Application of UV Cure Technology and Progress in Photopolymerization in China

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This report summarizes the 2007 output and production values of 129 leading Chinese coatings industry companies, including 40 that produce raw materials, 81 that manufacture UV formulations (some of them supply multiple products), and eight that supply UV lamps and equipment. A total UV/EB cure technology growth rate of approximately 13.5% in 2007 was estimated. It is noted that all the statistical data were from UV curing industries, because EB curing is still limited. Some recent progress in the application of UV technology in China is also briefly reviewed.

INTRODUCTION

The development of the coating industry is an important symbol of a country's industrial level. As concern about the environment increases, the coating industry is facing tremendous challenges. The market share of conventional solvent-based coatings has been reduced rapidly because of ongoing legislation to cut VOC emissions. In contrast, radiation curing, including ultraviolet (UV) and electron beam (EB) curing technology, is now being increasingly used in various application sectors because it is a clean and green technology that increases productivity as compared with other traditional curing methods.

Institutions and companies in China have been researching applications of UV/EB cure technology since the 1990s. While the market share of radiation-curable products is still small compared to that of the U.S., Europe, and Japan, the technology has been greatly expanded over the past 10 years, and is growing along with the Chinese economy.

RAW MATERIALS

Figure 1 shows the output and production values in China of raw materials, including monomers, oligomers, and photoinitiators, for the period of

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2003–2007. The output volume of monomers remained nearly the same in 2007 (49,213 tons) as in 2006 (48,024 tons), while production value decreased from US$ 205.71 million in 2006 to US$ 196.15 million in 2007. This is the first decline seen in recent years. The output of TMPTA and TPGDA was 15,480 tons and 16,250 tons, respectively, and HDDA and DPGDA were both more than 3,000 tons. The total export volume was over 15,972 tons with a dramatic increase rate of more than 100%.

Oligomers are the main block of UV coatings, and dictate the properties of cured films. Although a majority of high quality oligomers were imported just a few years ago, the production of oligomers in China has increased rapidly in recent years. In 2007, the output of oligomers was 31,595 tons with a growth rate of 15.2%, compared with 27,420 tons in 2006. Not only has the output of oligomers increased, but also the variety has broadened. Most of the produced oligomer products were consumed in domestic markets, and about 3,288 tons were exported to foreign countries including the U.S., Europe, and Asia.

Photoinitiators play an important role in UV curing. Both the production value and output of photoinitiators still show the fastest growth rates during the last year. The production value increased to US$ 217.85 million in 2007 from US$ 170.3 million in 2006 (an increase of 13%); and the volume increased 33.9%, from 22,053 in 2006 to 29,531 in 2007. Besides meeting the needs of domestic markets, more than 20,970 tons of photoinitiators were exported to foreign markets.

FORMULATION PRODUCTS

In 2007, the growth of domestic output, quality, and value of radiation-curing products was even more significant in comparison with past years. *Figure* 2 shows the output and production values for the UV curing market in China from 2003 to 2007 in detail. UV coatings and inks still remained the largest application areas in China. The total output of UV coatings (produced by 51 manufacturers) and inks (37 manufacturers) was 32,530 tons and 14,648 tons with growth rates of 12.1% and 13.6%, respectively, in 2007 compared with 2006. The production values had corresponding increases—US$ 180.2 million for UV coatings and US$ 151.79 million for inks with growth rates of 30% and 24%, respectively. Most impressive was the output and production value of UV adhesives, which increased by 73% to 846 tons and 110% to US$ 10.13 million from 2006 to 2007. These UV adhesives are used not only in medicine, glass, craftwork, packing, and fishing equipment, but also in LCDs, DVDs, instruments, and optic parts.

Wood coating is still the largest application market in China, with the parquet flooring segment still

Figure 1—Output (ton) and production value (US$ millions) of raw materials (2003–2007).

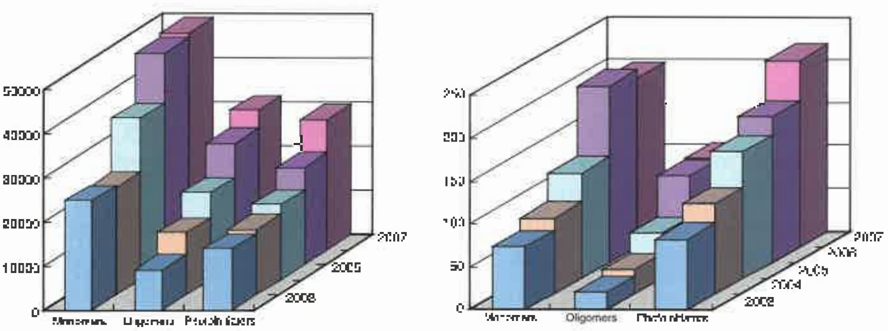


Figure 2—Output (ton) and production value (US$ millions) of formulations (2003–2007).

