buildings and floorings, and hard coatings for plastics. Polystyrene (PS) offset plates are one of the fastest developing products in China. By the end of 2000, the consumption of coatings, inks, and adhesives expanded 11,270 tons, 2070 tons, and 10 tons, respectively, compared with the total consumption of coatings and inks of 8,500 tons in 1998. The output of domestic coatings and inks were 10,680 tons in 2000, while those in 1998 were 6,130 tons. However, the total consumption of UV curable coatings and inks was only about 1,200 tons in 1990 and 3,000 tons in 1994. The application areas for UV curable coatings and inks in 2000 are presented in *Table* 4.

Although a considerable amount of the raw materials for UV curable formulations is imported, domestic products are increasing rapidly. The output of oligomers increased from 150 tons in 1999 to 700 tons in 2000. The comonomers produced in China for UV curable formulations are mostly trimethylolpropane triacylate (TMPTA), triproplyene glycol diacrylate (TPGDA), neopentyl glycol diacrylate (NPGDA), 1,6-hexanediol diacrylate (HDDA), and pentaerythritol triacrylate (PETA), and so forth. The output of comonomers increased from 850 tons in 1998 to 1,300 tons in 1999, with an annual growth rate of 53%. By the end of 2000, the output of co-monomers was 5,436 tons, almost five times of that in 1999. The output of photoinitiators, such as benzophenone (BP), 2,2′-dimethoxy-2-phenylacetophenone (651),1-hydroxycyclohexyl phenylketone (184), 2-methyl-(4-[methylthio]phenyl)-2-(4-morpholiny)-1-propanone (907), 2-hydroxy-2-methyl-1-phenylpropan-1-one (1173), isopropyl thioxanthone (ITX), and others produced in China increased from 610 tons in 1998 to 3,760 tons in 1999, and expanded 5,020 tons in 2000 with an annual growth rate of 34% above that in 1999.

The UV curing equipment market has also grown rapidly to meet the increasing demands. There are several UV equipment manufactures with strong success in the markets of China. A total of 30,000 UV lamps and 50 lines was in use in 1998, and this grew to 66,000 lamps and 114 lines by 1999. In 2000 there were about 130,000 UV lamps and 318 lines in use for a variety of applications. In the 1980s there were about 50 EB lines in use for heat shrinkable materials and for cross-linked coatings used in the wire and cable industry. In addition, there are several EB units for research in the area of coatings. The EB lines for industrial coating production are just coming into use.

Table 8—Markets for Coatings, Printing Inks and Photolithography

Application	Volume (Tons)
Coatings	13,750
Wood coatings	8,000
Optical fiber coatings	1,920
Optical disk coatings	600
Hard coatings	2,000
Metal coatings	300
Film coatings	230
PVC floor coatings	700
Printing Inks	7,940
Offset inks	5,830
Silk screen inks	400
Metal inks	450
Gravure inks	1.260
Photolithography	14,728
Liquid resist	5,780
Dry film resist	2,486
Photopolymer plate	2,130
Semiconductor resist	1,657
Barrier rib for plasma display panel	52
Color filters resist	940
Resist for liquid crystal display	1,383

The total production values of radiation curable products from 1998 to 2000 are listed in *Table* 5. The values in 2000 nearly doubled those of 1999. In addition, the total production values of printing plates, photoresists, and conformal coatings were over $48.7 million U.S. in 2000.

Although the production of radiation curable products has achieved a certain level, it is unable to meet the rapidly increasing requirements of domestic markets. Remarkable progress in basic research and applications has been achieved in recent years in China. With increased competition in China, significant price reductions for radiation curable products, especially comonomers and oligomers, have resulted. The photoinitiators for long wavelength photopolymerization system, e.g., photocurable dental materials and imaging applications, coumarin dye/iodonium salt, and camphorquinone/peroxide initiation systems have been successfully studied. In order to increase photosensitivity of cationic UV curing systems, sulfonium and iodonium salts with photosensitive groups have been developed. Other new types of photoinitiators have been also widely investigated in universities and institutes. The dendritic oligomers end-capping with (meth)acrylic groups are investigated for coating applications. These materials with 3D molecular structures offer most intriguing properties with great potential value for applications such as low viscosity in molten and as solution, high reactivity, and high adhesion on substrates, which are different from those of their linear counterparts.

