BEYOND THE FIG LEAF

By Philip Brown, 2023 Olney Award Recipient, Clemson University

ABSTRACT

Since the demise of the fig leaf, it appears that garments, including their individual parts, are meant essentially to cover and protect the users. Additionally, garments convey many signals such as power, sex, importance, and status. However, it seems that these signals cannot be effectively communicated if one ends up looking and smelling like a wet soggy dog.

From my youth, it was apparent that approaches that can mitigate the water saturated, dank, waterlogged effects that drizzle and deluges can have on people and their clothes were needed then and are still needed today.

In essence, this story revolves around the development of fibers and textiles that possess hydrophobic and oleophobic properties for extended time periods by making use of replenishing additives and specific fiber geometries.

BACKGROUND

Chemical surface modifications on fibers are literally "as old as the hills" considering that evolutionary processes have been modifying plant and animal fibers for survival over eons. Humans have applied this concept to textiles, developing finishing techniques to modify fibers to suit our current and future needs, whatever those may be. Despite years of technological advances, our modifications are yet imperfect. Looking over the textile research of the past 100 years, we find that some problems and issues continually resurface.

In 1905, Percy Bean published a rather extensive two-volume book about the chemistry and practice of textile finishing, in which he outlined ways to enhance fibers by making them softer, rot proof, waterproof, flame resistant, and bug resistant.[1] Since then, advances in polymer science and organic chemistry have greatly expanded the range of solutions for those and other problems that arise from the inherent properties of natural and synthetic fibers.

In 2023, one might ask the question, what else is there to do? Certainly, many of the basic issues—such as repellency, softness, anti-static, flame resistance, crease resistance, insect resistance, and antimicrobial issues have been addressed/solved in many ways over many decades.

Consequently, innovations today must solve not just the same age-old problems, but also enhance fiber and fabric functionalities beyond those expected by the consumer. These functionalities should also embody sustainability and environmental concerns.

Plus, there is a need to make money. My thoughts are that in 2023, our targets are much broader in scope than they were some 40 years ago, when I was a student. Thus, we should be adding functionalities that are all-encompassing i.e., those that have both high technical performance and green perspectives. In this way, manufacturers can create fresh marketing opportunities and more ways to distinguish their brands.

RESURFACING PROBLEMS FROM IMPERFECT SOLUTIONS

The chemical and textile industries have developed many solutions to big problems, only to learn later down the line they have become a problem themselves. This is nothing to be ashamed of, rather it is an opportunity to create new solutions.

Resurfacing problems are not restricted to the textile industry. For example, a big advance in the automobile industry was the use of "Ethyl." Riding with Ethyl became a good thing as it prevented engine knocking, which occurs when fuel detonates without being initiated by the spark plug. However, many years later, it was realized that Ethyl, developed by Thomas Midgley, had problems.[2] Tetraethyl lead, while being a great octane booster, led to environmental problems. The problem of lead as a potential health hazard was known, with some saying it contributed to the decline of the Roman Empire. Nonetheless, Ethyl solved a big problem at the time. In the 1920s, we can imagine they did not foresee the huge growth in the automobile industry. Today it seems everyone in a household has their own automobile, including a spare truck for the dog.

Another example would be the development and use of DDT (dichloro-diphenyl-trichloroethane) in the 1940s. As an insecticide it was used to kill mosquitoes and other insects. It found uses in homes, gardens, institutions, and crop and livestock production. It was very effective in reducing the problems of malaria in many regions around the globe. In 1972, DDT was banned in the USA. DDT is now regarded as a probable carcinogen with human reproductive defects suspected, known to be environmentally persistent, bioaccumulative, and can travel significant atmospheric distances. Nonetheless, Paul Hermann Muller received the Nobel prize in 1948 for Physiology or Medicine "for his discovery of the high efficiency of DDT as a contact poison against several arthropods."[3] It has been estimated by the World Health Organization that the use of DDT did save approximately 50 million lives. Although DDT is banned, the problem continues in 2021 when there were an estimated 247 million cases of malaria worldwide.

The textile industry is also a large chemical industry, and as with the examples mentioned, many groundbreaking ingenious solutions were later found to have their own problems regarding toxicological and environmental effects. Examples include fluoropolymers for oil and water repellence.

As a student at the University of Leeds, UK, in the 1980s, it was explained to me by my lecturer in chemical finishing, Ian Holme, known to us as Ian or sometimes Him Alone, that if you need both water and oil repellency you need to use fluoropolymers. In terms of repellency, fluoropolymers like PTFE (polytetrafluoroethylene) and fluoroacrylates are immensely impressive due to their low surface energy characteristics. At that time, I considered their performance to be outstanding. I was proud to be a textile chemist, a newbie in a field that made better products for a better world. They were considered inert, and as such, I could not see any drawbacks. Now this inertness is referred to as "forever chemicals." It is now known, just like DDT, the downsides of PFOAs (perfluoroalkyl substances) include that they are environmentally persistent, they are found in groundwater, and they bioaccumulate. Again, this is nothing to be ashamed of. Instead, we should approach the problem of repellency (particularly oil repellency), as a challenge and approach such problems with the sentiments of Horace Mann, who said "be ashamed to die until you have won some great victory for humanity."

