

A Method of Specimen Preparation for Reducing Colorant Flooding Errors in the Determination of Ink Strength using Spectrophotometric Measurement of Bleaches.

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Abstract: At the 1999 TAGA Conference a comparison of the many variables that can affect the reliability of the determination of ink strength using a universal bleaching white was presented. The most significant error was the time-dependent flooding of the ink or flush colorant at the surface of the bleach. This flooding was shown to produce changes of up to 8% in relative tinting strength during the time required to prepare a specimen and present it to a spectrophotometer, depending on the colorant being measured. Small secondary errors contributing to random fluctuations in tinting strength involved the motion of the wet bleach and possible distortion of the cell cover glass.

This report documents a new method of specimen preparation that reduces the time-dependent errors down to the level of the random errors. The mixing process is done with a centrifugal mixer to assure uniformity of the bleach. In addition, a new universal bleaching white was developed that incorporates an ultraviolet – visible activated vehicle and curing agents. The curing process is photo-initiated by exposure to radiation from an inexpensive, low power UV-LED array. The photo-polymerization solidifies the surface of the ink-bleach mixture down through the top 20-30um of the mixture, preventing any temporal drift of the colorants, and thus stabilizing the strength during the measurement period.

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Introduction

In a paper given at the 1999 annual technical conference of TAGA (Rich and Bassemir, 1999) we presented the results of a year-long study on the operational parameters that adversely affect the results of tests for ink or flush strength by the method of bleaching. The study focused on the use of the NPIRI 95 Universal Bleach (NPIRI 1996). This bleach is no longer produced and distributed by NPIRI, due to lack of demand.

The report identified three major processes that contributed significant errors to the reproducible determination of the tinting strength of an ink or flush. One of those errors was the method of computation of the relative strength. We demonstrated that, in some cases, the same measurement data could result in an assessment of a test ink being weaker, equal or stronger than the standard ink, depending on which equation was used. It was suggested at the conference that the FIAF (an acronym in German *Farbstärke durch Iterativen Angleich der Farbtiefen*, meaning, “color strength by iterative application of color depth”) be used. This method is documented in textbooks (Völz 1995) and in ISO standard 787-24 (ISO 1985) and is in common use in the European colorant industry and among paint producers. The method, often called “B depth”, is modeled from visual evaluations of strength and is considered one of the most reliable methods. We have adopted that method in this study.

The second parameter identified in the report was the process of mixing the ink or flush into the bleach. That process was found to be very dependent on the skill and experience of the operator and on the viscosities of the ink or flush and the bleach. Since the time when the paper was published, a dual-asynchronous, centrifugal mixer (FlackTek 2001) was introduced and is now in wide use in the industry. The use of this mixer to replace hand mixing with an ink knife is being written into the next revision of ASTM standard D 2066.(ASTM 1997) This mixer was utilized in this study as well.

The third and most significant parameter identified in the report, was the physical incompatibility of the rheology of the ink or flush with that of the bleach. This led to the flooding of the pigment to the surface of the bleach and resulted in an increase in the measured strength as a function of time after the preparation of the bleached specimen. This strength increase began the moment that mixing ceased, or that a new surface was formed on a puddle of bleach, and continued for as long as the mixture was being characterized. In the study, the drift in apparent strength was observed to continue to change for measurement times as long as an hour. This has been happening in the past but was never observed to be a problem because the standard practice was to bleach both the standard and the trial for every test. Therefore, since both were flooding at the about the same rate, any relative difference between them would still be consistent. The current practice of reading and storing the spectral signature of

the standard bleach demands that the trial bleach be processed in such a way that the flooding condition be taken into account or preferably eliminated.

This study reports on a project to devise a bleaching method to reduce or eliminate the effect of colorant flooding on the assessment of strength.