There is a great potential market of UV curable products in China. Some foreign companies have entered into the markets, including Sartomer, UCB, Ciba-Geigy, First Chemicals, Fusion Systems, and others.

Japan[4]

The greatest applications of UV/EB radiation curable products are prima-

Table 9—Markets for Photoinitiators in Europe (2000)

Photoinitiatator	Volume Share (%)
Benzophenone	42
Benzyl dimethyl ketal	19
Acetophenone	9
Thioxantone	4
Phosphine oxides	3
Amine synergists	23

Table 10—Market of Radiation Curable Materials in North America by Volume (2000)

Segment	2000 (Tons)	1997 (Tons)
Graphic arts paper, film, foil and board		
Overprint coating, clear-general purpose	17,000	13,000
Clear—specialty	1,900	1,200
Offset (litho)	6,300	4,000
Screen	5,200	4,000
Flexo	3,500	2,500
Letterpress	500	600
Wood Finishes		
Filers	6,000	4,500
Stains and sealers	500	300
Pigmented coating	2,500	1,800
Clear finishes	5,000	3,200
Flooring (prefinished)	1,100	700
Plastic Coatings		
Vinyl flooring (tile & sheet)	4,500	3,500
Automotive lens & sheet	750	500
Interior trim	100	60
Silicone Release Coating	750	550
Adhesives		
Optical	15	6
Pressure-sensitive	350	150
Laminating	1,900	1,200
Metal Decorating (can coating)		
Inks	850	700
Overprint varnishes—clear	675	500
Can end varnishes	425	350
Optical fiber-coatings, inks, and matrix	5,000	2,000
Printing plates (flexo and offset)	12,000	5,000
Stereolithography/solid modeling	200	25
Dental applications	22	9
Medical apparatus	14	10
Electronics		
Adhesives	350	250
Photoresists (chips)	4,700	2,500
Conformal coatings	600	600

Table 11—Estimated Volume Growth Rate in North America (2000)

	Growth rate (%)
Ink jet printing	37
Fiber optics	35
Medical devices	30
Solid modeling/prototyping	25
Adhesives	25
UV cured powder coatings	20
UV flexo inks and coatings	18
Automotive applications	16
Plastic coatings	15
Wood products, filler, sealers, finishes	12
Sprayable coatings	12
Metal decorating	11
Release coatings	10
Flooring frinishes	9
Screen inks	8
Clear overpint coatings (paper/paper board)	7
Offset inks	6

rily for opto-electronics in Japan, wood and furniture varnish in Europe, and graphic systems in North America, even though the graphics sector [printing inks and overprint varnishes (OPV)] is important. In addition, UV coatings and adhesives for CD-ROM, CD-R/RW, and DVD as well as photoresists for flat panel displays (FPD) such as LCD and plasma display panels (PDP) are promising new market leaders. The comonomers and oligomers for such applications are mostly being supplied domestically, although a large quantity was being imported from 1993-1995.

By the end of 2000, there were 200 EB processors, compared with only a few for research uses in China, although some of production lines are not fully operational. The accelerators with energy below 100kV have been accepted in the EB curing markets.

The consumption of comonomers, oligomers, and photoinitiators in 1999 showed a consistent tendency to increase based on 11,000, 13,200, and 1,140 tons in 1998, respectively. However, the consumption of acrylates was rapidly increasing after the summer of 1999, especially for optical fiber coatings, optical disk coatings, and film coatings, which had an annual growth of 30%. Inks and printed circuit boards had a 10% growth rate. The markets for raw materials in 1998 and 2000 are given in *Table* 6.

