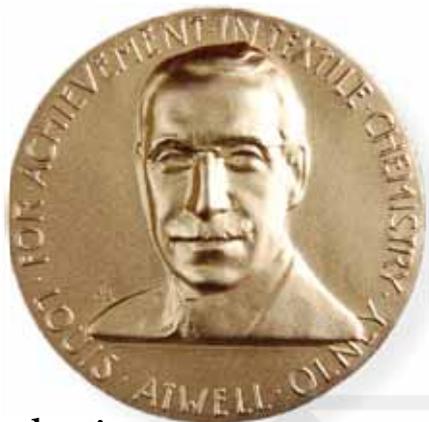


# In Praise of Textile Chemistry

By Martin Bide, University of Rhode Island, 2011 Olney Medal Award Winner



## Introduction

Since being notified of this honor, I have enjoyed thinking of what form this address might take. I have listened, often in awe, to many previous Olney medal addresses and it has been enjoyable and instructive to reread several of them. This is an attempt to live up to a no(ta)ble history and in doing so, to recognize some themes that most textile chemists will understand.

## Why is Textile Chemistry Special?

### Textile Chemists Benefit From a Long History

Clothing has been a human essential since we lost body hair and migrated out of Africa. For much of the time since the industrial revolution, any significant technological advance has been applied primarily to textiles. The power harnessed for the industrial revolution drove spinning machines and looms. Inorganic chemistry produced bleaching powder and mineral colorants. Industrial organic chemistry was first of all dye chemistry. Polymer chemistry found its first wide application in manufactured fibers. Textile chemists stand on a foundation of knowledge that we take for granted, but which “visitors” to our discipline often do not readily appreciate. That foundation is both wide and deep, within which are many fascinating niches. Some of these are explored and then forgotten: a discipline with such an extensive background will have its share of those who “fail to read history” and it is not uncommon to read a recent paper that doesn’t recognize a previous and similar approach.

For those who do read history, the treasure trove of the past leads to the observation that no knowledge is valueless. We are probably familiar with the refrain of “why do I have to learn this?” But what might at first glance seem an unimportant piece of trivia can illustrate a principle that can be applied in a totally different setting. A problem solved decades ago might reveal an inventive approach to dealing with a problem of today.

### Textile Chemists Know More Than They Realize

The broad foundation of our discipline leads to this observation. It becomes apparent when trying to explain, for example, the subtleties of dye-fiber interactions to students, historians, medical researchers, or chemical engineers (all of whom tend to start from the position of “how hard can dyeing be, anyway?”). It is a constant but enjoyable challenge. Our (textile chemical) world comfortably describes objects that are a few microns in diameter, within which are regions of more or less molecular order; polymer chain segments whose mobility we posit; and water swollen pores through which nanometer-scale dye molecules will diffuse. Without knowing it (or at least without giving it its *nom du jour*) textile chemists have been nanotechnologists for a century or more.

That diffusion takes place across a boundary that we refresh with dye by controlled agitation, at a rate that we influence with temperature, pH, electrolyte, and perhaps a well-chosen blend of... (well, that’s proprietary!). Our tender care will, we hope, produce fabric that is evenly colored, is the right shade, and leave a dyebath that contains the minimum of waste. If we have chosen the dyes well, and applied them correctly, the color will be fast (as assessed, of course, by AATCC test methods!).

Textile chemistry is rooted in the very practical, but its successful understanding requires some detailed scientific hypothesizing and experimentation. In other words, textile chemistry neatly bridges the gap between the academic and the industrial. At either end of the bridge are the practitioners who ignore theory, and the academics whose work is inherently impractical or adds little to fundamental under-





standing. More than 200-years ago, that sentiment was expressed most elegantly on the frontispiece of an early text on practical chemistry as “It is a pity so few chemists are dyers and so few dyers chemists.”<sup>1</sup>

### There Are No Dumb Questions in Textile Chemistry

AATCC stands comfortably on the bridge and has lived up well to its stated aims of increasing knowledge, encouraging research, and providing a forum for professional interactions for many years. Textile chemistry conferences, symposia, and meetings are a wonderful source of knowledge, of answers to questions, or even more questions that one can go away and try to answer. I do not envy those who attend conferences populated largely by other academics where attacks on ideas can become attacks on individuals: the more trivial the topic, the greater the vehemence, it seems. The cliché “there are no dumb questions” applies well to textile chemistry: the cliché relies on the patience to stop and think about where and how the question arose. AATCC is full of talented individuals who routinely spend their time and expertise to cheerfully answer what might initially appear to be dumb questions, and thereby contribute greatly to the “interchange of professional knowledge.” Similarly, most teachers have been forced to think differently about something when challenged by a student with what, at first glance, is a dumb question, but which contains an interestingly unorthodox view of the world.

