The Evolution of Tinting Dyes and Optical Brighteners in White Papers

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(where Green is not just a color anymore)
The World of White Paper Changed a Lot in 2005

• In that year, International Paper led the move to higher whiteness/brightness papers in North America.

• The changes were substantial – from a TAPPI directional brightness of 84, on average, to 92 and a change from roughly 100 CIE D65 whiteness to 146.

• The changes were made to combat the influx of cheap foreign papers which were coming to the North American marketplace and claiming share.

• Numerous changes were necessary at mills making these papers to continue competing in this arena.
White Papers - Purpose

• The main reason that white papers exist is to communicate a message – be it in the form of a letter, a book, a direct mail advertisement, a billing statement, or a myriad of other possibilities.

• It is a visual media.

• So, the appearance of the media upon which the message is printed is very important to the party trying to be heard.

• Visual appeal can be influenced in a number of ways – brightness, whiteness, shade, and even surface texture (e.g. smooth versus vellum).
White Papers – What Had to Change?

- To get from 84 TAPPI directional brightness and 100 CIE D65 whiteness to values of 92 and 146, respectively, is no simple task.
- In most mills, three (3) things had to change:
  1. Increased bleaching of the pulp;
  2. Alternate tinting of the paper;
  3. Greater use of optical brightening (use of fluorescent whitening agents) in the paper.
- It all begins with the raw materials – in this case the pulp. Most mills had to make a considerable increase in pulp bleaching in order to get the starting brightness high enough.
Why Did the Tinting Dyes Need to Change?

• Before the increase in brightness and whiteness, most paper machines employed a 3-dye system for shade tinting/control. These systems were typically: black/red/blue, or blue/red/yellow.

• Prior to 2005, there was excess brightness, and tinting dyes were often even used to dull the furnish slightly to the targets of 84 TAPPI directional brightness and 100 CIE D65 whiteness.

• After the change, there was not enough brightness “to give” in order to allow use of a 3-dye system and still meet the final optical property targets.
Why Did the Tinting Dyes Need to Change?

• Many thought that they needed a 3-dye system to control shade: L*, a*, b*. Indeed, that was necessary for tight shade control — but then the world changed.

• Now the key is to achieve the b* value while maintaining the L* value and brightness by employing pulp bleaching and fluorescent whitener (OBA). The a* value is allowed to “float” somewhat, but most bright, blue tinting dyestuffs do not move a* very much.

• So paper machines dramatically changed how they tinted the paper.
How Did the Tinting Dye Systems Change?

• The “new” paper made in North America is much bluer than what was made previously.
• This change was in line with the papers from Europe, Brazil, and Asia.
• Therefore, a shift was made to a dye system with just a single “blue” (more violet) dyestuff.
• Changes were made until a happy medium was achieved between cost of the dyestuff and its shade (not too dull or too red or green).
• At first, many machines switched to a direct dye.
How Did the Tinting Dye Systems Change?

- One of the most common “bluish” direct dyes selected was Direct Violet 35.
- This dyestuff is one of the brightest direct dyes available. It also has the right “tint” on the a* scale. Its redness is desirable for the end shade as opposed to dyes like Direct Blue 199 or 218.
- However, as always, there has been an ongoing desire to cut costs.
- Direct dyes are not as bright as many pigmented dyes.
- Some of the most brilliant tinting pigments include Pigment Blue 14 and Pigment Violet 3.
What Are Other Tinting Dye Considerations?

• Selection of a tinting dye (or system) isn’t always about lowest cost or selecting the brightest ones.

• Some mills have to concern themselves with food contact grades and dyestuffs that are appropriate for use in those applications – pre-58 dyestuffs.

• Pre-58 dyes are those which were in use prior to 1958 in food contact applications and for which the FDA has said they will not take regulatory action regarding their continued use in those applications.

• They are a “select” list of dyestuffs, by nature of their small number, which are grandfathered in.
What Are Other Tinting Dye Considerations?

• Some mills have a difficult time with tinting pigments.

• The reason for this is that the pigments tend to be very good at finding and “marking” deposits in the machine piping, headbox, etc.

• If a machine is not kept very clean, then when these deposits break free, they can form dreaded “Blue Spots” in the sheet.

• Pigments also tend to bubble to the surface if there is a foam issue in a machine’s wet end, causing similar defects.
What About Mills Using Mechanical Fiber?

• Mills using mechanical fiber can not achieve the very high brightness levels of bleached kraft mills.

• However, they make a very good sheet, all the same, and brightness is still very important.

• For machines using mechanical fiber there really aren’t any options which are better than Basic Violet 4 and Basic Red 12.

• There are more modern dye systems, though, for delivering these pH sensitive dyes to the machine and preventing them from agglomerating in dye lines. These dyes should always be kept “neat” (or undiluted) for best application.
What Changed With OBAs (Optical Brightening Agents)?

• Prior to 2005 there was one main type of OBA used in North America. It was tetrasulfonated OBA.

• Some mills continue to use only tetrasulfonated OBA to achieve 92 TAPPI directional brightness and approximately 146 CIE D65 whiteness. But, their pulp quality (brightness) has to be good.

• Other mills have moved to hexasulfonated in the size press because it builds to a higher brightness and whiteness level before “greenover,” which happens when the OBA is saturated.
What Changed With OBAs?

• The same is true for some coated mills. Tetrasulphonated OBA was used in the coating in the past, and now hexasulphonated OBA might be used in the coating.

• Another reason to use hexasulphonated OBA has come with the advent of ColorLok® technology. ColorLok® and OBAs do NOT get along well together.

• The ColorLok® salt can cause OBA to precipitate out of the starch, but hexasulphonated is the most soluble OBA. Therefore, it is often preferred in the size press by those making ColorLok® grades.
What Changed With OBAs?

• OBAs are now used in much greater quantities than they were when North American papers had lower brightness and whiteness.

• Despite upheavals in OBA prices due to availability and raw material shortages, they have recently come down considerably in price. The price gap between the different types has also closed tremendously, too.

• Rather than being a specialty additive, OBAs are now a commodity. However, their proper use (addition point, type, etc.) and dosage can still have a strong impact on final product cost.
What Changed With OBAs?

• There is presently a cost/performance based trend to utilize disulphonated OBA in the wet end of many paper machines.

• Disulphonated is the most expensive of the three OBA types, but it is also the most efficient in the wet end and has the least charge impact.

• Remember, though, for those making Food Grade products, there is only one OBA type which presently has FDA certification for this application. That is tetrasulphonated OBA.

• What’s the best OBA combination to use? It all depends on the machine, furnish, and end product.
SUMMARY

• The North American white papers market has changed tremendously in the last 5 years.
• Tinting dyes and OBAs should be optimized to keep manufacturing costs as low as possible.
• Consider having an evaluation done on your dye / OBA system. The field of knowledge continues to grow.
• Work with your team of experts and try things to determine what works best for your machine and grades.
• Be aware of special situations, though, that lock you into particular products.