

Light-Induced Color Change Technology

Introduction

Design is an important part of being interested the customer’s attention in the handheld devices and electronics that fill our lives. Light curing resins are widely used in the manufacturing of these because they shorten manufacturing tact time and do not require a heat source. However, in a world where design is important, resins that change color as they cure have not yet come into heavy usage as transparency issues make them inferior in molded products and solvent resins. At ThreeBond, we have been developing light curing resins with an emphasis on design in recent years, and within these projects, we have also looked into light-induced color changing technology as well as how to overcome weaknesses in color-changing light curing resins.

In this issue, we would like to introduce this light-induced color changing technology, its possibilities and its application.

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1. Pigment and Dye

Some kind of coloring agent must be used to make a resin change color, and these are broadly divided into pigments and dyes.

Pigments exhibit powerful opacity with a very clear tone. For example, inorganic compounds such as carbon black, iron oxide, titanium-oxide, etc., where black pigment exhibits the most powerful light blocking effects. Black pigment is well-known for its carbon black transmissivity as it absorbs the light of the entire visible range that the human eyes is capable of seeing.

Dye, on the other hand, is less opaque than pigment, with a tone that gives a sense of depth. Dyes are characterized by the way they absorb specific wavelengths of individual molecules. However, it is difficult to make a substance with a complicated structure that will absorb the entire visible light range equally with only a single type of molecule.

Therefore, black dyes are often composed of several different color compounds rather than a single black compound.¹⁾

2. Instances of Deep Coloration in Light Curing Resin

There are several cases where light curing resin is made to produce a black color for the purpose of blocking light. However, when even a small amount of jet black high-carbon black pigment is added, curing deteriorates considerable, so the compounds base light curing resin characteristics are not displayed at all.²⁾

Because dyes contain a mixture of various tints, they can be designed to allow a specific wavelength to pass, such as 365 nm. These dyes already exist on the market, so if they can be designed in line with the specific wavelengths emitted in high-pressure mercury lamps, such as 365 nm or 405 nm, light curing with a deep color is possible.³⁾

Unfortunately, the small amount of black dye used in situations such as the one described above is insufficient for producing a jet black color. As a result, this is not suitable for use in thin films because in order to achieve jet black, the film thickness must be increased.

In both these cases, we can see there is always a tradeoff between how jet black the color is and the curability of deep areas. To achieve the desired results considering both, we must make a dual curing resin that combines curing mechanisms that react due to applied heat as well as via moisture in the air same as a caulking agent. We focused on leuco dye as the material that would solve these coloring issues.

3-1. Leuco Dye

The basic structure of leuco dye is shown in Figure 1. In leuco dye, the lactone ring inside the molecule reacts with acid to open the ring and release color. But when a base makes contact with the ring, it closes and the color fades. In other words, tone can be tuned on and off using acids and bases.⁴⁾

By taking advantage of these features, leuco dye is used in heat and pressure-sensitive paper⁵⁾, and in recent years has also be used in the rewriting⁶⁾ technology used on IC cards. Various tones are combined with a developer and a discoloration temperature adjuster to form an ink whose color disappears in frictional heat. This is used in many familiar products, such as stationary.⁷⁾

