

## History of and potential for optical bonding agents in the visible

James T. Magyar

Summers Laboratories Optical Division  
E.M.S. Acquisition Corporation  
Fort Washington, Pa. 19034

### 1. HISTORY

Nature was the original producer of optical coupling agents. Canada Balsam, the sap from a balsam tree, when distilled and filtered, yielded an extremely viscous bonding agent for optical elements. At moderate temperatures, Canada Balsam was an almost ideal bonding agent. It had a refractive index of approximately 1.5, transmitted light in wave lengths from 350 millimicrons to over 1 micron in very high percentages and could fill minor differences between the surfaces of a crown and flint element. However, "moderate temperatures" was the problem area. In microscopes or telescopes that would be protected from severe temperatures, Canada Balsam performed just fine. But in fire control systems in tanks during desert warfare or optical systems in high altitude aircraft, Balsam thinned in high temperatures and crazed in low. World War II drove these facts home very clearly.

Between 1945 and 1946 the United States Military contracted researchers at the Mellon Institute of Industrial Research to develop a synthetic resin adhesive to replace Canada Balsam. The result of their work was a synthetic polyester resin dissolved in styrene, and cured with one percent of t-butyl perbenzoate at 100°C for 16 hours. This thermosetting adhesive broadened the wave length transmission to 325 millimicrons through 2.5 microns at greater than 95%. It also withstood a temperature range of -50°C to +100°C and had a refractive index of 1.55. This adhesive was also considerably easier to apply than Canada Balsam by allowing the technician plenty of time to remove entrapped air and to center the optics. The big disadvantage of this adhesive was the curing temperature. The bond achieved at so high an elevated temperature resulted in stresses that cracked elements as they returned to room temperature. This cement was given the military designation of FXS-1057 and later changed to M1-10-2A in 1950. It found broad use in the military and the private optical industry.

By about 1959 it became apparent that M1-10-2A cement would have to be modified in order to reduce the strain caused by high temperature curing.

Souren Sadjian and Marco Petronio of the Pitman-Dunn Institute for Research at the Frankford Arsenal were charged with modifying M1-10-2A adhesive to a room temperature curing cement. Their work led to the addition of a metallic promoter for accelerating the reactivity of the peroxide catalyst. Their most successful cements were those containing

.6% cobalt naphthenate 6% with 1 to 2 percent t-butyl perbenzoate catalyst which cured in 6 days at room temperature and .15% manganese naphthenate 6% with 1 to 2 percent methylethylketone peroxide catalyst which cured in 4 days at room temperature. They also discovered that these mixtures could be very rapidly cured at 70°C. The cobalt variety cured in 2 hours at 70°C. and the manganese cured 1 hour. The cobalt variety was chosen by the Military for its use and given the designation MIL-A-3920. Eastman Kodak and Summers Laboratories both produced this cement. Eastman Kodak, under the designation HE79 and now HE80 and Summers Laboratories under the names Lens Bond Type C-59 and Type M-62. MIL-A-3920 optical adhesive became the standard with thousands of bottles being sold to the American and European optical industry throughout the 1960's and even up to the present day.

The Space Program, the war in Viet Nam and optical non destructive testing equipment all served to push production of optical elements to an all time high by 1965. Not only the volume but the tolerances that were required were now demanding a cement that could pre-cure in seconds instead of minutes and full-cure in minutes instead of hours. Holding devices were being precluded because of the sheer number that would be needed.

At the urging of John Plummer of Plummer Precision Optics, Summers Laboratories embarked on the development of an ultra-violet curing optical cement. In 1966 Summers introduced the first UV curing optical cement. This cement utilized a sunlamp for curing and was rather "rough" by today's standards. In 1965 the UV initiators tended to absorb too much UV light and showed a tendency toward yellowing over long term exposure. The printing and paper coating industry pressed technology for better UV initiators in their areas which had the effect of offering the cement manufacturers better, more effective and more stable UV initiators for their adhesives. By 1974, Summers Laboratories was offering 3 ultraviolet initiated adhesives all of which were variations on the original MIL-A-3920 cement. Norland Products was offering a UV initiated urethane/mercaptan adhesive which was now on the qualified product list for MIL-A-3920C, Dymax Inc. was offering an acrylate/epoxy combination and Epoxy Technology, a straight epoxy, both of which were ultraviolet initiated. All of these cements offer good transmission in the visible range but only now are beginning to show some drawbacks or compromises for the optical industry. To understand these drawbacks, one must consider what takes place when adhering two substrates.