THE AVANT-GARDE APPROACH

The avant-garde approach to surface science (chemical finishing/physical featuring) finds us revisiting "the hills" and the art of nature for inspiration. In copying nature, plants, and animals via biomimetics, textile functionalities can be reinvented to enhance and address current issues with repellent technologies.

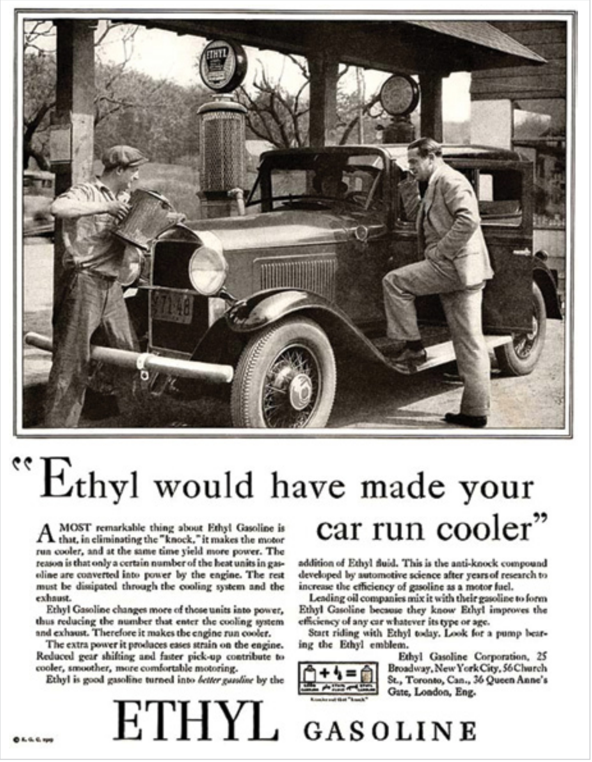
One such inspiration has been the lotus leaf, which demonstrates what is now known as the lotus effect. The properties of these leaves have been described as ultra-hydrophobic, super repellent, and self-cleaning. This is due to the leaves having an inherent micro- and nano-roughness (small hills developed via adaptive/evolutionary processes) allowing the plant, which inhabits a muddy swamp-like environment, to self-clean, therefore aiding in its photosynthesis.

I first came across the idea of the lotus effect when working at the University of Leeds while collaborating with Phil Sams, a scientist from Unilever. At that time, (around 1999) we were examining ways to make fabrics hydrophilic or hydrophobic with the use of plasma etching or plasma polymerization. Back in 1992, Sams had been examining the effects of surface topography on wettability. He mentioned to me that asperities on plants, feathers, and insects could make them "fully repellent."[4] I remember thinking that was interesting, but was not sure how to do that with plasma polymerization. Nonetheless, I thought this was something I wanted to get involved in as it intrigued me. Not long after, in 2001, I moved from Leeds, UK to The School of Materials Science and Engineering at Clemson University, SC, USA.

Different environment, different people! One day while sitting in my office, my friend Igor Luzinov popped in. All of a sudden, we were talking about the lotus effect, and I remember looking at Luzinov and saying, "let's do it." With a big grin, he said, "okay!" At that time, Luzinov was working on a "macromolecular anchoring layer" chemical technology based on PGMA (poly-glycidyl methacrylate). Looking back in time, it all seems terribly simple. It wasn't, but the excitement was real. Now we needed to add asperities. I remember thinking, *this has to work*.

So, the question became where are we going to get nanoparticle hills? Fortunately, again, the answer was very local, and we enlisted the help of George Chumanov in the Department of Chemistry at Clemson University. Chumanov makes metallic nanoparticles of different types. His favorite is silver due to their photonic 'colorful' abilities i.e., plasmon resonance.

From a color/materials science perspective, perhaps the most beautiful object ever made that used metal particle



nanotechnology was fabricated 1600 years ago by the Romans. You could also, it seems, drink out of it on special occasions.[5]

The idea/plan was becoming a reality. In addition, not only would silver nanoparticles provide the bumps, they could also potentially contribute inherent antimicrobial action to the system.

ANY FIBER + COATING 1 (PGMA nanolayer) +
SILVER nano BUMPS + COATING 2
(F-POLYMER nanolayer) = SELF CLEANING &
BUG FREE CLOTHES!!