The total volume of radiation curable coatings, inks, photoresists, adhesives, and others in Japan was estimated to be as much as nearly 37,000 tons in 1999, as shown in *Table* 7. The annual volume growth rate was estimated at 9.4%.

Wood finishing in the coating industry remains the largest market for radiation curable products in Japan, as shown in *Table* 8. Recently, interior and exterior building materials by EB-finishing have been greatly increased. The market of UV/EB boards reached 1,150 tons in 1999, and 1,450 tons in 2000. The markets of hard coatings for headlight lenses, reflectors, audio parts, cellular phones, and optical fiber coatings have grown at high rates of over 17%. Japanese scientists have developed photocationically polymerizable materials with pencil hardness of over 7H, low volume shrinkage during photopolymerization, and good adhesion to glass. The largest markets for UV printing inks and photolithography are offset process and liquid resist, respectively. The in-line process consisting of UV-curable clear varnishes on oil-based lithographic printing is now being replaced by the

process of using both UV-curable varnishes and inks as a result of pricing decreases. New UV offset inks, which are soluble to conventional wash-up, with high gloss and good workabilities but low cost, or combining UV curing and conventional inks, have been also developed. Printing on CD is mostly performed by a UV process. Photocationic inks for can coatings are coming into the market. A photolithography process based on the demand of high resolution (L/S 50-70 μm) has been developed rapidly in recent years. Liquid resist including solder and etching resists, and etching mostly consist of acrylated epoxides modified with carboxylic acids.

EUROPE[5,6]

The total market for radiation curable resins in Europe was estimated to be between 50,000 and 85,000 tons in 2000, compared with 32,000 tons in 1995. The forecasted average annual growth rate is believed to be over eight percent for the next five years. Less than five percent of the total resins is used in EB curing. It is the still prohibitive cost of equipment and the rapid progress made in UV curing technology that caused the decline of EB curing technology.

In consumption of resins, acrylates represent the lion's share at 75%, whereas unsaturated polyesters are 24% and cationically cured resins only one percent. Cationically cured resins and UV curable-powder coatings are future growth areas. Epoxy acrylates still dominate the oligomer market, which shares 48% of acrylate comsumption, while the total volume share of polyester acrylates and polyether acrylates is 40%. Parallel with the development of cationically cured resins, the market of cationic photoinitiators is expected to grow. The European photoinitiator market in 2000 was estimated between 3,500 and 4,000 tons. *Table* 9 presents the relative share of each photoinitiator category. Acetopheno-type photoinitiators are expanding their market because of the decrease in cost. Multi-functional monomers TPGDA and dipropylene glycol diacrylate (DPGDA) are expected to grow at eight percent for the next five years, with three percent for HDDA and TMPTA.

Table 12—New Potential Growth Radiation Curing Markets

Applications	Probability of Commercial Success (%)
Pressure-sensitive adhesives	40-85
Wide web flexographic ink	40-80
UV cured powder coatings	49-90
Impactless printing (jet inks)	40-80
Clear coatings for exterior matalized plastics	40-80
Rotogravure inks	30-70
Clearcoats for exterior automobiles	20-70
Magnet wire insulation	20-70
Exterior coil coatings	20-70

The coatings market is still the largest sector for radiation curable resins in European market. UV curable-powder coatings are gaining increased interest due to their ability to flow out at low temperature and cure by very fast radiation-initiated crosslinking via radical polymerization.[9] Presently, there are two lines in operation and another two or three lines are expected by the end of the year. The development of low temperature curable powder and near-infrared curing powder will determine the future growth in such area. A waterborne UV technology, polyurethane dispersion (PUD) used in wood coating and packaging industries, is another one of high interest, because of advantages such as low viscosity, faster drying speed, no solvent, no isocyanate crosslinker, no monomer, and less shrinkage.