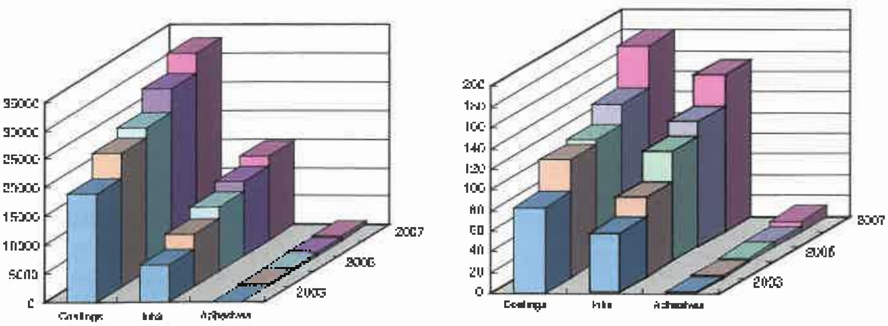


Figure 3—Output (ton) of coatings and inks with significant growth rates.

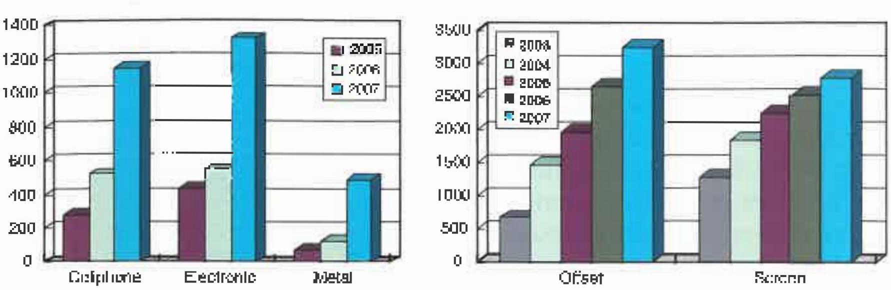
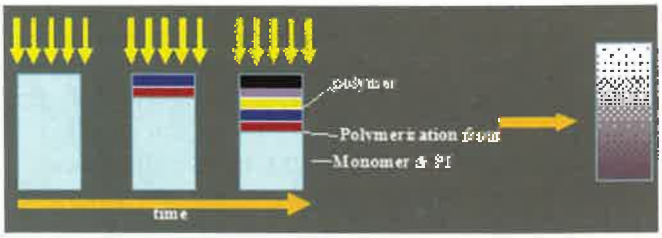


Figure 4—Schematic process of Frontal Photopolymerization (FPP).



the primary consumer. The output of wood coatings grew gradually from 2003 to 2005. However, it increased rapidly in 2007—up to 16,815 tons with a growth rate of 22%. This healthy spike should continue for another three to five years. Plastic coating steadily retains its market share mainly with PVC for tiles, flooring, and motorcycle applications.

As shown in *Figure* 3, UV coatings have become widely used for cell phone, metal, and electronic applications, which posted dramatic growth rates of 94%, 300%, and 120%, respectively, in 2007. It proves that some special-use coatings will be new growth spots in the Chinese market and will initiate ardent competition in the foreseeable future. The offset and screen-printing applications also maintained a steady increase and will persist for several years.

UV LAMPS AND EQUIPMENT

In 2007, 288,000 UV lamps and 2,497 UV-curing equipment pieces were manufactured and 59 lines were established by eight companies. Both the quality and the variety of lamps and equipment were improved. Some unusual lamps that were imported a few years ago are now presently manufactured by Chinese companies on a large scale. Moreover, UV measuring instruments such as UV radiometers, UV energy meters, and even on line UV monitors (display and control panel) are produced domestically.