Theory

In the assessment of the strength of cold-set inks and liquid inks, bleaching is used much more reliably. In the case of cold-set inks, the flooding is not as significant a factor as it is with heavy paste inks. This may be due to better compatibility of the cold-set formulation with the NPIRI bleaching white used in the cold-set industry. With liquid inks, the bleach can be produced from a white-pigmented base which is similar in chemical nature to ink base being tested or it can be quite distinctly different from the ink and the method will still work because the ink is drawn down rather than being placed into a cell and sets almost instantly. Such is the case in ASTM standard D 6531 (ASTM 2000) which recommends the use of a commercial house paint as the universal bleach. In packaging applications, there is often an opaque white ink in the palette of ink bases that can be used as a bleach for the colored inks. In the liquid ink cases, the unique feature of the bleach system is the ability to set or cure the "bleached" ink. This freezes the surface of the bleach and prevents the pigment from flooding up to the surface. This effect can be observed if one follows the ASTM method, using the water-based house paint as the bleach. The coalescence of the latex through the thick film requires some minutes. If during this drying phase the surface of the paint film is broken – by touching a finger to it – one immediately observes a bloom of color as the ink floods to the now exposed surface. This bloom results in a stronger and but less uniform appearance of the specimen.

The desire then is then to have a paste ink bleach which can be made to set instantly after the cessation of the mixing process. Heat-set inks can be made to set quickly by the introduction of an intense source of heat. Such heat sources can be bulky, expensive and potentially dangerous to operate. Oxidative setting inks will require some minutes of heating to set, even under such an intense heat source and during this process the flooding behavior may continue to occur. The immediate setting of a paste ink occurs after printing with energy-cured paste inks. But this curing requires the use of high intensity discharge lamps or an electron-beam unit. Both of these devices are large and expensive, and need shielding to protect the operator. The cost and size of traditional UV and EB curing systems eliminates their usefulness in laboratory determination of ink strength.

Recently, however, some new UV sources have been developed, based on solid state technology. These devices are light emitting diodes (LED) with emission

bands between 370nm and 400 nm in the near UV. They are small, inexpensive, but intense solid-state sources which can be easily utilized in an ink laboratory environment. These sources are beginning to find application in traditional areas of UV-VIS curing such as certain electronic adhesives, dentistry and small inkjet printers. It was felt that such short-wavelength, solid state source would be ideal to use in a bleaching application.

An experiment was undertaken to develop a bleaching white that could be set with these LED-based UV sources. The bleach would be formulated with a near-UV to Visible light activated photoinitiator and then optimized to cure in this spectral range. There are many specialized UV activated materials in use today (paints, adhesives, furniture coatings and specialty inks). Most are very expensive, compared to their conventional counterparts. – yet one of the goals of this study is to develop a method that is as inexpensive and easily reproduced as possible.

Experimental

After surveying the literature on available white materials, such as inks, paints and fillers, that could be cured with a near-UV (370 nm – 400 nm), Visible (400 nm – 420 nm) radiations it was determined that all of these specialty materials were far too expensive to use as a disposable ink bleach. Therefore, a Sun Chemical EB white ink (Sun Chemical 2003) was selected and then modified with an acrylic cross-linking agent, DIPETA, in the ratio of 75% of white ink and 25% of the DIPETA. Next, CIBA[®] Specialty Chemicals was contacted and they recommended a mixture of two photoinitiators, Irgacure[®] 184 and Irgacure[®] 819, (CIBA[®] 2003) for use with white pigmented coatings. Since these chemicals are solids, a diacrylate solvent was used to make an initiator compound. This compound was then added to the modified white ink in amounts to yield 10%, 9% and 8% photoinitiator compound and 90% to 92% white ink. The final concentration of initiators in the bleach mixture was approximately 1% of Irgacure[®] 819 and 3% of Irgacure[®] 184.

The UV source used was a UV Process Supply, Inc.(UVPS 2003) Con-trol Cure-All™ LED array. This source is composed of a square grid of UV LED chips mounted at the focus of a parabolic reflector. A plastic collection lens is then placed over the open reflector to focus any light that is not collected by the reflector. Figure 1 shows the lamp and associated heat-sink to keep the LED chips cool.



