Tech Talk

Fine Lines in High Yield (Part CLVIII)

Forty Years of Dry-Film Photoresist Technology

Karl H. Dietz (for CircuiTree Magazine, November, 2008)

When Jack Richard Celeste of the DuPont Company submitted his patent application for a dry film photoresist to the US Patent Office on September 11, 1968 (see Fig. 1) he could have hardly imagined how his invention was going to change the world of printed circuit board fabrication. My reflections on the forty year history of dry film resist is somewhat anecdotal and may not be always perfectly accurate for which I want to apologize in advance.

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3,469,982
PROCESS FOR MAKING PHOTORESISTS
Jack Richard Celeste, 40 Cameron Court, Freehold, N.J. 07728
No Drawing. Continuation-in-part of application Ser. No. 477,016, Aug. 3, 1965. This application Sept. 11, 1968, Ser. No. 759,217
Int. Cl. G03c 1/90, 5/00; G03f 7/10
U.S. Cl. 96—35.1 15 Claims

ABSTRACT OF THE DISCLOSURE

A process for forming a photoresist which comprises:
(1) applying to a surface the surface of an unexposed photopolymerizable layer, the other surface being adhered to a film support, then in either order
(2) exposing the layer, and
(3) stripping the support, and finally,
(4) washing away the unexposed areas of the layer. The surface bearing the resist can be etched, plated, or treated in other ways.

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films. Still further objects will be apparent from the following description of the invention.

The process of this invention for forming photoresists on metal or other surfaces, including glass, ceramics, etc., comprises:

(1) applying to a surface a solid photopolymerizable layer having a thickness of at least 0.00005 inch and low to moderate adherence to a thin, flexible, polymeric film support (e.g., .00025–0.008 inch or more); preferably with heating or later heating at a temperature from 40° C. to about 150° C. to increase the degree of adherence between said surface and said layer; then, in either order,

(2) exposing the layer, imagewise, to actinic radiation to form a polymeric image; and

(3) stripping the film support from the resulting image-bearing layer;

(4) washing away the unexposed areas of the layer to form a resist image of polymeric material; and

(5) permanently modifying the adjacent areas on said surface which are unprotected by the resist image by using a reagent capable of etching said areas or depositing a material on said areas. Where the surface is inorganic, step 5 can be eliminated

Figure 1: The J. R. Celeste patent for dry film photoresist

The technical team in Parlin, NJ under the direction of Abe Cohen had started work on dry film photoresists in 1963, and was able to commercialize the first solvent processable dry film (Riston® Type I) in 1968. Earlier research on photopolymers conducted by Louis Plambeck at DuPont's Central Research facilities in Wilmington, DE had yielded fundamental knowledge but had not led to a commercial product. Since the printed circuit board industry had no infrastructure for processing dry film, novel wet processing

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equipment, imaging systems and processing chemicals had to be introduced along with the dry film. Since early dry films were solvent processable, solvent processors, strippers (chlorinated hydrocarbons), solvent stills and solvent decanters had to be introduced. The transition to aqueous processable resists, was pioneered by Dynachem (Morton Electronic Materials). Hoechst was a later entry and its dry film business was later acquired by Dynachem. Semi-aqueous processable dry films were introduced by DuPont in 1971 (Riston® Type II). These new resists required different developer and stripper chemistries. Developer chemistries typically used mixtures of borax and alkoxy-alcohols (glycolethers), and strippers were alkoxy-alcohols, sometime mixed with ethanol amines. It should be noted that solvent processable and semi-aqueous processable dry films had excellent processing latitude, and that aqueous processable films had to come a long way to gain acceptable performance. So it is not surprising that solvent processable films were around for quite some time, especially at large OEMs, long after the introduction of aqueous resists.

The adoption of the new dry film technology was facilitated by the establishment of Technology Support Centers such as DuPont's Imaging Technology Center in Newark, Delaware in 1973. Dry film quickly replaced, but never completely eliminated the incumbent photosensitive liquids, such as Kodak's KMR and KPR. The liquid coatings at that time were more prone to defects and suffered lower yields than dry films. The transition from solvent processing to aqueous processing was spurred on by environmental concerns. In this context, it should be noted that DuPont developed a solvent-less coating technology for the manufacture of dry film.

Dynachem's first fully aqueous dry film was Laminar® A which was beta site tested in 1969-1970.followed by Laminar® AP (1970) which had limited success. Dick Beaupre who formulated Laminar® A remembers that he used only off the shelf commercially available materials for this composition. The very successful Laminar® AX had its debut in 1971. The "X" in its name stood for "experimental", but it stuck. Notable members of Dynachem's technical and business teams were Mike Gilano, Mel Lipson, Dick Beaupre, Gene Weiner, Dan Feinberg, Walt Custer and others I may not remember. They helped Dynachem succeed at Western Electric and IBM. Other suppliers entered the field in the US such as Xidex (later Hercules), then MacDermid. In Europe, BASF and Hoechst entered the market for a few years but exited later. In Japan, Hitachi Chemical was the first supplier, followed by Asahi, TOK and Mitsubishi. Kolon became a local supplier in Korea and several Taiwanese suppliers emerged, notably Eternal which is now one of the largest global suppliers. The field had opened up with the expiration of DuPont's basic patent in September of 1986.

The better known leaders on DuPont's team in the early years are probably Bill Wartel, Carl Gates and Jim Hickman. DuPont had licensed technology to Dynachem, and after settling an infringement suit with Hitachi, Hitachi started to coat dry films in Japan. When Dynachem had grown so fast that it had outstripped its cash resources it was bought by Thiokol and continued to prosper. Gene Weiner reminisced old war stories, when he killed a peel-apart dry film development at Dynachem in the early 1960s because the technology always gave ragged lines and would not be suitable for the anticipated finer lines and spaces. Gene also shared with me a story about a most unusual cold storage facility to supply Litton in Springfield, Mo, with dry film. There were nearby caves that served as "air-conditioned" warehousing.

In the mid70s, DuPont introduced a variety of process equipment that became quite popular: the first hot roll laminator (HRL-24) in 1974, a vacuum laminator (SMVL), and a PC Printer featuring double-drawer high-intensity dry film exposure. The first dry film soldermask was also introduced in 1974.

Japanese suppliers had developed very high resolution dry film resists and good tenting resists in the 1990s. In this context it is worth mentioning the acquisition of the Nippon Gossi Dry Film by Morton from Nippon Chem which resulted in the Nichigo Morton J. V., later a part of Rohm & Haas.

In more recent developments, most suppliers now offer high speed dry films for laser direct imaging (LDI) and specialty plating applications. Dry film photoresists also found new applications beyond PWB fabrication, such as graphic arts, phone cards, sandblasting, wafer-level packaging, and displays.

Not surprisingly, new coating capacity is only being installed in Asia where most of the dry film is used today.

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