The total consumption of radiation curable printing inks and adhesives in Europe was estimated to be 10,000 and 5,000 tons in 2000, respectively. Offset and letterpress are still the primary applications of inks, representing 73% compared with 17% for screen and 10% for flexographic, while the future growth of inks mainly depends on the increase of the latter. With the replacement of mechanical fastening and welding by chemical bonding, adhesives are predicted to grow between 12% and 20% per year. The structural adhesives used in electronics, optical fiber, automotive components, medical, jewelry, and opto-electronics will grow over 30% per year over the next five years, based on their current small markets. The coatings for printed circuit boards (PCB) applications are the most important areas in the electronics market. The market for PCB resists in Europe represents about 12% of the worldwide markets.

Many new technologies have emerged to overcome the major shortfalls of traditional radiation curing technologies. Dual-cure system using a UV flash following conventional curing is a promising technology for car makers and paint companies, because it improves scratch resistant and reduces dry time of refinish paints.

NORTH AMERICA[7-9]

North America is the largest market in the world for radiation curable materials. The total volume of materials consumed was estimated to be over 80,000 tons in 2000 (*Table* 10) with a growth rate about nine percent, over 90% of which is believed to be cured with UV systems. *Table* 11 presents the growth rates of market segments in 2000. The relatively more mature segments such as wood products and

Table 13—Limitation of UV-Curable Systems and Technological Developments

Limitation	Technological Development
• High shrinkage	• Dual cure, water-borne UV, cationic systems
• Spray application problem	• Waterborne UV, UV-curable powder
• Difficult to cure 3D objects/insufficient cure in shadow area	• Dual cure, cationic systems, equipment adaptation
• Irritating formulation	• Waterborne UV, UV-curable powder, new monomers
• Insufficient surface cure	• Excimer lamps, dual cure, UV-curable powder, nitrogen blanketing
• Mainly indoor uses	• Daylight curing, UV-stablized UV-cured systems
• Applicable film thickness limited	• UV-curable powder

graphic inks have slowed, in comparison with some new market segments such as fiber optics, adhesives, and medical devices. The price of monomers and oligomers has been reduced by about 15%, and the most frequently used raw materials are still acrylates, representing 86%.

Developing raw materials with lower cost is one of the most necessary improvements for a radiation curing system in the next years. A great deal of work was engaged for reducing expensive urethane-based oligomers by replacing these with polyester or acrylic "backbone." The future growth rate for the next three years is estimated to be 8-10% per year, depending on the success of UV curing technology in new areas. Pressure-sensitive adhesives, wide web flexographic inks, and UV curable powder coatings are three of the areas with the most potential for growth (*Table* 12). The first two began their first large-scale operations in the late 1990s. Two lines of UV curable powder coatings were also set up in the U.S. in 1999. Clear coatings with good exterior durability have received great attention since they were described in several papers at RadTech Europe in 1999. Recently, much work has been done with aliphatic urethane oligomers and nonyellowing photoinitiators, which have been formulated into clear coatings with remarkably improved properties.

BARRIERS AND DEVELOPMENT

Major shortcomings of UV-curable systems and corresponding technological developments are listed in *Table* 13. Future developments in UV systems are concentrated into improving UV output at specific wavelength, excimer lamp, high-power (300 W/cm) lamps, high peak irradiance, reduced heat output, cold mirrors, dichroic mirror, compact UV sources, and variable powder output UV sources. Optical applications (DVD, LCD, Plasma filters), UV powder coatings, waterborne UV coatings for wood and plastic substrates, PCB (rigid and flexible), and composite materials are regarded as the most promising developments.

CONCLUSIONS

During the past years, the success of radcure technology has been sustained by specific characteristics which rapidly led to heavy crosslinked networks. Taking into account developments related to radcure such as lower viscosity oligomers, more efficient lamps, and photoinitiators generating less extractables, we may be sure of the expanding market for radiation curing.

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