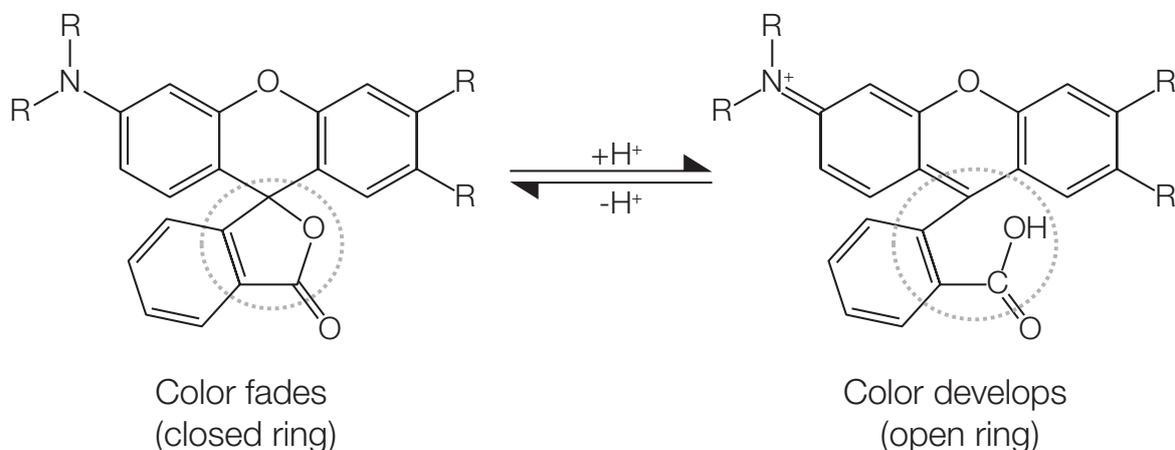


Fig. 1 Leuco Dye Structure and Reversible Reaction

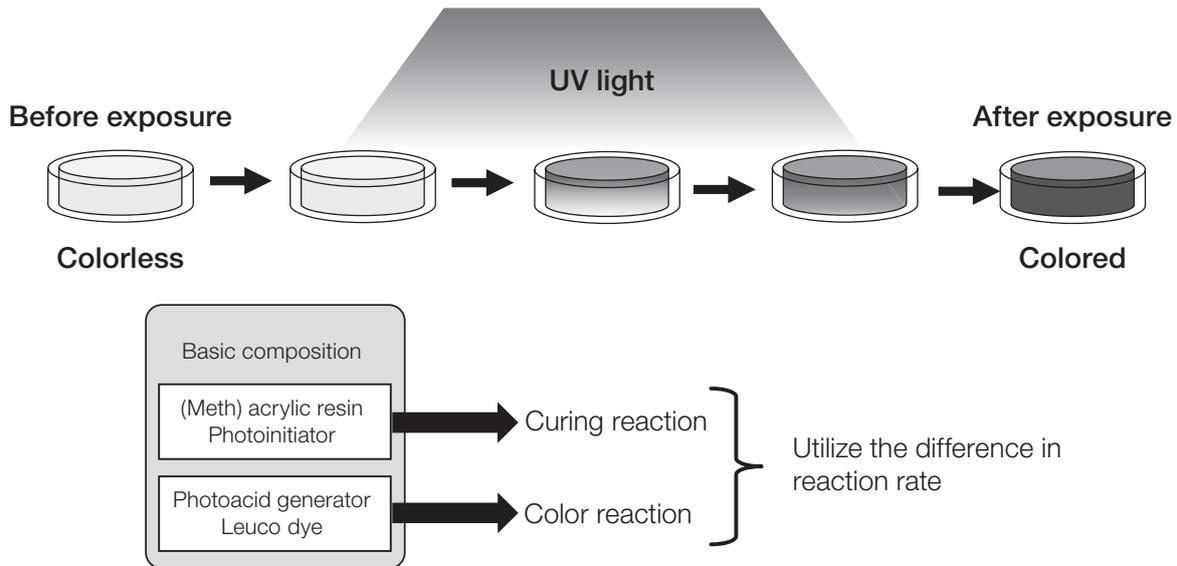


Fig. 2 Curing and Color Development Mechanisms in Previous Leuco Dye Technology

3-2. Light Induced Color Change Technology in Leuco Dye

Applying a low energy light source such as a blacklight to leuco dye can be used for both light curing and light-induced color change.⁸⁾

The basic composition is that it is a liquid before light exposure and made of (meth) acrylic resin, photoradical polymerization initiator, leuco dye and photoacid generator. The curing reaction progresses through photoradical polymerization just like in general light curing resins. The color develops when the leuco dye contacts the acid generated by the photoacid generator. The point to note in this procedure is that by utilizing the difference in reaction rates, inhibition of curing caused by color development can be reduced.