DEVELOPMENT OF COMPANIES INVOLVED IN UV CURING

The UV-curing market continues to experience positive growth rates in China. As a result, there are favorable opportunities for many companies to flourish in the radiation-curing market. According to the current survey, the scale of manufacturers has been expanding. Twenty-six companies each produced more than 2,000 tons of UV curable formulations in 2007; among that group, seven corporations manufactured over 5,000 tons. A production value of over US$ 30 million was obtained by eight corporations during 2007.

EB-CURING TECHNOLOGY IN CHINA

Limited by the high price of accelerator, the development of EB applications is still slow in contrast to UV applications. However, as the price of low energy accelerator decreases in the future, EB technology will be very promising in the radiation curing market in China. An EB-curing trend has already started to gradually reveal itself in the past few years. Several EB lines for printing applications were installed in recent years and an EB-curing technology center for research and development of EB-curing technology was established in Chengdou by Sichuan University and NHV (Japan) in 2006. The research and development of EB-curing technology in China will enter into a new stage.

RECENT PROGRESS IN UV PROCESSING TECHNOLOGY

Great attention has recently been paid to the research and development of UV processing technology in China, and some remarkable progress has been achieved. The following is a short review of research conducted by Chinese scientists.

Frontal Photopolymerization

Frontal polymerization is a reaction mode of converting monomer into polymer via a localized and propagating reaction zone (see *Figure* 4). Yang et al. have extended this technology to UV photoplymerization and have done extremely good work.[1,2] In contrast to the traditional thick film photopolymerization, a pure polymer without residual monomer was produced with frontal photopolymerization. The vertical gradient distribution of the molecular weight and its

Figure 5—UV irradiation unit and production line of cable.

polydispersity of the frontal photopolymerized rod are found, which is in accord with the attenuation of light intensity in a polymerization tube. Using the frontal photopolymerization of acrylates in the presence of organic zirconate and iodonium salt, an axial gradient polyacrylate/nanozirconia hybrid rod was fabricated. The nanozirconia, in-situ generated in the frontal polymerization matrix with the photocatalysis of iodonium salt, was presented with top-down distribution in the hybrid rod, both in particle size and in particle concentration. A mechanism of induced enrichment of iodonium salt and organic zirconate during frontal photopolymerization process was proposed. The refractive index of the hybrid rod increased along with the front traveling direction and reached 1.540 at the depth of 7 cm from the top.

Photo-crosslinking of Polyolefin

The photo-crosslinking process for polyethylene and its industrial irradiation apparatus have been developed recently by Qu and coworkers and applied successfully for industrial manufacture of photo-crosslinked polyethylene (XLPE) insulation wires and cables[3,4] (see *Figure* 5). The photo-crosslinked XLPE insulation low voltage (1 kV and below) and medium-high voltage (10–35 kV) power cables possess excellent electrical and mechanical properties, and have much lower operating costs compared with traditional crosslinking techniques such as peroxide chemical crosslinking, alkoxy silane crosslinking, and high-energy electron beam irradiation crosslinking methods. Moreover, the photo-crosslinking technique has unique advantages such as low investment cost, easy operation and maintenance, energy savings, environment-friendly, high production efficiency, etc. Four Chinese patents were authorized for the photo-crosslinking invention and an international (PCT) patent application has been submitted.

Photografting Used for Superhydrophilic Polymeric Films[5,6]

The UV irradiation-induced surface-grafting approach for producing superhydrophilic polymeric films has some advantages, such as ordinary facility, lower invested capital, and easy operation (see *Figure* 6). Moreover, the homogeneous products generated during grafting reaction are easily removed by simple water washing.

Figure 6—Sequential processing instrument for superhydrophilic films with UV lamps.

The charge transfer complex (CTC) system consisting of maleic anhydride (MAH), vinyl acetate (VAC), butyl vinyl ether (BVE), or N-vinyl pyrrolidone (NVP) containing high reactive group was used to graft with polymeric films. The higher monomer conversion, grafting degree, and efficiency were obtained. The relationship of surface grafting degree, morphologic behavior, and surface composition was investigated in detail. This technique can be used to prepare various functional materials, such as antibacterial nonfabric.

CONCLUSIONS

As the Chinese economy develops steadily and quickly, growth in the radiation curing industry will continue in well-established areas—for instance, wood and paper coatings, screen and offset inks, etc. A major effort will be made to develop new technologies and new raw materials for the radiation curing industry, and to enter into new application fields such as composite and gel coats, automotive OEM and refinish coatings, and so on. CT

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