The dynamics of adhesion are such that the first and weakest aspect is intimate mechanical contact of the adhesive with the substrate. This contact is attained when the surface tension of the adhesive is much lower than the surface energy of the "clean" substrate. Surface energy and surface tension are measured in dynes per centimeter. Since most glass and metal exhibit surface energies greater than 100 dynes/cm and most optical adhesives have a surface tension of 30 to 35 dynes/cm, the adhesives wet and intimately contact the glass.<sup>2</sup> But optical elements have a highly polished surface and even though the surface is intimately contacted, the mechanical grip of the adhesive is quite weak. However,

optical glasses are generally alkaline and if the adhesive is acid the next stage of the thermodynamics of adhesion takes place. This stage is called the Acid-Base reaction. During cure the intimately contacted alkaline optical substrate will exchange ions with the acid adhesive, creating a chemical and electrostatic bond between them. The third aspect of adhesion is the van der Waals attractions some of which take place between the adhesive and substrate but are primarily cohesive forces within the cured adhesive and impart some chemical resistance. If the base of the adhesive is primarily a thermoset then there are chemical bonds between the molecular chains called crosslinks that are far stronger than the van der Waals forces found in for instance a thermoplastic adhesive.<sup>3</sup>

Therefore, if the optical adhesive being used has a surface tension of approximately 30 dynes/cm and a pH of 3 to 4 and also is based on a thermosetting polymer; very strong, chemically and thermally resistant bonds can be expected. With these aspects of adhesion known, we can now address the drawbacks of ultraviolet curing adhesives.

Optical companies as well as independent testing laboratories have for some time now been aware that the bond strength of UV cured adhesives is less than that of two component adhesives. Tests seem to indicate that the acid-base reaction is left incomplete due to this speed in which the adhesive is converted from liquid to solid. Chemical resistance is also lowered. This may be caused, in the case of thermoset based adhesives, by the UV initiator causing the long chain molecules to link but leaving the crosslinks to occur by themselves over a longer period of time. Tests conducted on thermoset UV initiated cements that were placed in an oven after the UV curing period, even at 40°C for 1 hour, showed markedly higher chemical resistance than those not exposed to oven temperatures. The conclusion seems to be that cements can be cured too quickly or that full linking and crosslinking is being misjudged.

## 2. POTENTIAL

Examining the potential for optical bonding agents would seem to require the examination of what the optical industry is now asking of adhesive manufacturers.

Two major challenges presented to adhesive manufacturers by the optical industry are mediums for replication and optical cements for plastic optics.

The difficulties in the production of a replication medium exist not only in viscosity control to attain an even undistorted surface but also in the development of a release agent that can be applied in a smooth thin layer and resist the solvent action of the monomer or polymer replication medium.

The bonding of plastic optics presents a challenge of considerable

magnitude. If we remember the dynamics of adhesion and consider that most optical adhesives are really liquid plastics of one sort or another, we realize first that the surface energies of the plastic substrates will fall somewhat between 29 and 40 dynes/cm. Most adhesive experts agree that not only should the adhesive have a surface tension less than the surface energy of the substrates but this difference should be greater than 10 dynes/cm<sup>2</sup>. The difference of surface energy of plastic substrates and surface tensions of present optical cements is within 10 dynes/cm. Therefore the cements do not wet the substrates adequately. The pH of plastic optics is also very close to that of the cements so we cannot attain an acid-base reaction. The result is a very inadequate bond.

One company that is presently marketing a device to increase the surface energy of plastics is Tantec Inc. in Schaumburg Ill. This equipment emits a corona treatment to three dimensional plastic objects that enables increased adhesion. An example of the result is that treated polypropylene needle hubs can be glued to stainless steel cannulas<sup>2</sup>.

A second and very promising area now being explored is the introduction of organo-functional silanes to existing adhesives. These silanes have the ability to chemically bond inorganic materials to organic polymers<sup>3</sup>.

The challenge will be to produce a single adhesive to bond the majority of optical plastics to the majority of optical glasses; eliminating the need for a special adhesive for a specific mix of substrates.

In conclusion, it should be understood that the performance and hence the potential of optical adhesives, whether it is those on the shelf today or some as yet developed, depend greatly on the user. It is incumbent upon optical engineers, designers and technicians to understand some to the basic forces at work during the adhesion process. It is likewise important for adhesive manufacturers to understand at least basic optics in order to assist optical engineers and technicians in attaining their goals. Some understanding of the physical and optical properties of the materials being bonded is imperative if a manufacturer is to give an informed answer to a potential cement user.

### 3. REFERENCES

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