Investigation of Spray Oxides

by Rudy Sedlak

Examining the effect of surfactants on oxide formations resulted in more than was expected.

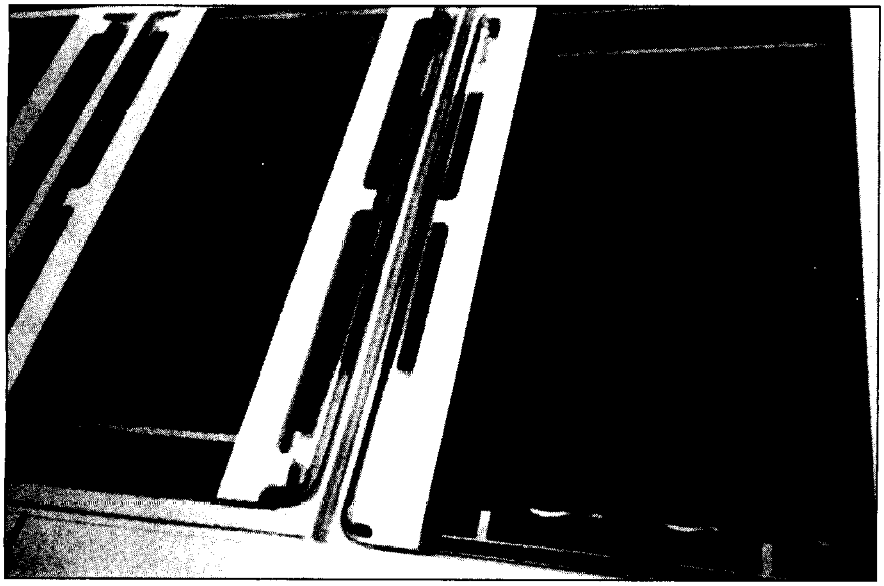

Figure 1. *Panels in spray oxide chamber.*

More than two years ago an investigation was started into the effects of organic crystal growth modifiers on the performance of conventional caustic- and chlorite-based oxide systems. The plan was to develop an oxide system that would create a smaller and more amorphous crystal structure. The new system would also have higher peel strengths and greater resistance to thermal stress and pink ring problems. These goals were subsequently achieved but proved to be only a fraction of the benefits discovered.

Water-soluble polymers and surfactants are well-known for their effect on crystal formations such as oxide growth. Both are used as agents for causing crystal formations to be smaller and less crystalline or more amorphous. Polymers are generally used at much lower levels and have a more subtle effect on crystal formations. Surfactants, on the other hand, tend to be used at higher levels in solutions and usually have more profound effects on the crystals formed.

THE EFFECT OF SURFACTANTS

Deciding which agent to investigate was easy because the use of water-soluble polymers in oxide systems was already patented. The question we had was why another major supplier had not already investigated the effect of surfactants on oxide formation. We quickly found, however, that almost no surfactants are compatible and stable to the aggressive conditions found in an oxide bath. Fortunately, early research revealed enough promising results to keep the project alive and ultimately led to our filing for patent protection on the use of surfactants in oxide systems (U.S. Patent No. 4,512,818).

Of the 50 surfactants examined, most actually caused the oxide performance to ı deteriorate. Seven were found to be acceptable and to significantly improve the performance of the oxide system. These surfactants had a number of effects on the oxide coating, al, good.

The firs beneficial effect we noted was that surfactants speed up oxide formation dramatically. A panel immersed into a conventional oxide system usually seeds (or initiates) at widely spaced points, and the oxide grows together from these points to cover the panel. The same panel immersed in the same chemical system with an appropriate surfactant seeds at so many points that it looks as if the panel is being uniformly and immediately covered, resulting in virtually instantaneous initial coverage. This combination produces shorter processing times. Speed, however, is not the most important effect of surfactants on the oxide.

It is commonly known that achieving a uniform oxide requires absolutely perfect cleaning and, occasionally, the help of the supernatural. Further, when the oxide coating is lighter (redder), the cleaning and rinsing requirements are more stringent and the peel strength is greater. Research revealed that the addition of a surfactant to an oxide system significantly minimizes color variation. This effect makes the use of high-peel-strength, red-bronze oxides a reality, instead of a technically desirable but unmarketable idea. By adding the proper surfactant to the oxide chemistry, we were able to achieve an extremely uniform oxide on a consistent basis, panel to panel and edge to edge, even in the tough red-bronze color range (Figure 1).

