

50 Years

of Epon®* Resins

By John G. Dickerson

Automotive Finishes

Epoxy resins, particularly Epon® resins, played a role in improving the performance of automotive finishes during the last half of the twentieth century.

Automotive finishes have undergone continuous improvement from the time the "Horseless Carriage" was introduced. Each improvement was the product of research and development by raw material suppliers, paint chemists, application equipment manufacturers and automotive engineers. The following summary of major developments in the resinous component of auto finishes illustrates the extent of improvements over the years, with no slowdown in sight. Similar strides were made in pigments — some readers will recall maroons, blues and grays that chalked prematurely — and in application systems, from brush to spray to powder.

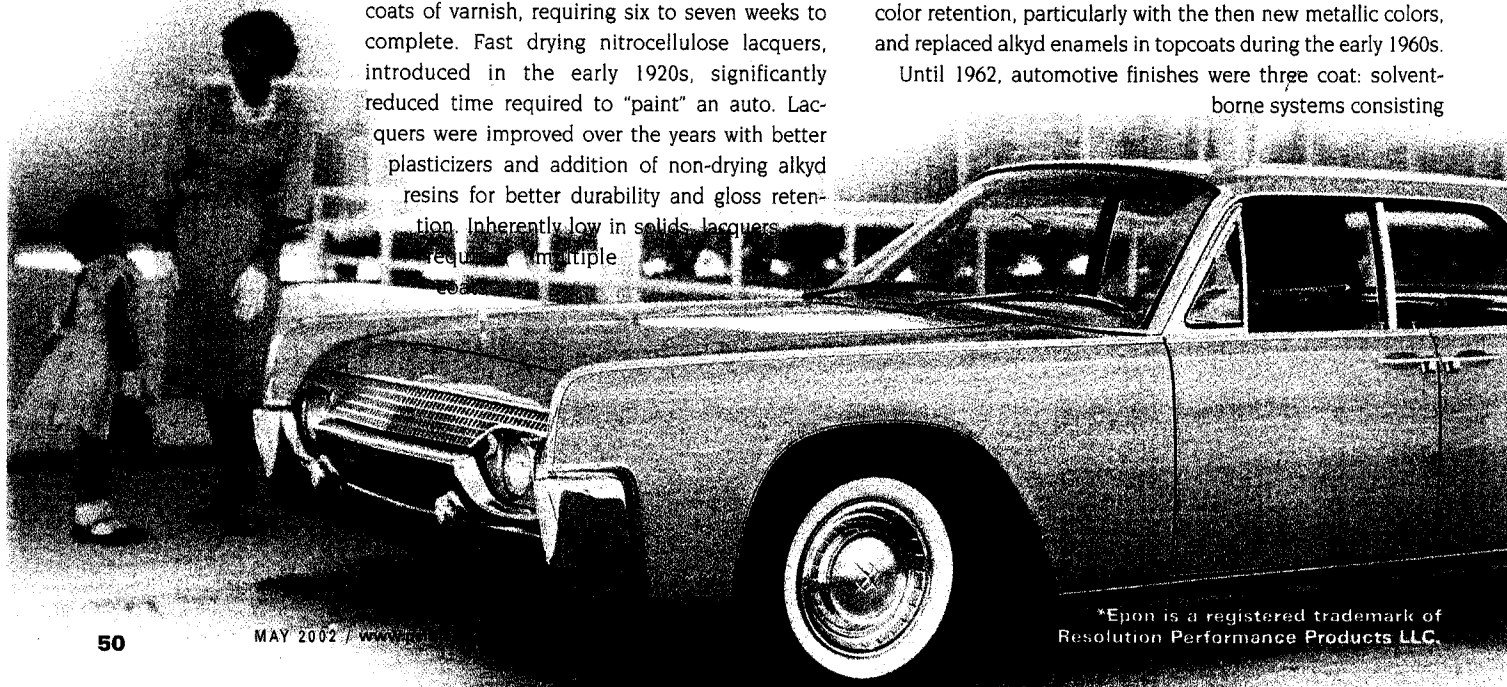
The first auto finishes were slow drying oleoresinous varnishes, a carry-over from the days of horse-drawn carriages. Fine carriages were finished with up to 16 coats of varnish, requiring six to seven weeks to complete. Fast drying nitrocellulose lacquers, introduced in the early 1920s, significantly reduced time required to "paint" an auto. Lacquers were improved over the years with better plasticizers and addition of non-drying alkyd resins for better durability and gloss retention. Inherently low in solids, lacquers required multiple coats to achieve sufficient film thickness for acceptable performance.

Despite this shortcoming, nitrocellulose lacquers were a dominant component of auto finishes for over 30 years.

Another major development occurred in the late 1930s with the introduction of drying oil phthalic alkyd resins, commonly referred to as "alkyds." Alkyd resins enabled paint chemists to formulate coatings with nearly twice the film build of nitrocellulose lacquers. Chrysler, Ford¹ and others adopted alkyd resin based finishes. General Motors continued to use nitrocellulose lacquer until the mid 1960s.

The 1950s brought several improvements. Alkyd topcoats underwent an improvement in gloss and color retention with the introduction of nondrying-oil alkyds crosslinked with butylated melamine resins. Epoxy ester primers and primer surfacers became available, significantly improving corrosion resistance of coating systems. Acrylic lacquer topcoats with improved gloss and color retention, replaced nitrocellulose. Thermosetting acrylic topcoats offered improved gloss and color retention, particularly with the then new metallic colors, and replaced alkyd enamels in topcoats during the early 1960s.

Until 1962, automotive finishes were three coat: solvent-borne systems consisting



of a primer, a primer-surfacer and a color topcoat. Application was by spray gun, except for one company that applied primer by dipping the entire body in a tank of primer. In 1962, Glidden and PPG introduced waterborne epoxy *anodic* electrodeposition primers to replace solventborne primers. Auto parts and complete bodies were dipped in tanks of primer. These waterborne primers improved corrosion resistance, eliminated fire hazard, and were adopted by most automakers. The term "e-coat" became the common abbreviated description of electrodeposition primers. In 1977, PPG Industries introduced an improved epoxy based aqueous *cathodic* electrodeposition primer that significantly improved corrosion protection. Cathodic "e-coat" soon became the primer of choice throughout the world, a position still held at the end of the century.