Figure 1.

Hi-Power Con-Trol-Cure-All showing large heatsink to dissipate excess power. Note the lens over the parabolic reflector to improve focus of the light.

The parabolic reflector and lens collect the radiance emitted by the chips and focuses to a spot about 25 mm in diameter. The spectroradiometric output of the LED source was measured using an Optronic Laboratories 754 spectroradiometer (Optronic 2002) and is shown in Figure 2. Two versions of the lamp were available to us, a standard, low-power version and the newer, high-power version shown in Figure 1. There is some variation in the actual central wavelength of an LED and the plots in Figure 2 show that the newer, high-power lamp was narrower and closer in central wavelength to 390nm nominal value. The variations in centroid wavelength are always to the longer wavelengths. LED suppliers seem to specify their products in terms of the shortest wavelengths observed in a production lot rather than the mean wavelength of the production. This meant that the photoinitiator would need to be designed to be tolerant of moderate shifts of the LED radiance into the visible spectral region.

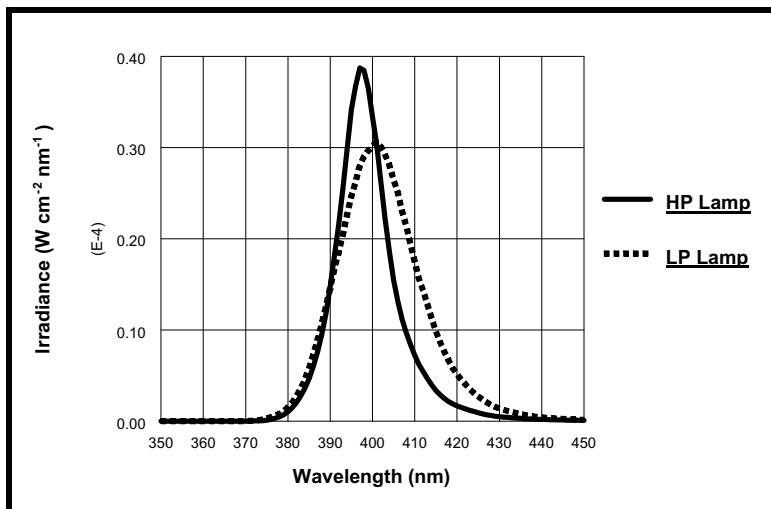


Figure 2 Spectral Irradiance of a Low Power and a High Power LED Lamp

A set of standard heatset, offset inks (Sun Chemical 2002) identical to those used in our previous study were obtained. They were weighed with the bleach in the ratio of 2% ink to 98% bleach and mixed in a small plastic cup (15 ml) on the centrifugal mixer for 3 minutes at 3000 rpm. As soon as the mixing process was completed, the inks were transferred to a special bleaching cell, see Figure 3, and exposed to the UV LED source for a specific period of time ranging from 30 seconds to 90 seconds. A baseline was also obtained by not curing the bleach in the cell.

The cell was mounted on a Datacolor Spectraflash[®] SF600plus spectrophotometer (Datacolor 1996) and the strength assessed as a function of time on the instrument relative to an initial reading, as was done in the previous study. The Spectraflash 600plus was controlled with the ColorTools[®] version 1.3 software. A custom macro was created that would take timed readings every 10 seconds after the initial reading. The measurement series were then saved to disk and exported to an ASCII file for offline analysis and plotting

The bleaching cell was assembled using a 50 x 75 mm precision glass microscope slide as the cover glass. (Corning 1999). The base of the cell was an approximately 1mm thick 2 x 3 inch cardboard spacer with an 18 mm diameter hole punched using a manual hole punch. The bottom side of the spacer was sealed with a piece of 1" cellophane tape. Figure 3 shows a schematic diagram of the construction of the cell that was developed. As there is nothing critical about the size and shape of the cardboard spacer, this could be ordered from a local paper supplier, cut and punched to specification to create a consistent supply. A sufficient amount of the bleach (about 3 gm) was transferred to the

cell and the microscope cover glass placed over the ink. The rim of the reflector of the LED source can be placed directly onto the surface of the cover glass to maximize the effect of the UV radiance available.