Additionally, tone depth is adjusted through the acid concentration. The color is still inferior to pigment, but as opposed to conventional dye, sufficiently deep color is still possible, even for thin film. This makes it easier to achieve a jet black color while ensuring that deep areas are cured.

The previous technology mentioned above has been developed for a limited number of manufacturing purposes, but due to the time required in exposure to light, it is not yet appropriate for adoption in designed parts for electronic appliances and other mass production.

Now, however, we have found a way to produce color development maintaining the short curing time that light curing resins excel in, which we will introduce below.

4-1. Light Curing Technology in this Technology

The following two methods were used to improve both deep area curing and curing speed.

1. Wavelength control via the light source (2-step cure)
2. Delay of color development using an amine compound

4-2. Wavelength Control via the Light Source (2-Step Cure)

Figure 3 is an image of the mechanism for curing performed via light exposure in two steps. The first step involves a curing wavelength of 400 nm or more, and the second step is where color is developed at a wavelength of 370 nm or less. This procedure keeps curing and color development separate to maintain adhesive effectiveness.

Although the basic composition of this technology is the same as the previous technology mentioned above, the focus here is the difference in the spectrum of absorption between the photoradical polymerization initiator and the photoacid generator.

This difference in the spectrum of absorption between the photoradical polymerization initiator and the photoacid generator is shown in Figure 4. As shown in Figure 4, there is a range where the absorbed spectrums of the two do not overlap (shaded area). We verified that by keeping in this range, we could cure without color developing.

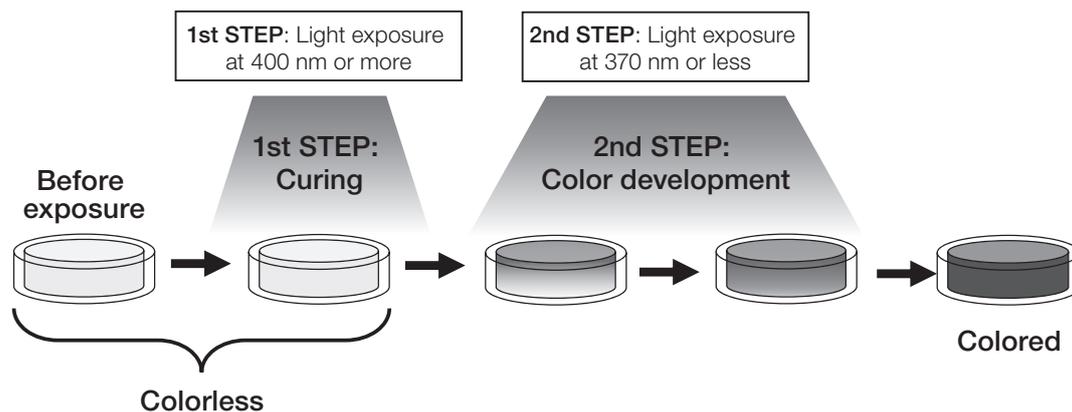


Fig. 3 Wavelength Control via Light Source (2-Step Cure) Mechanism

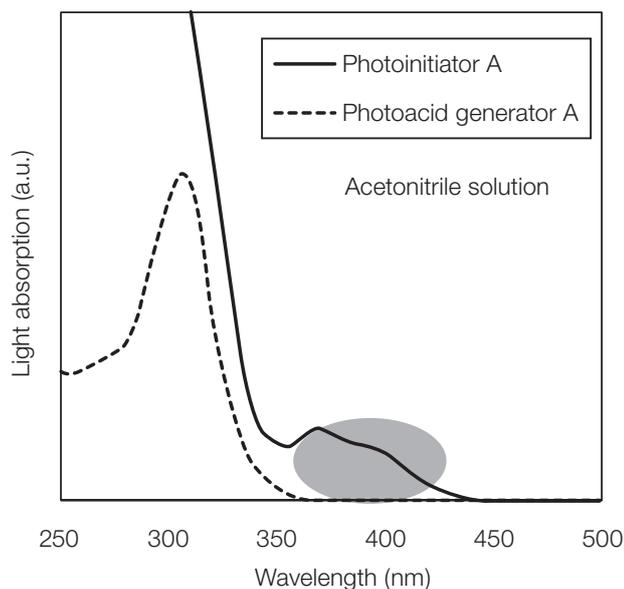


Fig. 4 Spectrum of Absorption for the Photoredox Polymerization Initiator and the Photoacid Generator