During the 1980s, the automotive industry replaced the single topcoat with a color coat and a clear acrylic topcoat, to accommodate new, more colorful pigments and increased use of metallics. This change provided a more durable, higher gloss appearance.

During the 1990s, several automotive manufacturers replaced spray applied primer *surfacers* with electrostatically applied epoxy-polyester hybrid powder. Today, automakers have generally settled on a four-coat system for automotive finishes — cathodic electrodeposition primer, primer-surfacer, color coat, and clear topcoat.

Solventborne Epoxy Ester Primers and Primer Surfacers

Epon Resin Ester Primers

When epoxy resins became available in the late 1940s, nitrocellulose lacquers and alkyd resins were the vehicles of choice for automotive primers, primer-surfacers, and topcoats. In their early evaluation of epoxy resins (1946/47), Devoe & Reynolds Co.² demonstrated that an alkyd topcoat applied over an epoxy ester primer was far superior to an alkyd topcoat applied over an alkyd primer. The epoxy ester primer improved adhesion to untreated or phosphate treated steel, provided better flexibility, improved resistance to corrosion from salt spray and detergents, and reduced blistering during immersion in hot water. These properties suggested a potential market in automotive and appliance coatings.

In 1950, shortly after Shell opened its Union technical service laboratory, chemists Bud Wittenwyler and Bob Bayes undertook an evaluation of Epon resin esters. They prepared Epon 1004 esters from

every commercially available fatty acid and evaluated a myriad of performance properties of both air-dry and baked coatings. They found that esters made from Epon 1004 reacted with tall oil or soybean fatty acids (the choice dependent on the price of the acid), when cured with a small amount of urea formaldehyde resin, could be formulated into outstanding automotive baking primers. These Epon resin ester primers provided at reasonable cost, several key properties desired and needed by auto manufacturers, particularly:

- outstanding adhesion to metal
- excellent corrosion resistance, including elimination of corrosion where two dissimilar metals meet - for example, where a chrome door handle meets the steel auto body
- good flexibility and impact resistance that contributed improved chip-resistance to the coating system

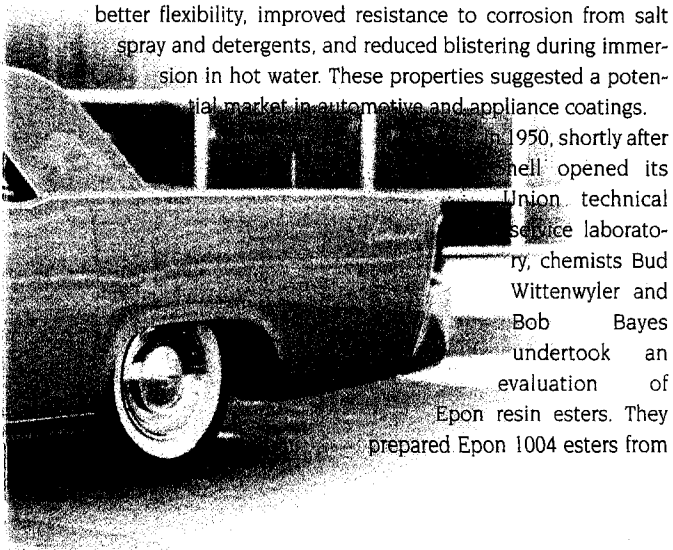
Despite these improved properties it was not easy to persuade paint companies to adopt and promote Epon resin ester primers to the auto industry. Most paint suppliers had their own alkyd kettles and proven formulations, so were reluctant to adopt and promote primers based on the more expensive, unfamiliar Epon resins. Shell elected to promote Epon resin ester primers directly to automotive manufacturers. Largely as a result of presentations directly to auto manufacturers by Harry Howard³ and others from Shell, auto manufacturers requested epoxy ester primers from their suppliers. By the early 1950s, epoxy esters became the principal vehicle for spray or dip-applied solventborne auto primers. They retained this dominant position for nearly three decades.

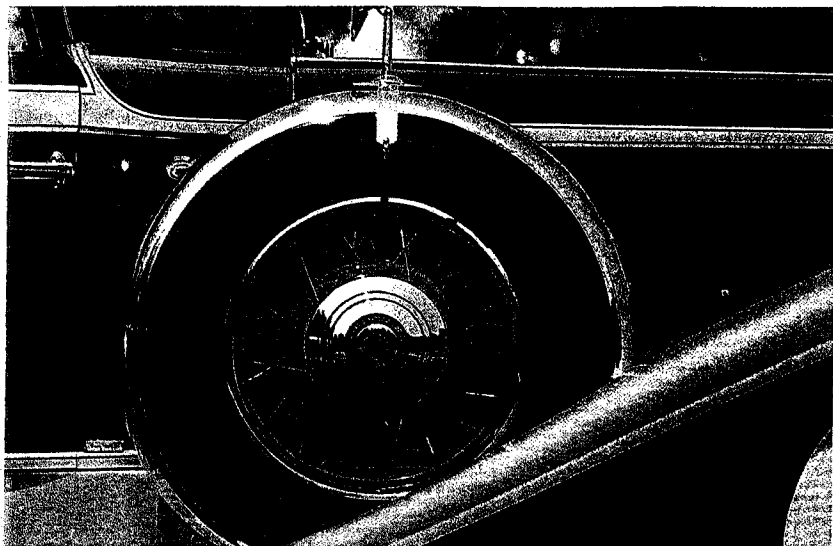
As best we can recall, major suppliers of epoxy ester primers to the auto industry during this period included the following.