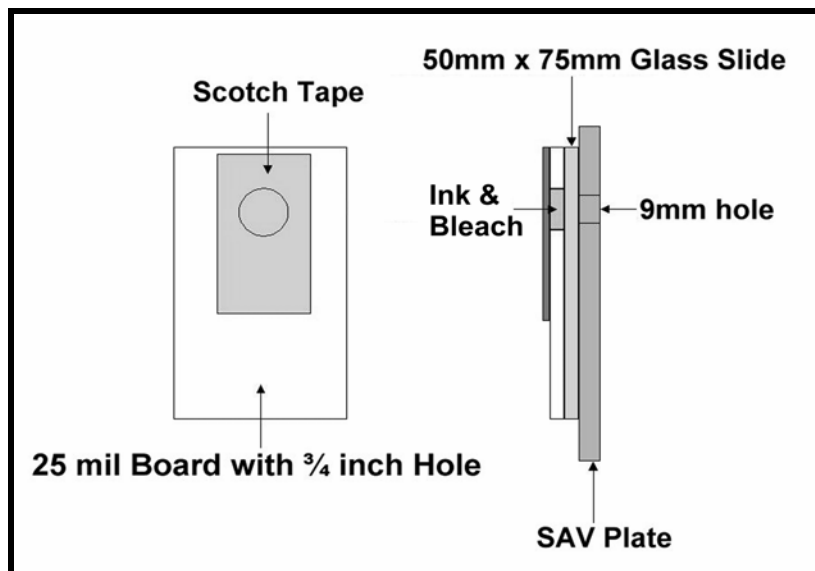


Figure 3 Schematic of the Cell where the Bleach & Ink Can Be Cured

As soon as the cell was assembled, the mixture was immediately exposed to the UV light through the cover glass. The transmittance of the glass was measured using a PerkinElmer Lambda™ 900 (PerkinElmer 1998) UV-VIS-NIR spectrophotometer and observed to have very little absorbance and only surface reflection losses in the spectral range from 360nm to 450nm where the UV LED source emitted radiation. The spectral transmittance of the cover glasses is shown in Figure 4.

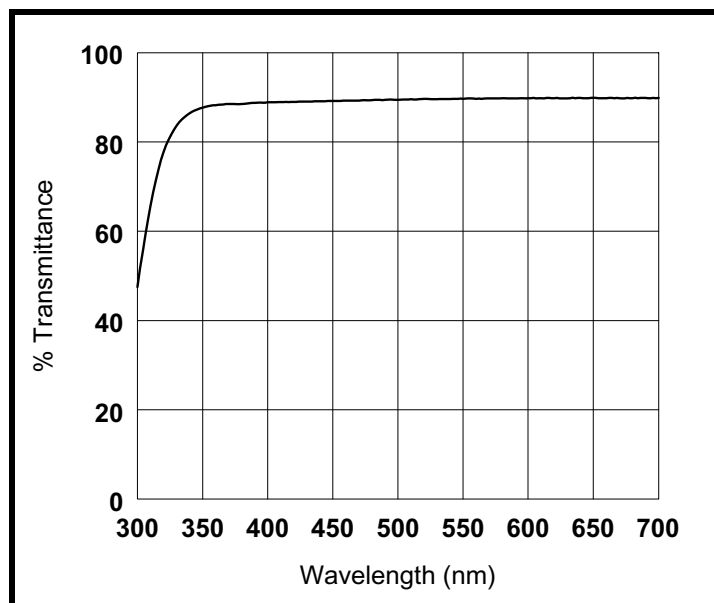


Figure 4 Spectral Transmittance of the Glass Slide

Results

To determine the effectiveness of the UV curing process, each ink was first bleached and measured without curing the bleach. The mixture of bleach and ink exhibited the same apparent strength drift as reported in our earlier study. [Rich and Bassemir 1999]. The relative strength would increase as much as eight percent over the period of the first few minutes. Figures 5, 6 and 7 shows the graphs of strength versus time from filling of the cell for each of the process colors with no UV exposure.