We began to collaborate. What happened next, though, was a little unexpected, a large understatement. Not results-wise, but the amount of attention we received was rather large. With the encouragement of Bill Pennington, a Professor in the Chemistry Department at Clemson University, I began organizing a conference session for the Southern Region of the ACS (American Chemical Society) on Textiles, "Can They Really Do That?" After the conference was announced, I got a call from Mark Sampson of ACS. After some discussions about what is "it" they can really do, Sampson prepared an ACS press release, "Self-Cleaning Suits May be in Our Future."[6] Many others followed, two of note being from *The Christian Science Monitor* and *Popular Science*.[7,8] After that, I was on the phone non-stop for about three months, with my left ear burning because my right ear was totally deaf.

Back to the process. This process can be applied to many fibers, as well as to other materials and substrates, such as glass and metals. In each case, the coating permanently bonds at a molecular level to the substrate.

When applied to fibers, the handle of the resulting textile (to my touch at least) seemed identical to that of the uncoated equivalent textile. This type of lotus coating offers enhanced waterproof capability and is suitable for all types of apparel, from shirts to jackets, to trousers, and pants.[9,10]

ELEGANCE VERSUS MANUFACTURE

Indeed, the method was elegant but also delicate in the sense that poor execution of the process could negatively affect the success of the coating. For example, prior to the treatment, both the fabric's surface and the application machinery must be spotless. In an industrial environment, focused on production rates, this might not be so simple. Nonetheless, simpler methods can be used to obtain similar results by applying hydrophobic polymer dispersions/coatings that have nanoparticles dispersed in them.

OLD SOLUTIONS—THAT LED TO NEW PROBLEMS

Around 2005, the problem of C8 fluorocarbons in the environment/bioaccumulation had become clear and the solution was to reduce the fluorinated moieties by two carbon atoms to reduce the problem. Legislation was passed such that by 2015, C8 based finishes could not be used.

Around 2008, it was evident from many conversations I had with companies applying C6, that the C6 replacement chemistry did not perform as well as the previous C8 chemistry. Between 2008 and 2015, other initiatives were examined, and these are still continuing today. To add further complexity to the situation, a number of things were ongoing from 2005. Firstly, there was an increased perception of the environmental problem. Global studies were performed looking at textile wastewater, highlighting many pollution problems, and pointing at the 'fashion and corporate labels,' not the chemical producers per se.[11] At this point, there were ideas of manufacturing with zero emissions and zero pollution. This is an interesting idea, as one would not be able to drive to work (pollution) or wear clothes (pollution) and thus one would walk to work naked.

Fortunately, while doing your homework, you realize you have a fig tree outside your house. Upon getting to school, you find your computer has been replaced with an abacus, and you have a quill to write with. All you must do now is get the blood of an albino vampire (used as ink) to write with on the back of a Dead Sea Scroll to be obtained from the Museum of Monty Python. And then you hear, “Sounds easy enough Brown, get on with it. I expect your answer by next weekend.” Yes sir!

As time went on, regarding chemical producers, a number of court cases found fluoropolymer manufactures guilty of what amounts to perceived ecocide, and/or simply bad decisions were pursued. These cases are likely to be ongoing for some time.[12]

The result of the above combinations was that a number of textile manufacturers totally abandoned fluoropolymer chemistries. The end result is previous performance standards cannot be met.

FUTURE SOLUTIONS OR NO SOLUTIONS

In my opinion, we do not have to abandon performance, cancel elements, and go back half a century.

I would like to suggest two approaches, which when combined, will lead to the desired water and oil repellency for synthetic fibers. In addition, since neither approach uses nor requires water as an application media for fluoropolymer incorporation, then the environmental wastewater burden is eliminated. One approach is to make fluorinated polymers of ‘low’ molecular weights that are melt stable and somewhat immiscible with the base polymer to be melt spun. Such polymers can have fluorinated groups that are shorter than C6 and yet demonstrate oil and water repellency at the polymer surface by making use of thermomigration.[13] The other approach is to make use of geometry at the fiber level. The geometries are chosen to attempt to optimize repellent effects. Such surfaces were described by McKinley[14] have been fabricated via fiber formation as demonstrated by Hoffman.[15]

This story has yet to be finished. For now, this story (my story) is ending but the pendulum continues to swing. If the shadows seem darker in 2023 it is only because the light is brighter and there is hope.[16]

LYRICAL MUSINGS

We need to take some time to be distant, need to take some time to be still.

Need to take some time to rethink the problem as our processes are making the world ill.

But canceling elements because you feel awkward will only sacrifice the performance, And if you’re going backwards, you’re not moving forwards.

So, let’s retool with intellectual evolution to enact revolution, and make use of geometry, a different way of thinking, a new theology, refreshing, replenishing chemistry to improve human life and prosperity, don’t be the poison, make the remedy.

—Phil Brown

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