- E.I. DuPont de Nemours and Co.
- Pittsburgh Plate Glass Co., which became PPG Industries in 1968. This included Forbes Finishes Division in Cleveland and Ditzler Color Division in Detroit.
- Rinsched-Mason in Detroit, subsequently acquired by Inmont and then by BASF
- Ferbert Schoendorfer in Cleveland, acquired by Valspar

PPG's Holste⁴ recalls that PPG's Milwaukee plant made their first solventborne Epon 1004-fatty acid ester auto primers in the early 1950s. American Motors Corp. used the primer in a dip tank for auto bodies at their Kenosha and Milwaukee assembly plants. Each afternoon PPG loaded a batch of Epon ester, plus pigments, solvents and additives into a 4,000-gal ball mill that ran overnight. The next morning the primer was transferred from ball mill to tank truck and delivered to American Motors.

This was the first attempt to dip auto bodies in primer to eliminate bare spots not reached by the conventional spray method. American Motors was the only auto manufacturer to dip complete auto bodies into a bath of solventborne Epon ester primer. (Other auto manufacturers applied primer by





conventional spray.) The dip tank released solvent vapors to the atmosphere creating a potential fire hazard, but American Motors used the system successfully for several years, eventually replacing it with waterborne electrodeposition primers when the latter became available.

Epon Ester Primer-Surfacers

When epoxy resins were introduced in the late 1940s, common practice in the auto industry was to apply a primer-surfacer over the prime coat. Primer-surfacers contained more filler pigment than did primers. They served as a sandable coating to provide a smoother surface for the topcoat. Primer-surfacers were also designed to promote adhesion between primer and topcoat. Epoxy ester primer-surfacers were developed soon after epoxy ester primers (early 1950s) and dominated the automotive primer-surfacer market for nearly thirty years. Their decline began in the mid-1980s, and by 1990 epoxy esters were completely replaced by solventborne polyester primer-surfacers.⁵ To a major extent, their demise was caused by the adoption of more transparent acrylic topcoats. Unless carefully formulated, the more transparent topcoats allowed ultraviolet light to reach and degrade the epoxy primer-surfacer, resulting in delayed adhesion failure of the coating system.

A New Way To Make Epoxy Esters

For many years the preferred method for making epoxy esters was to react a medium molecular weight solid epoxy resin such as Epon 1004, with varying amounts of fatty acids depending on the desired "oil length". In the late 1950s, Union Carbide Corp. intro-

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duced a method of manufacturing epoxy esters from 1) Union Carbide's liquid resin, ERL-2774 (similar to Epon 828), 2) additional bisphenol-A (BPA) and 3) fatty acids, in sequential steps in one kettle. The procedure involved first reacting a calculated amount of liquid resin, BPA and a small amount of fatty acid, plus a processing catalyst. By selecting various ratios of resin and BPA, resin chemists could produce the equivalent of a solid epoxy resin of any desired molecular weight. After the reaction of resin, BPA and part of the fatty acid was complete, additional fatty acid was added to the kettle and the reaction continued, to make an epoxy ester of the desired oil length. This method gave coating and resin chemists wide formulating latitude with respect to molecular weight of the resin component and oil length of the ester, all in one kettle. In addition it eliminated handling 50-lb bags of solid resin, and slightly reduced overall manufacturing costs compared with making esters directly from solid resin. Resulting esters were dark in color, apparently caused by the processing catalyst, but color was not a problem in formulating auto primers. The first epoxy ester primer vehicles made at PPG's Springdale, PA plant used this process.

High Molecular Weight Epon Resin Primers

In the late 1950s Rinshed-Mason Co. requested Shell's assis-

tance to develop a flash dry-primer. R-M wanted a primer that could be top coated right after the primer was applied so the entire coating system could be baked in one operation. R-M also wanted primer that would improve chip resistance of the total coating system. Joe Manasia and his group at UTSL found that a primer formulated from Eponol® 55-B-40, met the customer's requirements. (Eponol 55-B-40 is a 40% solution of a very high molecular weight linear epoxy resin dissolved in methyl ethyl ketone.) Film formation is by solvent evaporation; no curing agent required. Rinshed-Mason used Eponol 55-B-40 for several years to make a flash dry primer for General Motors. It was applied on areas that were prone to chip and rust caused by small flying stones, especially around headlights, on rocker panels under the doors and around fenders.

Wyandotte Paint Co., Wyandotte, MI, also used Eponol 55-B-40 to make a zinc-rich primer. The product, trade named "Zincrometal®," was used to coat coiled steel to replace galvanized steel. Much of the Zincrometal coated steel found application in automotive parts.

Waterborne Primers

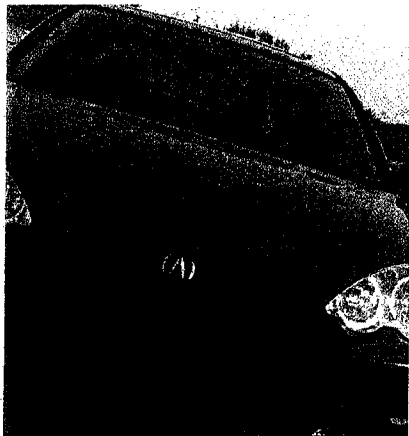
On August 12, 1953, a disastrous fire occurred at General Motors' four-year-old Detroit Transmission and Ternstedt



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Instrument plant at Livonia, MI. The fire started when sparks from an outside contractor's welding torch fell into a drip pan filled with a low flash point rustproofing compound. In less than an hour the 1.5-million-square-foot plant was a burning ruin. The response throughout the auto industry was a drive for less flammable materials. Auto makers particularly wanted a less flammable coating system.

An Epon Ester Water-Dispersible Primer

In 1958 Shell undertook a project to develop a water-reducible auto primer.

Chemist John Lopez and his group at UTSL discovered a way to emulsify a 50%-solids solution of Epon 1007-soya fatty acid ester and dilute it with water to make a satisfactory coating. Auto primers made from this system exhibited outstanding salt spray resistance, flexibility and improved chip resistance. This system had one drawback: it could not be applied satisfactorily by electrostatic spray, a method rapidly being adopted by the automotive industry. Soon after Lopez's water-reducible Epon resin formulation was introduced to

the paint industry, the auto industry began moving toward electrodeposition. This once promising waterborne epoxy primer was never used commercially.