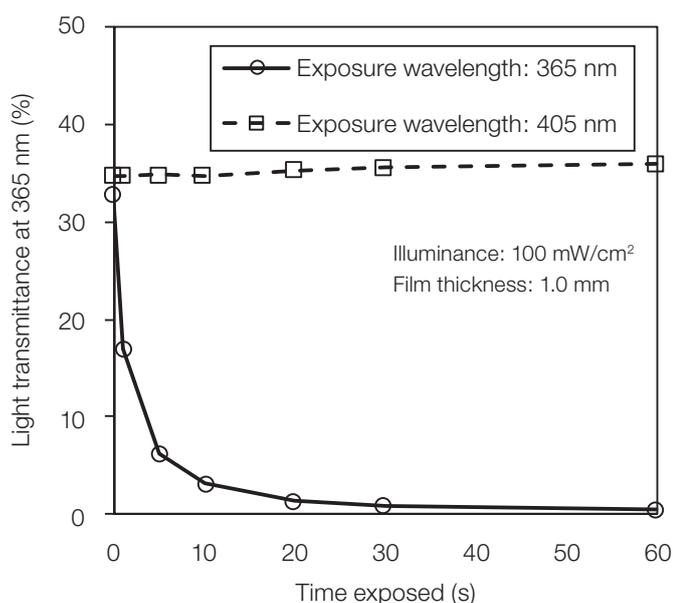


Fig. 5 Changes in Light Transmittance versus Time at 365 nm Exposure Wavelengths

We exposed the adhesive to LED light at both 365 nm and 405 nm wavelengths. Light transmittance and reactivity for 365 nm exposure versus time is indicated in Figure 5 and Figure 6, respectively. Light transmittance decreases immediately after exposure at 365 nm, whereas it maintains its initial value at 405 nm. Additionally, Figure 6 shows that the reaction reaches equilibrium more quickly and is more highly reactive at 405 nm than at 365 nm.

Figure 7 shows a picture of cured material. These results show that exposure at 405 nm results in complete curing of even the deepest areas without color developing, while at 365 nm curing was hindered due to color obstructing light transmission.

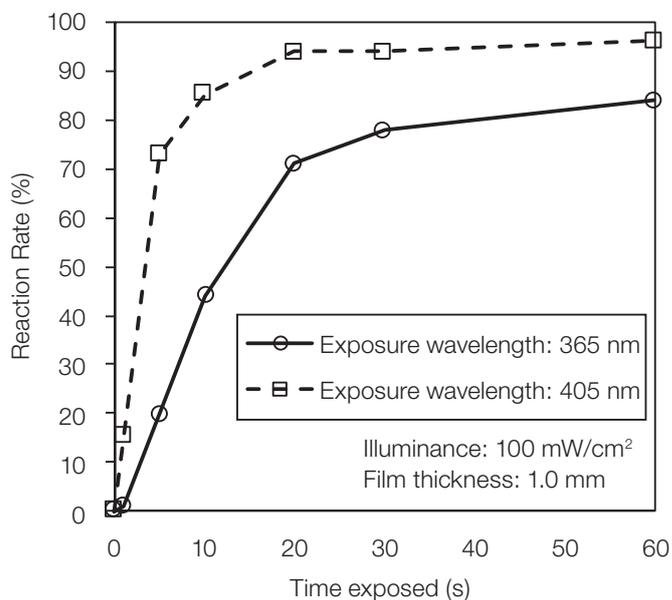


Fig. 6 Reactivity versus Exposure Time

Even after curing is completed at 405 nm, exposure at wavelengths of 370 nm or less produces the same color change as in other previous technologies.