### It’s a Small (Textile Chemical) World

Given the vast size (70 million tons of fiber per year) of the global textile industry, the textile chemical world is surprisingly small, and, with connections made more apparent with search engines and social media, getting smaller. The degrees of separation between textile chemists are often few. Maintaining those connections provides a rich source of expertise that is usually just an email away. The connections span generations: in addition to the obvious interactions with contemporary colleagues, students past and present can provide challenging questions, and professors’ former professors can still supply some interesting knowledge. And it can be interesting to follow the “family trees” of professorial expertise: I can trace my dye chemistry to W. H. Perkin in four “generations.”



### The More You Know, the More You Know You Don’t Know

Color and dyeing seem simple and obvious to the uninitiated, but it doesn’t take long before the complexities reveal themselves. Thus, textile chemists typically recognize early in their careers that the more you know, the more you know you don’t know. Fortunately, the corollary is the more you know the more chances you get to learn. Dip your toe into a new pool, get involved enough to dive in, and before much longer, others are asking you about the water. Textile chemists are typically adaptable creatures, and the broad background they enjoy lets them wander usefully into many areas that at first glance may seem unrelated.

### Textile Chemistry in Practice

#### The Way In: the 1970s

As I hope is conveyed above, the world of textile chemistry is a rich and fascinating one. I didn’t realize that I was headed there when I considered “Colour Chemistry” as a degree, sounding, as it did, much more interesting than plain chemistry. It turned out to deal predominantly with textiles and dyes, and my interest was piqued on touring a university lab in which freshly tie-dyed T-shirts were draped over dyeing machines. Being given a colour blindness test appealed to my sense of logic.

My classmates and I spent four years dealing with the intricacies of polymer structure, dye chemistry, dye application, dyeing and printing technology, and textile finishing. We suffered the principles of mass and heat transfer, and fluid flow through pipes. We learned about XYZ, FMCII and ANLab40 from pioneers of color science in pre-CIELAB days. We wrestled with kinetics and thermodynamics and their application to heterogeneous systems; how non-steady state diffusion led eventually to equilibrium (albeit rarely achieved in practical dyeing processes). We marveled at the delicate experimental techniques that were used to derive the equations. We wondered “why are we learning this?” but enjoyed the moments when the light bulbs lit and we finally “got it.” And, of course, we tie-dyed T-shirts!

Three years of postgraduate research gave the world some charming fluorescent yellow and orange disperse dyes with remarkably long names of no commercial value and provided a dissertation, published papers,<sup>2,3</sup> useful lessons on careful gathering



and analyzing data, heat resistant fingers (so one does not drop the beaker containing the product of five reactions and six weeks' work, no matter how hot) and pre-word-processing typing skills.

The 1970s were a twilight of the times when dyes were profitable and specialty chemicals and (manufactured) fibers were not yet the commodities of today. Dye and fiber companies undertook research that extended far beyond the immediate need to support sales. Textile chemistry was a more prominent academic discipline in which many talented scientists plied their trade. Then, as now, textile chemistry seemed comfortably to bridge the worlds of industry and academia: scientists from each area published significant, fundamental, pioneering papers that developed the understanding of the interactions between dyes and fibers. Even today, one can learn much from browsing *American Dyestuff Reporter* or the *Journal of the Society of Dyers and Colourists* from the mid-20th century.

The textile chemical world has changed since then. Dyes and fibers have become commodity products and profits can no longer support the same level of industrial research, particularly in the US and Europe. In the meantime, other research areas, notably those with the prefixes medico- or bio- or pharmaco- have more money to play with, and represent a richer field for research chemists, both academic and industrial. While dyehouses have embraced the joys of  $\Delta E$  and Instrumental Match Prediction, few dyers have heard of Langmuir's isotherm, or if they have, consider its implications in their day-to-day work. The range of fibers has grown, but the existing knowledge base lets us understand them fairly readily. It has been more than fifty years since the last new class of dyes was introduced.

### Industry and Academia

Standing on the bridge between the academic and the industrial, a textile chemist will often benefit from both. Industrial chemistry is instructive: 1. The need to answer to the bottom line is lurking in the background, no matter how interesting the research is. 2. The customer is right. 3. Minimize waste, and use it if you can. 4. The environment is important. These principles were brought together in an interesting multi-year dye project.