Electrodeposition: Anodic and Cathodic

In the early 1960s, a group at Ford Motor Co. under the leadership of Dr. George E.F. Brewer introduced a revolutionary new concept of applying primer to auto bodies. They called it electrocoating. The process, more precisely defined as anodic electrodeposition (AED), was based on the principle of a negatively charged waterborne primer being attracted to and plated out on a positively charged auto body.

Clayton May, a researcher at Shell's Emeryville research laboratories, recalls Dr. Brewer explaining the new process during a visit to Emeryville in 1964. The entire auto body is immersed in a tank containing a low solids aqueous dispersion of primer. The auto body serves as the positive pole in a direct current system; the primer receives a negative charge from the tank or metal electrodes in the tank. Negatively charged primer particles are drawn to the metal auto body, forming a uniform, continuous film over its entire surface. After about two minutes the deposited film insulates the body so no more primer is deposit-



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ed. Dr. Brewer noted the following advantages of the process.

- **Complete coverage:** All metal surfaces were covered, particularly recessed areas previously missed or inadequately coated because of geometrical constraints during spray application.
- **Reduced fire hazard:** Water was the major component of primer in the tank.
- **High primer utilization:** No primer lost to overspray.
- **Better handling on production line:** Auto body could be washed and coated with primer-surfacer immediately after being primed.

Brewer's group proved the principle of applying primer by electrodeposition, but first attempts to develop a practical, effective low solids water dispersible primer were unsuccessful. Ford invited three paint companies, Glidden, PPG and Ferbert-Schoendorfer, to develop and supply a functional anodic electrodeposition primer suitable for use on a commercial scale. Glidden⁶ and PPG accepted the challenge and within approximately two years, developed suitable waterborne AED primers. Glidden's Alan Gilchrist is credited with developing the AED primer first used by Ford in 1962 at its wheel plant in Wixom, MI. About the same quantity of steel was primed in small tanks at the wheel plant as would be primed in large tanks in a body plant. In this respect, the Wixom plant served as a pilot application to refine the primer and process before proceeding to a full body application. Gilchrist patents were assigned to Ford Motor Co., some say to help ensure Glidden's position as a supplier of AED primer to Ford.

Following successful application at Wixom, Glidden and PPG supplied AED primer to several Ford body and frame plants, one of the first being at Mt. Clemens, MI.

The first AED primers were maleated oils and typically consisted of linseed oil reacted with maleic anhydride, copolymerized with vinyl toluene or styrene; some were modified with a phenolic resin. Water reducibility was achieved by treatment with ammonia. These were soon superseded by more complex molecules such as maleated epoxy esters, and styrene-allyl alcohol copolymers (Shell's RJ-100[®] resin⁷), modified with fatty acids. The move to these higher molecular weight resin systems was an attempt to improve penetration of primer into recessed parts of auto bodies - or to use the technical vernacular, to increase the "throw power"!

Even these higher molecular weight systems left much to be desired with respect to corrosion protection. Shell's George Velten recalls a visit to Ford's Dearborn, MI facilities where he observed results with RJ-100 based AED primers. Ford chose to evaluate the R-J 100 primer system on their Lincoln Continental[®] line because performance could be monitored best on a line of cars built in limited numbers and generally returned to an authorized service center for check-up. Velten observed premature corrosion on several fairly new Lincolns that had been removed from service and cut open to examine recessed areas. Primer performance was less than satisfactory.

Even during the early stages of development, Ford's Dr. Brewer reportedly believed that *cathodic electrodeposition* (CED) was the better way to apply primer than AED (in CED the auto body is



negatively charged and the primer positively charged.) Because technology was not available, Ford and their principal suppliers, Glidden and PPG, continued developing AED primers.

Glidden developed a butadiene-styrene water dispersible system that provided better corrosion resistance than the maleated oil systems. PPG's final and best AED primer vehicle was a dispersion made by polymerizing styrene and butadiene on a "soap" prepared from a maleated epoxy ester. About that same time in Europe, Kurt Herberts, (a Hoechst company), developed an AED primer based on maleated liquid 1,4-polybutadiene. Ford was impressed with the performance of the Herberts primer on Ford autos produced in Germany. The Herberts primer had good salt-spray corrosion resistance, but became brittle over time.

Shell Research on Electrodeposition

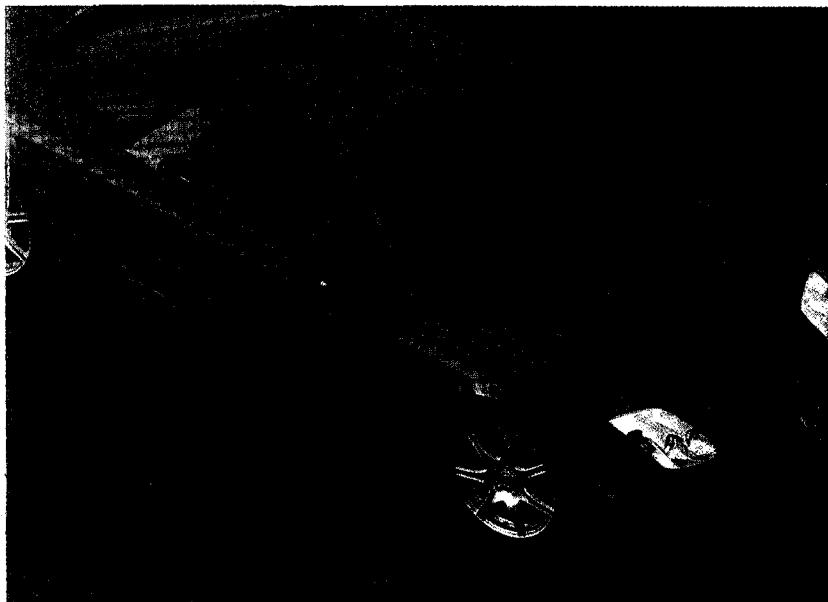
Spray-applied epoxy resin fatty-acid-ester primers had dominated the auto primer market for over a decade beginning in 1950 and represented a significant market for Shell's Epon resins. Revelation of this new electrocoating process which could threaten a major part of Shell's epoxy resin business, spurred research activity at Shell laboratories in the U.S. and overseas. In the U.S., Shell Development Co. Emeryville Research Center (ERC) concentrated on the theoretical aspects of electrodeposition while the overseas product applications laboratories at Egham, England and Delft, The Netherlands, worked on formulations and performance testing. Results of the early work by Shell were presented in the spring of 1966 at a European Paint Society (FATIPEC) meeting in Holland. Shell Development, ERC contributed the theoretical portion and Delft presented practical formulations.