The uniformity seen is due to the fact that the oxide seeds simultaneously over the whole surface rather than at widely dispersed points. Thus, no one area has time to develop more thoroughly than another. The fact that the surfactant turns the oxide into a mild cleaner also helps in obtaining uniformity.

SPRAY APPLICATION

The next step was to investigate the possibility of spraying this new system, enhancing speed and uniformity characteristics. Other oxide systems have been sprayed, but they require titanium spray modules. The results were so nonuniform that the boards produced were not commercially acceptable. (One major captive producer dubbed his spray oxide Rambo because it resembled camouflage.)

Initial testing was done in a converted conventional (horizontal) dry-film stripping machine. The results were gratifying. The spray system retained a.1 the benefits that we had seen in an immersion system.

All this research was being done under the assumption that polypropylene spray modules would be used to keep the capital investment required for this process at an acceptable level. It was also presumed that polypropylene could easily handle a temperature of 160°F. With our system, were able to produce any color oxide in two minutes. However, just about the time the process had been put to bed, we were told no manufacturers would guarantee their equipment using oxide chemistry at temperature over 140°F. Decreasing the temperature would have required a four-minute process time in the oxide. This would have doubled the cost of the oxide module and jeopardized the commercial acceptance of the program.

So we went back to the laboratory and found that by increasing the oxidizer concentration and adjusting the rest of the system to compensate, we were able to lower the process time to two minutes at 140°F.

SURFACE PREPARATION

To ensure consistently uniform results even with the light (red) oxide, the preparation line must be appropriate. During our research of the oxide, another industry-shaking development was revealed. Mechanical scrubbing, even the hallowed pumice scrub, was detrimental to oxide uniformity at any point in the process. The presumption was that the pumice particles were embedded so deeply, only an extremely excessive microetch would return the panel's surface to pure copper. The good news was that the further away from the oxide the mechanical scrubbing was performed, the less detrimental its effect. Thus, scrubbing prior to dry-film lamination has negligible effect compared with scrubbing immediately prior to oxide.

During the course of the research, it was noticed that although a good photoresist stripper can make an alkaline cleaner appear unnecessary, a properly formulated, fresh alkaline cleaner is crucial to a perfect oxide. If the dry-film stripper is older and loaded with copper and stripped dry film, this is even more critical.

RINSING

Another unexpected finding was the importance of using a deionized water rinse prior to the oxide (or oxide predip, if one is used). This type of rinse is especially important for red oxides but less so for darker (heavier) oxides. Although the exact chemistry of this procedure is not understood, enough experiments were run to show that the result was definitive. The total rinsing system before oxide does not need to be deionized water, only the final rinse before the oxide (or predip). If the line has a deionized water final rinse, as is frequently the case, it could be cascaded into the rinse prior to the oxide, making the addition of another tank the only increase in cost.

Thus, we concluded that the optimal process line should consist of the following steps:

1. Alkaline clean 1 to 2 minutes at 1400 to 160” F; rinse; rinse
2. Microetch 30 seconds to 1 minute at 80° to 90° F; rinse; rinse; deionized rinse
3. CHEMBOND oxide 2 minutes at 1400 F; rinse; rinse; deionized rinse.

FIELD USE

Since February, this line configuration has been used for production at ACT II (Advanced Circuit Technology II, Tempe, **AZ).** ACT II’s experience with the process has been overwhelmingly positive. The work coming through on ACT II’s automated line has a better appearance and is much more consistent than the work produced in its old immersion oxide process. Even better, chemical and labor costs have been lower than when the company was using the old nonautomated line.

Dennis Opheim, ACT II president, and Doug Woodworth, engineering manager, were able to design a line that maximizes the advantages of using spray oxide. They have configured a continuous line of products that automatically processes panels from chemical clean prior to photoresist through oxide. This line has established new standards for quality and efficiency in innerlayer production. It produces perfect layers with no rack marks.

SUMMARY

By incorporating surfactants, this oxide improves the peel strength and thermal stress resistance. It offers better uniformity in oxide color, edge to edge, and panel to panel, as well as a significant increase in speed. Combined with discoveries about the pretreatment line, the chemical system has allowed the fabrication industry to progress ,0 a practical spray oxide system. ■

Rudy Sedlak is technical director and sales manager for RD Chemical Co., Mountain View, CA.

I