

By Alexander Ross, PhD

## THE PROBLEM

Ground level ozone is one of the major air pollutants that the EPA is trying to control. Not only is it a major cause of smog, but it is a health threat especially for persons with lung, bronchial and other breathing problems. The EPA reports that more people in the USA are exposed to unacceptable levels of ozone than all the other criteria pollutants combined. Ozone is also harmful to growing plants resulting in agricultural losses. This low-level ozone is not a natural air constituent. It is generated from the reaction of volatile organic compounds (VOC) with oxides of nitrogen (NOx), another major pollutant. Until now, we have not been successful in reducing the Nox levels in the air. The task of removing the ozone from the air therefore falls on the control of VOC. The major sources of VOC are the industries that use them as solvents under conditions that release them to the atmosphere.

Until now, whenever a manufacturing process required the application of thin layers of polymeric materials to large surfaces, it was customary to dissolve or disperse that polymer in solvents, spread them on the substrate and then drive off the volatile solvent with heat. This has been typical of paints, coatings, inks, adhesives and similar materials. The major solvents used are VOCs, including benzene, toluene, xylenes and other aromatics as well as acetone, methyl ethyl ketone, methyl isobutyl ketone and some alcohols. Some of these solvents, such as the aromatics and the ketones are also listed as Hazardous Air Pollutants (HAP) which are subject to special federal regulations by the EPA. The amounts of such pollutants emitted by industry are huge. For example, the latest Toxic Chemicals Release Inventory (TRI) for 1997 shows the following emissions data:

## VOLATILE ORGANIC COMPOUND/HAZARDOUS AIR POLLUTANTS POUNDS EMITTED

Toluene 113,000,000

Xylenes 80,000,000

Methyl Ethyl Ketone 53,000,000

Methyl Isobutyl Ketone 16,000,000

(All the above are listed as Hazardous Air Pollutants as well as VOC)

Attempts have been made to reduce these emissions by minor changes in the resins used in the subject products. The advent of high solids products and water dispersible products has succeeded in emissions reductions in the early years of EPA control. More recently, however, the steadily growing economy has overcome the partial advantage of the minimal change approach and emissions are again high. The only way to handle the emissions and maintain a thriving growing industry is to remove the culprit solvents completely, at the source. This approach has bred powder coatings, which contain no solvents. Powder Coatings have been successful in replacing solvent based coatings on many heavy metal substrates. Because of their high temperature cure requirements, conventional powder coatings cannot be used on

temperature sensitive substrates such as paper, plastics and wood.

## **THE SOLUTION**

The development of ultraviolet (UV) and electron beam (EB) technology has succeeded in the generation of solventless, liquid products that perform as well or better than their solvent based counterparts as paints, coatings, inks and adhesives without the emissions into the atmosphere. This development involves a basic change in the composition and chemical reactivity of resin ingredients.

Instead of using large molecule polymers, the UV/EB approach uses short chain oligomers (more about these later). The oligomers are dissolved in monomers with similar reactivity. These mixtures can then be formulated with pigments and other additives used in the respective trades and applied to the surface to be treated using conventional techniques. In the case of EB, simple exposure to a stream of electrons causes copolymerization of the oligomers with the monomers to form a solid surface containing 100% of the component materials without any emissions. For UV curing, photoinitiators are incorporated into the formulation. These materials break down under the influence of the ultraviolet light generating free radicals, which then propagate the copolymerization in much the same way as in the EB case. In a newer version of this technology, the initiators generate cations which then initiate cationic polymerization with the oligomers and monomers to generate virtually 100% solids.

The free radical approach is based on acrylate polymerization and most of the monomers used are acrylates. The oligomers however are much more diverse. The basic resins used can be any of the resins traditionally used in such products, e.g. acrylates, urethanes, polyesters, silicones, epoxies, etc. such polymers are reacted with acrylic acid, hydroxyethyl acrylate or other such reagents to attach acrylate end groups on the resins, making them UV/EB polymerizable. Using these resin ingredients have allowed UV/EB to provide a very wide range of performance properties, to meet virtually all needs of the target industries.

This radiation curing technology has been around for some 30 years, but only recently has it begun to achieve solid growth in the industrial world. Industry, in general, is reluctant to accept new technology, especially when it requires equipment changes, product changes, re-educating production staffs and convincing their customers that the new product is as good or better than the previous products. With the advent of non-volatile monomers and improvement in equipment design and costs, UV/EB technology has begun to take off in the past five years. It now has a steady annual growth rate of 10-12% in the coatings/ink industry where overall growth is 1-2%/ year. Although the environmental advantages of the products has been a driving force in getting industrial establishments to consider this new technology, it has been some of the other, unique advantages of the system that have led to the modern, rapid commercial growth of the technology.

## **ENVIRONMENTAL ADVANTAGES**

UV/EB systems generally contain no HAP chemicals, thus totally relieving users of the special regulations covering such materials.

Because UV/EB systems may have negligible emissions (some by-products from photoinitiator reactions), operators who switch to them can show tremendous reduction in emissions, generally removing the operator from the "major source" category. As an example, the Coors company who makes over four billion beer cans a year switched their production entirely to UV curing. They reduced their emissions in the manufacture of each billion cans from 28.9 tons /year for a water based enamel to 1.677 tons/ year for a UV cured acyclic (free radical) enamel and thence to 0.224 ton/year for a UV cured epoxy (cationic) enamel. In short they reduced their emissions by 94% using the acrylate and over 99% using the epoxy, without the use of add-on pollutant collection and destroying equipment.