Derek Shingleton, a chemist at Shell's Egham (England) Laboratory, recalls a humorous incident that occurred later when he was on temporary assignment at Union technical service laboratory in New Jersey. A Shell Chemical technical sales representative took Derek to PPG Industries to discuss water

dispersible maleated epoxy resin esters that Derek had been working on at Egham. The following week, Derek was amused to read in the Sales Rep.'s visit report that "Shingleton presented Shells new *marinated* Epon resin ester."

Research on electrodeposition theory at Shell Development Co.'s ERC, conducted primarily by Clayton May and his group, continued for about six years, from 1965 thru 1971. May's work covered almost every aspect of electrodeposition. He conducted a wide range of studies on theoretical and practical aspects of electrodeposition. For example he evaluated numerous different types of vehicles, including maleinated Epon esters, butadiene polymers, diallylphthlate and many more. He studied effects of anode and cathode selection and voltage requirements; anionic valence state; metallic ion concentration and weight of primer deposited as a function of deposition time; and a host of other variables.⁸

May's studies resulted in several surprising discoveries. For example, May determined that during *anodic* electrodeposi-



tion, significant quantities of iron and zinc, from the galvanized steel auto body, were dissolved into the primer coat, resulting in large concentrations of iron, zinc and other metal ions at the primer-metal interface. These metal ions formed a convenient bridge for passage of corrosive materials, such as moisture and salt, through the coating to the interface and were the cause of premature failure of the coating system. He also pictorially demonstrated that positive and negative poles were formed during electrodegradation of anodic coatings by salt water. He showed that application of primer by *cathodic* electrodeposition (wherein the auto body is negatively charged and the primer bath positively charged) did not cause metallic ions to migrate into the applied primer. The obvious conclusion was that for maximum salt-spray resistance, primer should be applied by *cathodic* electrodeposition, not *anodic*.

May presented the results of his work at the 46th Annual Meeting of the Federation of Societies for Paint Technology in New York City on October 24, 1968. He won the prestigious Roon Awards Competition prize for his contribution to the science of coatings technology. May won a second Roon Award in 1970 for a study on the effects of electrodeposition on galvanized metal surfaces. May lectured on his research and conclusions at local Paint Club meetings across the country and made several private presentations to major customers.

PPG Industries was the only company to "grab the ball and run with it." They were major suppliers of AED primers and were already researching cathodic electrodeposition when May presented the results of his research. Whether encouraged by May's research or not, PPG did an outstanding job of developing and patenting CED primers and application processes. PPG became the principal supplier of CED auto primers worldwide, a position they still hold.

As the result of PPG's major research effort on Epon resin based CED systems and the apparent lack of interest by other paint companies, Shell reduced its research and development effort on CED, to technical service support and Epon resin quality improvement.

The move from anodic to cathodic electrodeposition was a major technological development that resulted in a landmark improvement in the performance of automotive finishes. The switch by automakers from anodic to cathodic, was accelerated to a great extent by results of tests conducted on complete autos at a test track in Arizona.

Dr. Ivor Pratt, retired Director of Worldwide Research at ICI-Glidden, and Hilary Holste, retired Director of Resin Process Engineering at PPG recall what turned out to be a defining test of electrodeposition primers. In 1976, Ford conducted extensive tests to determine the best AED auto primer. They finished 40 Mustangs® and tested them under the worst possible conditions at a test track in Arizona. This was the largest scale test Ford had ever conducted. Primers tested included Glidden's butadiene-styrene system, Herbert's maleinized polybutadiene, PPG's styrene-butadiene maleinized epoxy ester and a few others. At the last minute PPG submitted a "new product" for inclusion in the Mustang fleet test. Ford allocated 4 mustangs to test PPG's new entry. The Mustang test fleet was driven 24 hours a day for weeks on a test track that included gravel sections and a "hot box" – a chamber in which the test vehicles were subjected to rain water, salt spray and 100% relative humidity at 100° F. One cycle on the test track and in the hot box was deemed equivalent to one year's driving under "normal conditions." The test was designed to provide the worst possible conditions a car could be expected to encounter. The tests were so severe that over a period of 5 to 6 cycles, gas tanks were sometimes corroded out!

Ivor Pratt was an observer at the Ford Development Center when the Mustang bodies and test panels were evaluated. Bodies were cut open to observe the extent of corrosion protection on interior spaces. Unlike the year 2000 Presidential race, the results were immediately conclusive and convincing.

Glidden's butadiene-styrene system performed better than the maleinized oil systems, but PPG's "new product" was far superior to all the rest. The winner was PPG's first CED primer. Ford had modified their electrocoating tank to accommodate the PPG CED primer to coat four Mustang bodies for the test.

Glidden decided not to pursue the automotive coating market and instead concentrated on appliance and can coatings. Glidden made a major technical breakthrough and as a result, achieved a dominant position in can coatings.