When the bleach was exposed to the near-UV radiation from the LED the surface of the bleach was cured and formed an intact, well cross-linked film. This prevented the colorants from flooding to the surface of the bleach. The apparent measured strength remained either constant or showed very slight (<1%) changes from the initial reading. The strength and color-difference remained essentially constant for five minutes. Figures 5, 6 and 7 also show the strength versus time for the UV-cured bleaches.

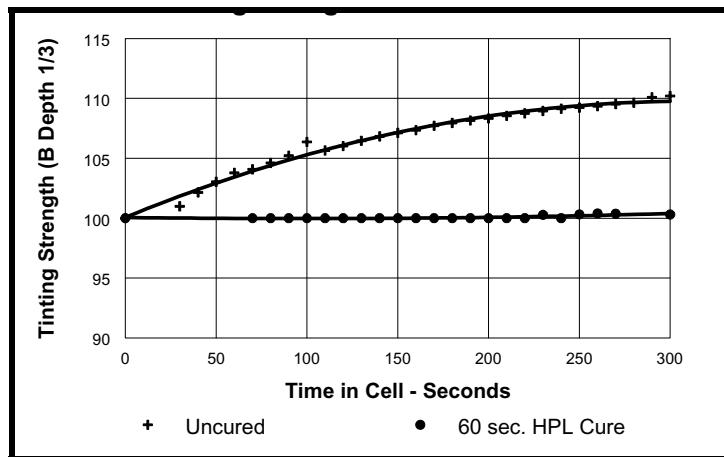


Figure 5 – The Variation of Tint Strength with Time for Cured and Uncured Cyan Ink

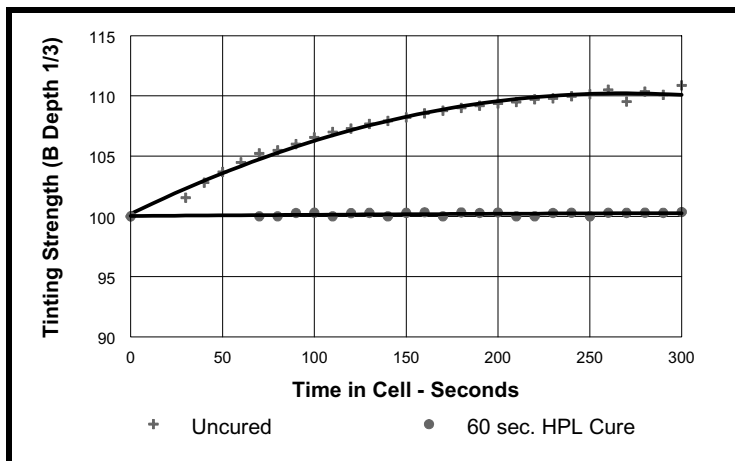


Figure 6 – The Variation of Tint Strength with Time for Cured and Uncured Magenta Ink

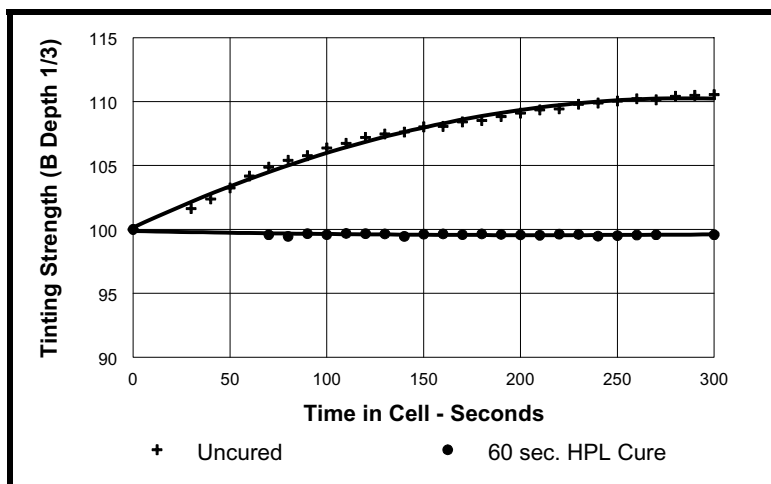


Figure 7 – The Variation of Tint Strength with Time for Cured and Uncured Yellow Ink