4-3. Delay of Color Development Using an Amine Compound

Figure 8 is an image of the curing mechanism. We have added an amine compound to the basic composition of the

previous technology. Amine compounds are sometimes used to improve stability of photo-cationic polymerized storage⁹⁾. This is because the amine compound traps the acid released by the photoacid generator to act as a polymerization inhibitor. We took advantage of this in our technology, creating a design which uses the amine compound to trap acid released by the photoacid generator during exposure to a single 365 nm wavelength. Doing this slows the start of

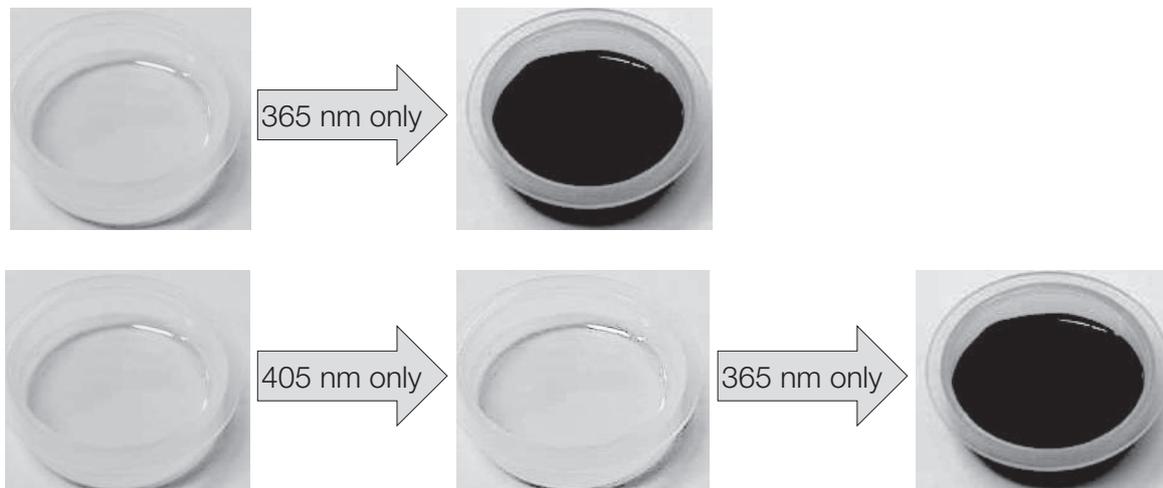


Fig. 7 Resin Appearance Before and After Exposure to Light