The first step for many anthraquinone ("AQ") disperse dyes is a (mercury-catalyzed) disulfonation.

The 1,5 and 1,8 isomers are isolated in about 65% yield. The rest is a mix of other isomers that were waste but could be retrieved as chloro compounds, then nitrated, hydrolyzed, reduced and brominated to make a workable navy blue. Optimizing the reaction for large scale production took two years of work, but scale up still had surprises, including a valuable lesson in the relationship between mass and surface area when 98% sulfuric acid at 130°C foamed up the stack! The resulting dye went for large scale customer trials. It failed: too much staining of cotton in blends, and some very interesting chemistry went onto the shelf. Many years later, the building in which these dyes were produced was demolished. The brickwork contained enough mercury that the whole building was hazardous waste. Outside the lab it became clear that the polyester boom of the 1970s was over, and that there was a limited future in industrial dye research.

So it was back to academia. For a new member of the faculty, there is inevitably a period of adjustment. For both teaching and research, it is typically a relearning time for a lot of that undergraduate material (no knowledge is wasted, and THAT's why I learned it). AATCC had (and maintains) a vital role in providing professional contacts at the local and national (and increasingly, international) level. And the contacts are both fellow academics and the "real-world" practitioners, between them providing continuing sources of inspiration, chemical samples, plant tours, and a chance to explore interesting ideas.

### Where's the Money?

Funding is important, and a researcher who relies on a single topic is at a disadvantage compared to one who is flexible enough to do what someone with money requires. Academic research is thus not too distantly related to the oldest profession. It's especially advantageous to have contacts with funding agencies near the end of the year when they may have to spend it or lose it. This was the genesis of a project on wool scouring funded by USDA, for which the idea was to solvent-scour wool "on site," recover the solvent, give the farmer clean wool, collect lanolin, and return the remaining waste to the field as fertilizer. A technically successful project, some wonderful new contacts in the wool business, and, in a triumph of comic timing, a paper published about six months before the solvent used, Freon, was recognized as a potent greenhouse gas!<sup>4</sup>





Spin-off ideas are interesting to explore. A study of spots appearing on army T-shirts, especially those worn by young recruits, turned out to be the effects of acne medication based on benzoyl peroxide, an oxidant powerful enough to destroy dye. Turning a problem into an opportunity led to a study of its use as a discharge agent for printing, and a first foray into AATCC's student paper competition.<sup>5</sup>

Many might remember the AATCC's intersectional paper contest. For several years, the RI section of AATCC put together a group (again, a combination of the academic and the industrial) to produce papers for the competition. An interesting exercise carried out in the evenings at various labs, it produced papers on rayon dyeability tests, moisture vapor transmission, and the drycleaning fastness of pigment prints.<sup>6,7</sup> It also meant good business for a number of local pizza restaurants!

### The Rewards of Former Students

Students inevitably become former students. They are often a rich source of interesting conversations as they come face-to-face with the real world and have the good sense to remember that professors might actually know something. One graduate working in dye research asked how to do thin layer chromatography on vat dyes. That became a Masters thesis.<sup>8</sup> Another series of discussions became an interesting study in print paste rheology.<sup>9</sup>

The most fruitful of these casual conversations came via a former student who married a biochemist, working in the vascular surgical research laboratory of a large NE hospital on knitted polyester artificial arteries. When his wife ran out of answers to textile questions, it started a collaboration that is now more than 20-years old. A textile chemist's shortcomings in biology matched the biochemist's in polymer and fiber chemistry, and the resulting "dumb questions" often led to the answer "I don't know, why don't we find out?"

The first task was to reduce infection over periods of days or weeks after implantation, more than could be achieved by local bolus at the time of the operation, and more elegantly than could be done with degradable binding agents. The work sought dyes with antibiotic properties, looked at mordant dyes mordanted with silver, used dyes as 'anchors' to which antibiotics might be linked, and found some success with the application of heat-stable antibiotics in a (textile-like) pad-heat process. This worked,

albeit inefficiently, as some of the antibiotic was held near the fiber surface and was released (measured as one would measure dye release) slowly enough to kill bacteria for several days<sup>10</sup> and which showed sufficient promise to be trialed.<sup>11</sup>