To evaluate the precision of the method, the same ink was bleached and cured multiple times. Table I shows the strength of replicate determinations. On the Cyan and Magenta ink, the apparent repeatability of the method is better than 1% in strength relative to the first determination.

Table I – Ink Strength of Replicate Preparations of the Bleach

	Cyan		Magenta	
	B-Depth Strength	CIELAB Difference	B-Depth Strength	CIELAB Difference
1 st Determination	100.00	0.00	100.00	0.00
2 nd Determination	100.29	0.19	99.16	0.54

Discussion

The Control-Cure LED source performed as advertised. The center wavelength and bandwidth will vary somewhat from unit to unit, in contrast to atomic discharge lamps such as xenon or mercury lamps. But the photoinitiator absorption band is quite broad, as shown in Figure 8, and can thus accommodate the small variations in the LED emission. Newer sources have greatly increased intensity and can thus cure the bleach faster and more deeply. As the technology of the LED fabrication improves, the bandwidth also narrows.

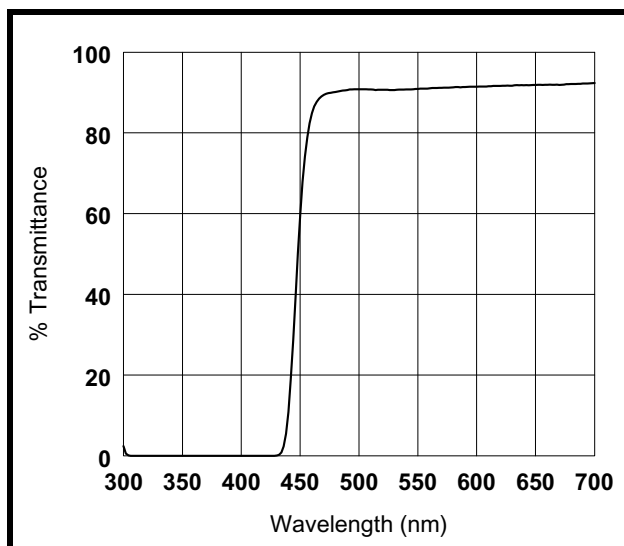


Figure 8 – Spectral Transmittance of the UV-VIS Photoinitiator Compound

It is known that the presence of free oxygen quenches the UV-activated curing of polymers. To overcome this effect, it is usually necessary to utilize very high flux levels from large discharge lamps or to saturate the surface of the coating with a flow of dry nitrogen.. It is believed that compressing the bleach under a plate of glass and irradiating the film through the glass minimizes the presence of free oxygen and allows the bleach to be cured sufficiently by the lower intensity of the LED source.

Measurements were also made of the cured thickness of the films produced on the inside of the cover glass, by wiping off the uncured bleach and rinsing with ethanol. Typical films were found to be 20 – 30 micrometers in thickness and were essentially opaque to any changes occurring in the underlying film of bleach.

Conclusions

1. It has been demonstrated that using an energy curable, universal bleaching white will greatly reduce or completely stop the flooding of colorant observed with traditional paste ink bleaches.
2. The Control-Cure LED source is capable of curing the upper layers of a thick layer of white bleach loaded with an appropriate amount of UV-VIS activator, when covered by a glass slide.
3. Using an LED cured bleach allows replicate bleaching to be performed with an absolute precision of better than 1%, even when storing the

color measurement of the standard instead of measuring it each time a determination of strength is performed.

Literature Cited

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CIBA®

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Corning

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Datacolor

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Sun Chemical

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UVPS

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