When an operation is no longer a major source, there are many advantages to the operator in terms of relief in obtaining and maintaining permits, keeping detailed records, making detailed periodic reports to the EPA, etc. Some states, e.g. California (South Coast) and New York already have regulations exempting UV/EB operations from obtaining permits.

### **HEALTH AND SAFETY**

Although early in its history, UV/EB used volatile monomers which caused irritation of the eyes and skin, the monomers now used are non-volatile and air borne irritation has been eliminated. Contact with the liquid products can still cause irritation to some susceptible individuals; however, the normal health and safety rules involving use of aprons, gloves and eye protection constitute a safe milieu for the workers. A two-year feeding study on selected acrylate monomers showed no negative carcinogenic or teratogenic results, leading the EPA to cancel the SNURs that it had proposed for the class of compounds.

### **ADVANTAGES FOR INDUSTRY**

As described above, the chemistry of UV/EB technology is based on backbone resins long used in the target industries. This means that almost any resin used in solvent-based products today can be made into UV/EB curable oligomers. This gives the technology a very broad scope of performance capabilities, enough to satisfy most industrial needs, as can be seen from description of some of the industries currently using UV/EB (see below). Other advantages of UV/EB are:

- \* Low temperature cures No heat is required for complete cure, allowing use on all heat sensitive substrates.
- \* No need for curing ovens. Elimination of curing ovens saves on cost of fuel for heating such ovens; saves on floor space taken up by such ovens; and eliminates the emission of air pollutants associated with the burning of fuels.
- \* High speed curing Cure time is reduced from the usual oven cure of 15 min or more to mere seconds or fractions thereof, thus allowing for higher production rates and greater efficiency.
- \* Coating Stability Most coatings lose solvent and hence increase in viscosity during application. This may require halting operations and making adjustments. In printing operations, loss of solvent causes inks to solidify on the presses requiring frequent shut downs for press cleaning. This results in loss of production time and materials. UV/EB materials have no solvent to lose, hence need not suffer these shut downs. In fact some UV/EB press operations are

stopped overnight and started up the next day without the extensive and expensive start up procedures.

\* No Add-on Controls needed Since there are no emissions from UV/EB it is not necessary to install collect-and-destroy equipment, thus saving on expensive capital outlays, cost of operation and emissions from burning fuel in the incinerators.

## **INDUSTRIAL USES**

Although UV/EB is still a rapidly developing technology, it is already enjoying some substantial uses in a number of varied industries.

**FIBER OPTICS UV/EB** is considered an "enabling " technology for the development of fiber optics, which require protection from breaking, fraying and other hazards in the manufacturing process. UV/EB provides all the necessary protection on the raw fibers and on the cables into which they are formed by curing thoroughly at the high speeds required for commercial operations.

Estimated Usage in 1999: 2400 tons

**WOOD PRODUCTS** Wood must retain a certain level of moisture to perform properly. It cannot tolerate high cure temperature. As a consequence cure times for wood products are excessively long. As a result much wood product manufacturing and finishing has converted to UV/EB. The very rapid complete cure allows for greater production rates. There is an added saving in time because the extensive cool down periods formally used prior to shipment are no longer needed in the ambient temperature UV/EB cure. This applies to furniture doors, paneling, flooring, molding and a host of other wood products.

Estimated Usage in 1999: 12,500 tons

**PLASTIC PRODUCTS** Most plastic products are thermoplastic and thus susceptible to heat, imposing temperature limitations on their finishing. Many of them have converted to UV/EB for the same reasons described above for wood products. These include such products as:

- \* Plastic Bottles - for toiletries and other chemical products.
- \* Sports Equipment - golf balls and clubs, skis, helmets, etc.
- \* Medical Equipment – fluid containers, syringes, blood pumps, etc. where the immediate setting of UV adhesives is a great boon.
- \* Cans and other containers
- \* Automotive Applications e.g. making headlamp assemblies, lens covers, wood trim

Estimated Usage in 1999: 5200 tons

**GRAPHIC ARTS** involving Lithography, Flexography, Screen Printing, Offset, etc. This includes the printing of magazines, annual reports, labels, catalogs, folding cartons, cereal boxes milk cartons, juice containers, etc. Includes inks and overprint varnishes

Estimated Usage in 1999: 36,000 tons

**ELECTRONICS** including coating of CDs, DVDs, circuit boards, conformal coatings, etc. The construction of DVDs requires several UV cured products, including inks, coatings and adhesives.

Estimated Usage in 1999: 4,000 tons

**SILICONE RELEASE COATINGS** used in labels, decals, etc.

Estimated Usage in 1999: 700 tons

**ADHESIVES** for laminating, pressure sensitive and structural adhesives.

Estimated Sales in 1999: 1500 tons

**GLASS PRINTING & COATING** Automotive glass, consumer bottles, etc.

## **CONCLUSION**

Virtually all users of UV or EB have been able to increase their production while keeping their emissions well below the standards of EPA and state regulations. Many have also been able to widen their product line as a result. In essence, UV/EB can give almost zero VOC emissions, the ultimate in ozone elimination, without impeding industrial growth. Indeed, the added efficiency, high performance, economic savings due to elimination of ovens and collect-and-destroy facilities can result in increased profits for the forward looking companies that employ the UV/EB technology.