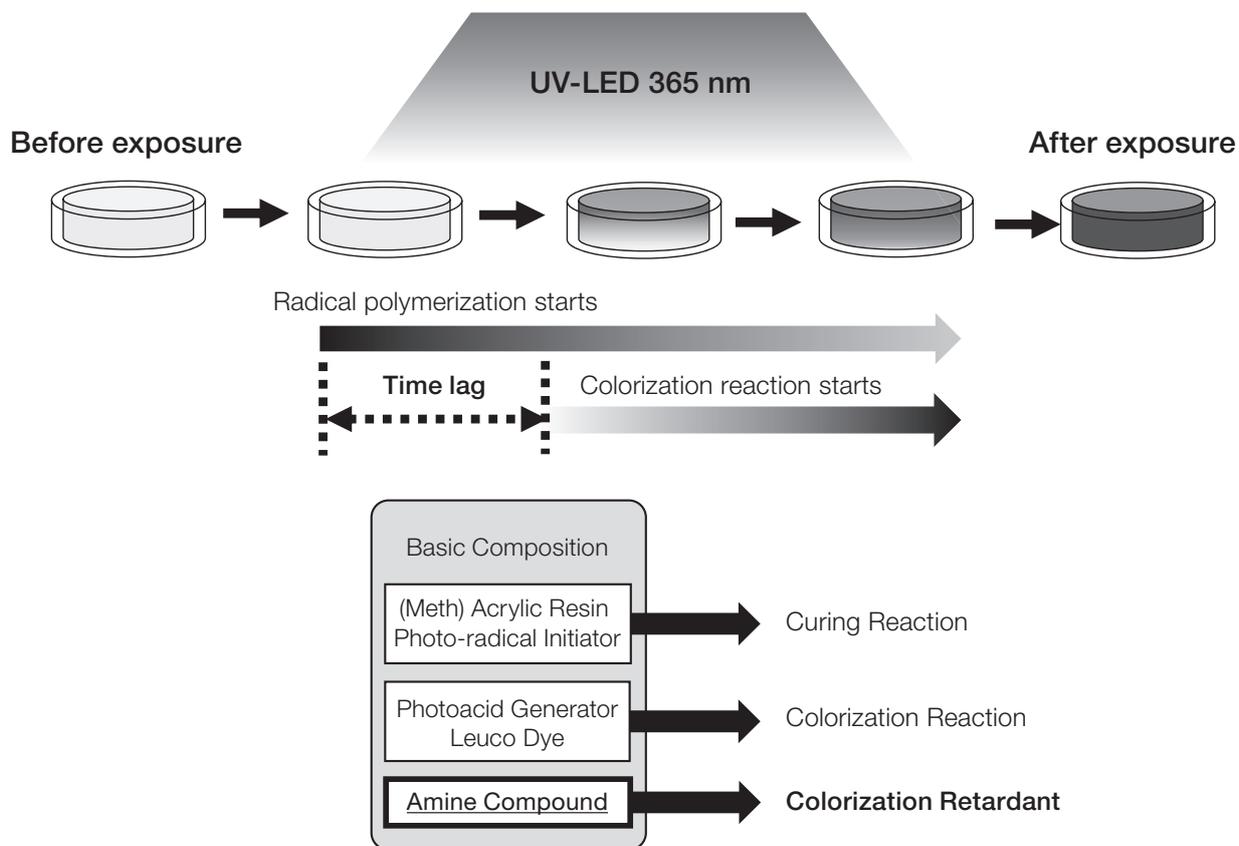


Fig. 8 Color Retardant Mechanism Using Amine Compounds

the reaction that develops color, creating a lag between the start of curing and that start of color development so that the curing of deep areas is improved.

Light transmittance over time at exposure to 365 nm is shown in Figure 9, and reactivity is shown in Figure 10. Light transmittance immediately weakens after exposure in products that do not contain the amine compound, while it is maintained for several seconds after exposure when the compound is added. The reaction rate in the figure indicates adding the amine compound to produce a time lag speeds up curing and also produces higher reactivity.