PPG Industries' Development of Cathodic Electrodeposition Primers

Dr. Roger Christenson, now retired from PPG, recalls that PPG had two groups working on cathodic electrodeposition under Dr. Howard Gerhart. One group, led by Dr. Marco Wismer, developed a CED primer system, based on a solid epoxy resin as the backbone, with quaternary amine groups. The system was made water soluble with organic acids. Cure was accomplished with melamine resins. Although suitable for appliance applications, the baking time and temperature were excessive for automotive applications. The colloidal stability of this system was poor, causing operational problems. Although Wismer's was the first commercial CED system, it was eventually discarded.

The second group, under the direction of Christenson with Robert Jerabek and Robert Zwack as principal investigators, followed a different approach. They developed a CED system based on an Epon resin with pendant amine groups, cured with blocked isocyanates, e.g., toluene diisocyanate. The system cured well at existing automotive production schedules. The epoxy backbone, which contributed the inherently good adhesion and corrosion resistance, was a major factor in the outstanding performance of this system.

Christenson had great confidence in his new CED primer and convinced Fred Rhue, then PPG's Automotive Finishes marketing manager, to promote CED against Kurt Herbert's apparently successful competitive maleinized polybutadiene AED system. As a protective measure, Rhue had taken a license for the Herberts AED system. Christenson's clincher in his discussion with Rhue was, "The worst case is they'll fire us both. The best case is we'll have a winner." The rest is history. Christenson's cathodic system was a resounding success as first proven on the Arizona test track. PPG obtained most of the significant patents on cathodic electrodeposition. Years later, on March 17, 1992, Dr. Roger Christenson received the prestigious Brewer Award "in recognition of outstanding contribution and service to the development and use of electrocoat."

The automotive industry was quick to accept CED after its commercial introduction in 1977 because it provided corrosion resistance far superior to any other primer system. PPG developed several types of "E-coat" to meet individual customer's needs by modifying the basic vehicle with plasticizers, flow additives and other proprietary compounds. Most CED primers now use oxime-blocked toluene diisocyanate as the curing agent.



Photo courtesy of PPG Industries Inc.

An auto body entering an e-coat tank.

PPG had to solve many practical problems to develop a complete system suitable for automotive production schedules. Design and materials for construction of the anodes had to be established. Conductivity of the system required close control. Completely new and different membranes had to be designed for PPG's CED ultra-filtration system, a major contribution to the commercial success of e-coat. [In the PPG process, the object being primed is given a clear water rinse immediately after passing through the primer tank to remove loosely held primer particles. This dilute solution is then subjected to ultra filtration. Clear filtrate is returned to the rinse cycle and retained solids are returned to the primer bath.]

There were scale-up problems in making the CED resin. Hilary Holste remembers that at the outset PPG had no commercial equipment to make the polymer. A 1,500-gal reactor at the Springdale, PA plant, normally used for another resin, was pressed into service and supplied resin for CED primer to two General Motor's plants over a two-year period. They moved up to a 5,000-gal reactor at the new Oak Creek plant, just south of Milwaukee, and were able to produce CED primer in 10,000-gal batches. Control of molecular weight was critical to avoid rough films. This problem was solved during the early years by adopting precise manufacturing specifications and controls and by monitoring customers' CED tanks continuously⁹. PPG's dedication to customer technical support was another key to early success. Teamwork and significant contributions by many people resulted in PPG's successful CED process. This development is reported to have required a team of 25 chemists, engineers, and technicians working for about nine years!

In a private communication to this editor, Dr. Christenson summed up PPG's CED development rather nicely: "There is a tendency for everyone who mentions cationic or cathodic electrodeposition to believe they invented the idea. There was



agreement that such systems would be better (than anodic) due to less attack on the substrate. The trick was to design a CED system that worked and cured at reasonable temperatures. This is what PPG accomplished."

An epoxy resin with narrow, tightly controlled specifications, particularly low saponifiable chloride content, was essential to the successful production of CED primers. Shell and PPG worked for several months to agree on specifications for a special quality Epon resin to meet PPG's U.S. requirements. Shortly thereafter, PPG began standardizing its CED technology worldwide and requested Shell supply epoxy resin meeting similar narrow specifications from its Epon®/ Epikote® resin plants worldwide. (Epikote is Shell's trademark for its bisphenol-epichlorohydrin resins outside the U.S.) This was not an easy task because Shell employed different processes to manufacture epoxy resins in some of its overseas plants. After many months of testing and collecting statistical manufacturing data from three Shell plants (Deer Park, TX; Stanlow, England and Pernis, The Netherlands) and of evaluating CED production from various PPG plants, agreement was reached on a mutually satisfactory set of worldwide specifications. George Velten, who coordinated this effort for Shell, credits PPG's Hilary Holste for facilitating agreement on worldwide specifications. Being from the manufacturing side, Holste was understanding of Shell's problems in developing one narrow specification for product manufactured by different processes, at different plants, in different countries.

PPG's patented CED product and process soon became the industry standard for priming automobile bodies. Within a few years, PPG had a major share of the worldwide CED auto primer business. This enviable position was achieved both by direct supply from PPG plants and by early licensing agreements with companies such as Ford Motor (Paint Division), and Inmont in the U.S., Nippon Paint in Japan, ICI and BASF in Europe, plus others in Australia and South Africa. Dupont acquired a license with its purchase of Ford's paint business. PPG later established their own CED primer manufacturing

plants worldwide. PPG continues to develop improved CED technology and remains the world leader in CED products.

Readers interested in more technical aspects of electrocoating may wish to read Brewer's "Electrodeposition of Paint", Chapter 34, in *Applied Polymer Science*, by Roy W. Tess, Second Edition, American Chemical Society, Washington DC, 1985.

Recent Developments in Primer-Surfacers Epoxy Polyester Powder Primer-Surfacers

Powder primer-surfacers based on epoxy-polyester hybrid resin systems, are a recent innovation in automotive coatings. Small volumes of epoxy-polyester powder primer-surfacers were used at two truck and auto plants in the mid 1980s. These first powders were applied directly over electrocoat primer primarily to improve chip resistance on rocker panels. In 1983, GM applied full body powder primer-surfacer (1-2 mils thick) to S-10 trucks at their Shreveport, LA plant. The powder was an epoxy-polyester hybrid supplied by Glidden and incorporated one of Shell's Epon 2000 series resins developed especially for powder coatings.

