The Evolution of Tinting Dyes and Optical Brighteners in White Papers

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ABSTRACT

The world of white papers changed tremendously in 2005 and since in North America. In that year, International Paper increased the TAPPI directional brightness from 84, on average, to 92. The concept of CIE whiteness was also introduced to the North American market in 2005, and the change in that parameter was from roughly 100 to 146. These changes in optical properties meant a "night and day" difference in the appearance of paper products for printing & writing grades, reprographic, book papers, etc. To make these changes in the optical properties of paper, mills in the U.S. and Canada, in particular, had to change the types and/or quantities of tinting dyes and optical brightening agents used in their manufacture. Ripples of change and optimization efforts continue today.

INTRODUCTION

Changes were made in the brightness and whiteness of North American white papers in 2005 in response to a growing influx of cheap foreign papers which were coming into the market here and claiming market share. There was also a threat to existing markets from groundwood grades which were looking for a new outlet as copier papers (and related uses). The brightness/whiteness increase made by all of the major (and minor) manufacturers of white papers in North America stemmed the tide of imports and cross-over grades, protecting their market share.

The main reason that white papers exist is to communicate a message – be it in the form of a letter, a book, or 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.

DISCUSSION

Visual appeal is impacted by properties which are described using a number of parameters: brightness, whiteness, shade, and even surface texture (e.g. smooth versus vellum finish). With the exception of the last, every one of these properties is influenced by the dyestuffs and optical brighteners added to the paper or board. The big change in white papers that happened in 2005 required three things:

- Increased bleaching of the pulp;
- Alternate tinting dye package for shading the paper;
- Greater use of optical brightening agents (OBAs, also called FWAs – Fluorescent Whitening Agents).

It all begins with the raw materials, in this case the pulp and the additives. Most mills had to make a considerable increase in pulp bleaching in order to get the starting brightness high enough to achieve the new targets of 92 TAPPI directional brightness and 146 CIE D65 whiteness.

Tinting Dyes

Before brightness and whiteness increased dramatically, most paper machines employed a 3-dye system for tinting shade control. These systems were typically: Black/Red/Blue or Blue/Red/Yellow. After the 2005 change, most paper machines making white papers moved to the use of a 1-dye system (2 at most). The reason for this is that prior to the change, there was often excess brightness, and tinting dyes were sometimes used to dull the furnish slightly to the targets of 84 TAPPI directional brightness and 100 CIE D65 whiteness. Also after the change, there was not enough brightness "to give" in order to allow use of a 3-dye system and still meet the optical property targets – because dye addition reduces L* and brightness. Many thought that they needed a 3-dye system to control shade: L*, a*, b*. Indeed, in the past, that had been necessary and was a best practice – but then the world changed

in North America. Papermakers in the U.S., Canada, and Mexico learned what their counterparts in Europe, Asia, South America, and other places had already concluded. A proper selection of tinting dye(s) means that those selected affect mostly b* value and CIE whiteness. These became the key parameters in the new white papers. So paper machines dramatically changed how they tinted white papers. The "new" paper made in North America is much bluer than what was made previously as well. If used properly, blue dye addition will cause the paper to which it is added to appear whiter. If pushed to the extreme, though, and overused, blue dye addition can cause the paper to start appearing dull and grayish. But, the changes in North America are in line with the practices in Europe, Asia, and South America.

At first the dye 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). Many selected a direct dye at first, and one of the most common of these 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 Direct Blue 218. However, as always, there has been an ongoing desire to cut costs.

Direct dyes are not as bright as several pigmented dyes, and more OBA must be added with them to achieve target brightness. Instead then, mills have begun turning to the brilliant tinting pigments. Some of the best of these include Pigment Violet 3 and Pigment Blue 14. The cost of the tinting dye is not often as significant (if chosen well) as the cost savings realized in using less OBA.

Selection of a tinting dye (or dyes) is not always about lowest cost or selecting the brightest ones, though. Some mills have to concern themselves with food contact grades, and dyestuffs that are appropriate for use in those applications are called pre-58. That name signifies that they were in use in 1958 or earlier and are grandfathered in as safe (unless specifically identified otherwise). In the 1980's, the FDA indicated that it will not take regulatory action against those who use pre-58 dyes in food contact grades.

Some mills also have a difficult time in managing tinting pigments. The reason for this is that the pigments tend to be very good at finding and "marking" deposits in the paper machine piping, headbox, etc. If a machine is not kept very clean and does not use a modern dye delivery system, then when the colored deposits break free, they can form dreaded "Blue Spots" in the sheet. These defects have caused a lot of paper to be rejected at some mills who've tried tinting pigments. Pigments also tend to bubble to the surface if there is a foaming issue in a machine's wet end, and this can also lead to similar defects.

What about mills using mechanical fibers as the main part of their furnish? For mills using mechanical fiber (lignin containing fiber), the very high levels of brightness and whiteness cannot be achieved. However, they still can make a very good sheet which is perfectly appropriate for many applications such as books and sales circulars. For these machines, there really are not any better dye options than Basic Violet 4 and Basic Red 12. There are better options for delivering these pH sensitive dyes which require acid to keep them in solution to the paper machine, too. Modern dye systems maintain the dyes in "neat" (undiluted) form for best application. Newer pumps can handle the very low flow rates of these dyes with great precision.

OBAs

What changed with optical brightening agents used in white papers? Well, prior to 2005, there was one main type of OBA used in North America. It was tetrasulphonated optical brightening agent (OBA). This is the least expensive of the OBAs, and some mills continue to use only tetrasulphonated product to achieve 92 TAPPI directional brightness and 146 CIE D65 whiteness. However, there pulp quality (brightness and shade) has to be very good. Other mills have moved to hexasulphonated OBA in the size press because it builds to higher brightness and whiteness levels before "greenover," which occurs when the OBA reaches saturation and begins to bind to itself.

Similar changes to what occurred in uncoated white paper mills also happened in coated mills. Tetrasulphonated OBA was used in the coating in the past, and it may well have been replaced by hexasulphonated OBA now. Another reason for using hexasulphonated OBA has come from the advent of ColorLok® technology. ColorLok® and OBAs do NOT get along well together. Typical ColorLok® chemistries can cause the OBA added to the size press of an uncoated paper machine to drop out of solution, precipitate, and fill the rods of a metering size press. But, hexasulphonated OBA is the most soluble of the optical brightening agents, and it is therefore sometimes preferred in the size press starch to avoid runnability problems when ColorLok® papers are being made.

OBAs are now used in much greater quantities than they were in North America prior to 2005. The higher brightness and whiteness targets demand it. Despite upheavals in OBA prices due to availability and raw material shortages, they have come down in recent times to much more reasonable prices. The price gap between the different types has also closed tremendously. Rather than being a specialty additive, OBAs are now mostly a commodity. However, there proper use (addition point, type selected, etc.) and dosage can still have a strong impact on final product cost. 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 the most efficient in the wet end and has the least charge impact.

Remember, though, for those making Food Grades, there is only one OBA type presently approved by the FDA for use in that application, and that is tetrasulphonated. So, what is the best OBA combination to use? It all depends on the machine, furnish, other chemistry, and end product.

CONCLUSIONS

The North American white papers market has changed tremendously in the last 5 years. Tinting dyes and OBAs were significantly modified to meet the new optical property targets, and they should continue to be an area of focus for optimization for keeping 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 execute trials to determine what works best for your machine and grades. Be aware, though, that some paper products STILL require the use of specific dyes and tetrasulphonated OBA.

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