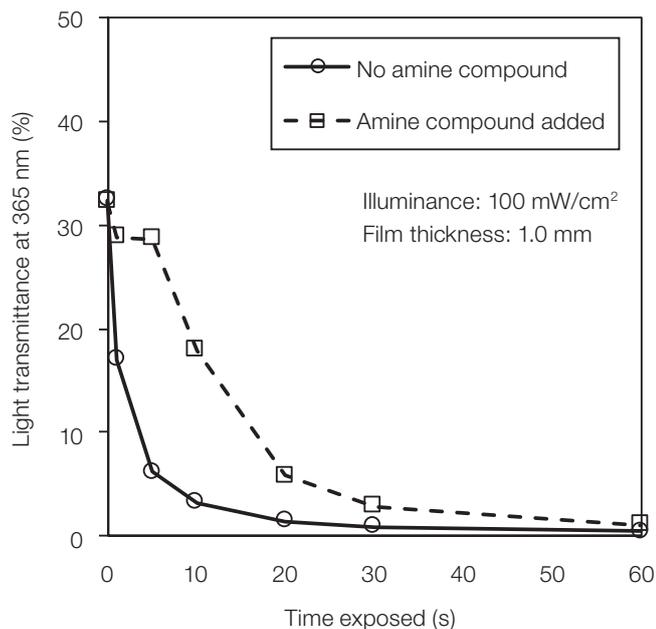


Fig. 9 Light Transmittance at 365 nm versus Exposure Time

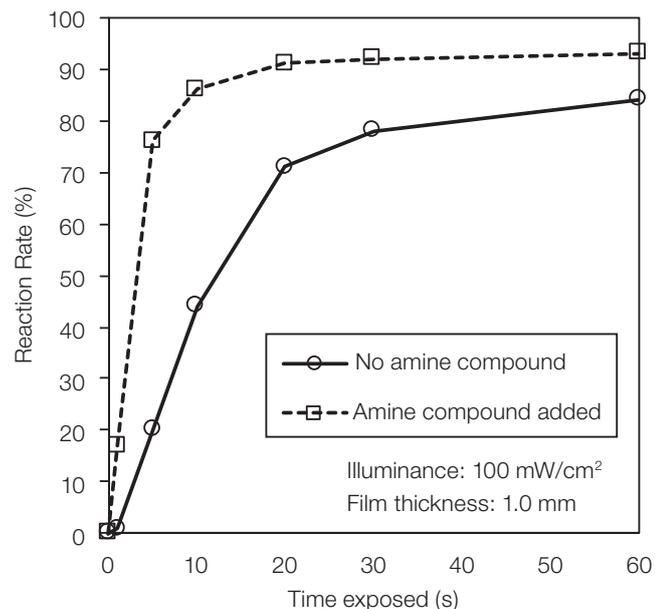


Fig. 10 Reactivity versus Exposure Time

The length of this time lag depends on the amount of amine compound added, its classification and functional group, and is also a factor of adjusting the level of black and deep area curability.

5. ThreeBond 3020

ThreeBond has adopted the technology described above and released ThreeBond 3020. ThreeBond 3020 is a single-liquid acrylic resin that cures through exposure to light at 200 to 420 nm. Table 1 shows values indicating its various characteristics. Before exposure to light, it is a pale yellow, but turns black once exposed to 370 nm or less. For ThreeBond 3020, we recommend the afore-mentioned 2 Step Cure as this ensures better curing of deep areas than exposure to a single wavelength.

6. Future Issues

All dyes, including leuco dyes, may fade over time¹⁰. Measures must be put in place to protect against environmental weak points, such as high temperature above the base resin's glass transition point, high humidity or expose light.

In addition, light-curing resins that use leuco dyes contain photoacid generators so the existence of incredibly powerful acids must be taken into consideration. This makes them difficult to develop and apply for electrodes, wiring areas and other places where acid is not compatible.

Moving forward, these issues must be addressed and solved.

Table 1 ThreeBond 3020 Characteristic Values

Features	Unit	2 Step Cure ^{*1}	Single 365 nm wavelength exposure ^{*2}	Test conditions	Remark(s)
External appearance (liquid)	—	Pale yellow	Pale yellow	3TS-2100-020	—
Viscosity (25°C)	mPa·s	1210	1210	3TS-2F00-007	Shear velocity 76.6 s ⁻¹
External appearance (cured)		Black	Black	3TS-2100-023	—
Thick film curing performance	mm	2.0	0.9	3TS-3160-001	—
Hardness	—	D65	D60	3TS-2B00-010	Type-D
Tensile shear bond strength	MPa	7.4 (material failure)	7.5 (material failure)	3TS-4100-013	Glass/Glass
Light transmittance	%	1.2	1.1	3TS-2940-003	Film thickness: 150 μm, wavelength: 550 nm

*1 Curing conditions: LED (405 nm) 100 mW/cm²×30s + LED (365 nm) 500 mW/cm²×30s

*2 Curing conditions: LED (365 nm) 500 mW/cm²×30s

Closing

This has been an introduction on light-induced color change technology that utilizes leuco dye.

This technology has finally been developed to the point where it can be practically applied. The future is certain to bring increasingly demanding requirements, so we at ThreeBond will continue to focus our efforts on product and technology development in line with market trends in order to ensure the contribution our products make to the industry.

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