By 1985, PPG had assembled a world class powder research team at Allison Park and in 1986 opened a powder manufacturing plant in Strongsville, OH. In the early 1990s, PPG initiated a serious research and development program to expand use of powder primer-surfacers on entire auto bodies. Driving forces for broader use of powder technology in the auto industry included:

- Enactment of the 1990 Clean Air Act, effective in 1996, requiring lower emission of VOCs. Powder coatings contribute essentially no VOCs, thus making it easier to obtain permits for new or expanded facilities, as well as meet reduced emission standards at existing plants, with minimum capital investment.
- Need for improved chip resistance due to the new, more aerodynamic, low slope hood designs.
- Need for improved ultraviolet light protection for electrocoat primer.
- Need to reduce/eliminate the cost of incinerating solvent vapors from spray booths.

Richard S. Tansey, who in 2000 was market development and technical manager, Automotive Powder Coatings at PPG's Strongsville, OH facility, has been directly involved in powder primer development since 1992. He describes the rapid growth of powder primer-surfacer, as "The Evolution Within the Revolution."¹⁰ The following summary of this revolution in powder technology is based largely on an interview with Tansey in October, 1999.

When PPG introduced their waterborne CED primer, "e-coat", to the auto industry in 1977, corrosion resistance was the major requirement considered. E-coat was applied at relatively thin films, 0.6 to 0.8 mils. Solventborne epoxy ester or polyester primer-surfacer was applied directly over e-coat. About 1981, PPG introduced "Uniprime®" a reformulated e-coat primer that could be applied in thicker films, i.e., about 1.2 mils. Uniprime served as a single primer for corrosion protection and chip resistance comparable to that provided by an e-coat and solventborne primer-sur-

facers. Several auto body plants adopted Uniprime and realized substantial savings by eliminating a primer-surfacer. As a result of developments/ trends in (color) base coat and (top) clear coat, these finish coats become more transparent to ultraviolet light. About the same time, after a few years of outdoor exposure, delamination of auto coatings at the e-coat interface was observed. The specific causes of delamination are complex and a function of the entire coating system. However the increased transparency of the topcoats and the potential of the epoxy based e-coat primer to degrade on exposure to UV light was thought to be a factor.

While nearly zero VOC was a major plus for powder primer-surfacers, several other attributes had to be addressed to develop a commercially viable product, namely:

- Appearance (smooth surface)
- Superior chip resistance
- Ultraviolet light protection for the e-coat primer
- Efficient powder utilization.

To produce a commercially acceptable powder primer-surfacer, all of the above had to be realized at an applied cost competitive with existing systems.

Appearance was found to be a function of base resin type, film thickness, powder particle size, type of application (electrostatic spray or bell¹¹), and baking schedule (time and temperature to melt, level and cure the powder).

Chip resistance was found to be a function of base resin type, film thickness, compatibility with topcoats, and body design. The new aerodynamic, low slope nose design was more prone to chip. As development proceeded, attention went from evaluation of chip resistance of the powder primer itself to consideration of design of the entire coating system, (e-coat, powder primer, base color coat and clear topcoat) as it affected chip resistance.

Ultraviolet light protection was found to be a function of base resin type and formulating techniques to maximize UV opacity.

Product utilization was found to be dependent on application equipment, design of the track that carries the auto body along the production line, air vent system, sieve screen technology and vacuum retrieval system.

Evolution of a commercially viable full body powder primer-surfacer was a result of successive incremental improvements in each of the above categories.

PPG evaluated four types of base resin systems for powder primer-surfacers:

- Epoxy-polyester hybrid: epoxy resin plus a carboxylated polyester.
- Polyester-urethane: polyester crosslinked with blocked isocyanate.
- Polyester- Primid^{®12}
- Acrylic crosslinked with DDDA (didecane dioic acid)

More detailed descriptions of evolutionary developments leading to commercially acceptable primer surfacers may be found in Tansey's articles and papers.

In 1993, Chrysler Belvedere, IL, plant expanded their use of epoxy-polyester based powder primer from rocker panels to

Several achievements account for the rapid escalation of epoxy-polyester powder primer from a few units at two plants in 1994, to over 2,000,000 units at eight Chrysler plants in 1998.

front hood and fenders, to improve chip resistance. Based partly on experience at the Belvedere plant, PPG made important modifications to their epoxy-polyester product, learned how to manufacture it better, and how to apply it better. By 1994 PPG was confident their hybrid powder primer-surfacer was ready for full auto body application.

In May 1994 Chrysler installed a full body, electrostatic epoxy-polyester primer-surfacer system at its Sterling Heights, MI, plant. A similar system began operation at Chrysler's St. Louis assembly plant in October of that year.

From this modest beginning, full body powder primer-surfacer has grown to nearly 3 million auto body units in the United States and Canada. By 1998, epoxy-polyester hybrid systems were in use at eight Chrysler plants; polyester or polyester-urethane systems were in use at five General Motors plants. Half a million more units are expected to use powder primer in the year 2000 and another half million in 2002. This substantial growth attracted the attention of all suppliers and has resulted in increased technological improvements in all aspects of powder primer-surfacer.

Several achievements account for the rapid escalation of epoxy-polyester powder primer from a few units at two plants in 1994, to over 2,000,000 units at eight Chrysler plants in 1998. One was PPG's ability to formulate a product that gave desired smooth appearance, good chip resistance, and eliminated the de-laminating problem, when applied in thin films (2.0 to 2.5 mils). Another was improvement in total product utilization, which turned out to be more difficult than simply vacuuming up unused powder in the application area. All plants are running at 96 to 98% total powder usage, with the potential to reach 99% utilization. Panel exposure tests in Florida and experience with automobiles on the road, indicate any UV degradation of epoxy resin in the epoxy-polyester system does not occur, as evidenced by elimination of delamination.