The next challenge was to reduce the incidence of clotting within the artery: good anti-clotting agents are known, but they must be immobilized to make them effective in a small area. The surface hydrolysis of polyester is well known (originally as "denier reduction") and it generates a surface rich in carboxylic acid groups.<sup>12</sup> These provided sites for crosslinking reactions to bind the anti-clotting agent hirudin to the polyester surface and show that it maintains its activity.<sup>13</sup> A similar approach bound a growth factor to the surface of the polyester so that the "right" cells would colonize the graft and extend its acceptance by the human body. The examination of other surface modifications led to ethylenediamine, and the expectation that an aminated surface could bind. Interestingly, both amine and carboxylic acid groups are produced simultaneously, providing a multifunctional surface.<sup>14</sup> Some flexible thinking turned the prevention of blood clotting into its promotion, and with similar antimicrobial and cell growth properties, the genesis of a wound dressing for major trauma in a relatively small package.<sup>15</sup> And while polyester has too high a Tg to absorb or release materials at normal temperatures, other polymers are more cooperative. A polyurethane with carboxylic acid functionality provided a chance to practice some of those equilibrium experiments and to postulate a sorption mechanism based on a Langmuir isotherm.<sup>16</sup>

Those important connections in the close textile world led to others joining the group, bringing electrospinning into the mix, and a chance to produce structural polymers, chiefly polyesters, in sub-micron sizes at ambient temperatures.<sup>17</sup> The different size and morphology allows for longer and steadier release, e.g. of antibiotics, and the low temperature means that bioactive proteins survive and maintain activity without the complexities of the crosslinking moieties. Playing with electrospinning conditions, and varying the polymers used (in layers or as alloys) means no shortage of research to do. In the meantime, the biochemist and his wife now have a successful research company, with a staff of scientists and a burgeoning portfolio of intellectual property.





## Right Place, Right Time

Timing can play a crucial role, such as when a chemical engineering department has finished a successful pollution prevention project in the jewelry industry, and a textile chemist shows up just in time to help develop a P2 project for the textile industry. Good professional contacts from AATCC meetings can open doors, and led to practical help for many of the 50 working dyehouses in Rhode Island, and some academic research on dyebath reuse and machinery modifications to avoid some unpleasant chemicals.<sup>18,19</sup> The associated learning led to a series of consulting projects with USAID in several exotic locations, working with talented environmental engineers who were happy to share their expertise. Many of those P2 principles have become the means to participate in current debates on sustainability.<sup>20</sup>

Changing institutions can provide new challenges and opportunities. Teaching courses in new subjects benefited from the wealth of knowledge that AATCC meetings and members can provide, and a chance to develop expertise in new areas.<sup>21</sup> New colleagues provide new areas of research. The University of Rhode Island (URI) has a large Historic Textile and Costume collection and the Northeast has rich repositories of dyers' and printers' notebooks from the nineteenth century. Reading them today is both challenging and rewarding. Understanding them and interpreting their use on historical textiles makes full use of a textile chemical education, and interpreting them for an historical audience requires some care. A "quilt documentation project" for the state produced a book that included details of printing processes of the 19th century.<sup>22</sup> AATCC's "Little Black Book" provided a fascinating study of printing techniques before synthetic dyes were available and an interesting lesson in early technology transfer.<sup>23</sup>

Meanwhile, stray encounters can lead in interesting directions. One spectroscopist with an interesting analytical technique was looking for new compounds to work with and asked a student to "go pick up some dyes" from textiles. Her jaw dropped when she looked in a cupboard with around 500 dyes in it. But it turned into some very rewarding research.<sup>24</sup>

A benefit of academic life is the opportunity to take a sabbatical leave. Finding something interesting to do is easy when one maintains contacts with ones student peers who are also in the academic world, and who are applying the same educational back-

ground in many different directions.<sup>25</sup> And who would have thought that measuring tooth color could be so difficult?

## Final Thoughts

Textile chemistry offers a vast array of possibilities. And as textile industries grow around the world and universities continue to teach the subjects, employing professors who need to publish to prove their worth, those possibilities are similarly increasing. New instruments, new chemical and physical techniques, the occasional new fiber, responding to the needs of the environment... Computing power of the 1970s and 1980s made possible Instrumental Match Prediction and represented a cutting edge in dye chemistry when molecular orbital theory was used to predict the absorption maximum of a given dye structure. But the orders-of-magnitude greater computing power of today is used where the money is, to predict drug-cell interactions, not to predict fiber-dye interactions. And only time and the marketplace can separate the true breakthrough from an academic curiosity, or an idea that is just not quite practical enough.

My undergraduate research project was a dye for olefin, my first job interview was to join a project on reducing oligomer from polyester dyeing, and one of my first students went to work on developing reactive dyes for nylon. It's been fascinating to see how much effort has been put into these ideas in the years since without achieving full success. But we will all keep trying!

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