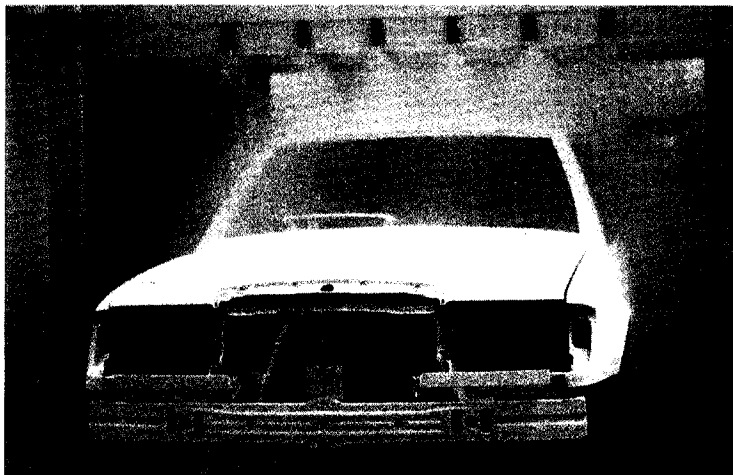
Powder primer-surfacer has established its place in the auto industry. The predominant auto finishing system in 2000 consists of four coats:

- Epoxy based aqueous cathodic electrocoat primer. Negligible VOC.
- Powder primer-surfacer. Dominant technology is epoxy-polyester. Zero VOC.
- Solvent or waterborne polyester base color coat.
- Solventborne acrylic clear coat.

Future Outlook

It would appear that the inherent properties of epoxy resins —

Photo courtesy PPG Industries Inc.



Horizontal Application of Hybrid Powder Primer Surfacers Using Bell Application

particularly corrosion protection, adhesion, toughness, and flexibility — will ensure their role in automotive primers for many more years. However in this dynamic industry we can certainly look forward to unique and unanticipated developments to reduce VOCs and to improve the durability, appearance and easy maintenance of auto finishes. At the turn of the century, it seems powder and waterborne epoxy systems will be the systems of choice for primer and primer surfacer. ●

Author's Note

For over 50 years, EPON® was Shell Chemical Co.'s registered trade name for its brand of epoxy resins. On November 14, 2000, The Royal Dutch Shell Group transferred its worldwide Resins and Versatics business to the New York based private investment firm of Apollo Management LP. The business now operates under the name Resolution Performance Products LLP, with headquarters in Houston TX. Resolution Performance Products acquired the former applicable Shell trademarks as well as R&D, production, distribution and sales of Epon® epoxy resins; Epi-Cure® curing agents; Cardura® and Veova® monomers; Bisphenol A; Allyl Chloride; and Epichlorohydrin. References to Shell with respect to the above noted products and trade names, relate to activities that occurred prior to sale of the business to Resolution Performance Products LLP.

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Editor's Note

This article is an edited excerpt from a book entitled "Fifty years of Epon® Resins, A History of the Epoxy Resin Business," in preparation by John G. Dickerson. Copyright to the book is held by J.G. Dickerson.

The author acknowledges the following contributors: Shell Chemical retirees Clayton May, John Lopez, George Velten, and C.V. Wittenwyler; PPG Industries retirees Hilary Holste

and Dr. Roger Christenson; Glidden retiree Ivor Pratt; and Richard Tansey, Market Development and Technical Manager, Automotive Powder Coatings, PPG Industries

Footnotes

- ¹ Ford operated its own paint plant at Dearborn, MI, for many years. DuPont acquired the Ford paint operations and plant in 1986.
- ² Devoe and Reynolds Co. was primarily a trade sales paint supplier but conducted research on resins and related materials. The Jones-Dabney Division developed, manufactured and marketed industrial finishes. J-D was a major supplier of automotive, appliance marine and container coatings.
- ³ Harry Howard headed application and technical service work on Epon resins at Shell's Union Technical Service Laboratory.
- ⁴ Hilary Holste, at the time of his retirement in 1998 was Director of Resin Process Engineering in PPG's coating business.
- ⁵ Epoxy- polyester powders and specially formulated e-coats are the newest developments in primer surfacers.
- ⁶ Glidden was acquired by SCM Co. in 1967 and for many years was known as SCM-Glidden. In 1984, the business was acquired by Hansel Trust and in 1985, acquired by the present owner, ICI
- ⁷ RJ-100 was a styrene-allyl alcohol copolymer developed by Ed Shokal and Paul Devlin at Shell Development Co., Emeryville California. Shell manufactured and marketed RJ-100 for a while as X-450. Marketing rights were later sold to Monsanto Chemical Co.
- ⁸ For more information on some of Clayton May's work, see "Dissolution of the Anode During Electrodeposition of Surface Coatings", Clayton A. May and George Smith, Journal of Paint Technologies Vol. 40, No. 526 November 1968, Pages 494-502. Also Smith, G., and May, C. A. Papers, Am. Chem. Soc. Div. Of Organic Coatings and Plastic Chem., 28, No 1, 480, San Francisco, April 1966.
- ⁹ A chemist who joined PPG in 1977 recalls that the first CED tank was filled that year at an assembly plant in Framingham, MA. He was assigned the responsibility of monitoring the CED tank and process He commuted weekly from Cleveland to Framingham for 11/2 years, an indication of the level of service required during the introductory period.
- ¹⁰ See "Automotive Powder Primer The Evolution Within The Revolution" presented at SUCAR XVIII, 1997. Copyright by SUCAR est organisé par SURFACES 25 rue Dagamo - 75012 PARIS. Also "Environmental Aspects of Automotive Powder Primer", International Body Engineering Conference, October 1996. Copyright International Body Engineering Conference, Warren, MI 48092.
- ¹¹ Auto body is positively charged; powder is negatively charged. Bell is an application process developed by SAMES around 1995. Powder is introduced through a center tube, falls onto a rotating disc where it receives a charge and is distributed onto the car body like a waterfall in the shape of a bell.
- ¹² EMS- Primid is a tetrafunctional crosslinker.