The Evolution of Durable Press and Flame Retardant Cotton

May 14, 2004

A National Historic Chemical Landmark

AMERICAN CHEMICAL SOCIETY

SCIENCE THAT MATTERS

"Chemical research at this laboratory [SRRC] on 'durable press/easy care'and 'flame retardancy' of cotton has been extremely significant for increasing cotton markets and market share and helping cotton compete against synthetic fibers."

– Phillip J. Wakelyn, Ph.D., Senior Scientist, National Cotton Council.

Celebrating Chemistry: The American Chemical Society designated the evolution of durable press and flame retardant cotton a National Historic Chemical Landmark on May 14, 2004.For additional information see our Web site: www.chemistry.org/landmarks.

Cotton under attack

King Cotton was about to be dethroned. By the middle of the 20th century synthetics were usurping cotton as the dominant textile. In particular, wrinkle resistant synthetics had captured a large part of the clothing market and had begun to be used in household items traditionally made of cotton.

Cotton is a natural seed fiber that exhibits many attractive qualities. It is comfortable; it breathes; and it can be dyed easily. These traits combined with its wide availability and renewability made cotton desirable for apparel and home use for centuries. As late as 1960, cotton accounted for two-thirds of the total retail apparel and home furnishings market (excluding carpet). But as the competition from synthetics increased, cotton's share of that market diminished to about one-third.

This was the situation that the scientists and researchers at the Southern Regional Research Center faced when they began studies designed to make cotton competitive with synthetic fabrics. One measure of their success is that by 2000 cotton owned a 61.5% share of the retail market for apparel and home furnishings (again, excluding carpet). The average consumer used thirty-seven pounds of cotton a year, half again as much as ten years previously. King Cotton was reclaiming his throne.

Cotton and science

Cotton farming in the early years of the 20th century, like much of U.S. agriculture, suffered from overproduction, a chronic problem that resulted in surpluses and low prices. In a sense, the American farmer was the victim of his own success as mechanization and newer and better crop varieties increased yields per acre. After World War I agricultural problems worsened. In the 1920s farmers were buffeted by inflation. Then the Great Depression, an era of deflation and lower and lower commodity prices, forced many off the land and impoverished those who stayed.

Congress responded to the farm crisis with the 1938 Agricultural Adjustment Act. One small part of the legislation instructed Secretary of Agriculture Henry Wallace "to establish, equip, and maintain four regional research laboratories, one in each major farm producing area, and at such laboratories to conduct researches into and to develop new scientific chemical and technical uses and new and extended markets and outlets for farm commodities…" The Southern Regional Research Laboratory was placed in New Orleans, and it was commissioned to focus on sweet potatoes, peanuts, and cotton – especially cotton.

Southern Regional Research Center (SRRC)

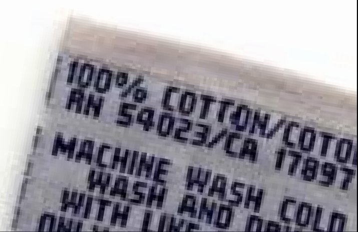
Durable press cotton

Much research interest centered on making wrinkle resistant or durable press cotton so that cotton could compete with synthetic fibers. Cotton is mainly cellulose, which is a polymer. The cellulose chains in cotton, organized into microfibrils, have only hydrogen bonds between them, so there are no covalent crosslinks to force the cellulose chains to return to their original position when deformed by wrinkling or laundering.

In the late 1950s SRRC scientists initiated work on wrinkle resistance so that fewer wrinkles would form and those that did would fall out on hanging. The next stage was wash and wear: making a wrinkle free garment that would come out smooth after washing. But wash and wear had a problem; it would not hold a crease. That led to the next stage, sometimes called permanent press, but more accurately termed durable press, in which wrinkle resistance and durable press creases could be achieved in cotton garments.

In the beginning, scientists used urea-formaldehyde resins, which are inexpensive, to produce cotton garments that had wrinkle resistance and shape retention. Later, melamine-formaldehyde condensates that produced fabrics with improved properties were introduced. SRRC scientists understood in the early years of research that wrinkle resistance could be imparted to cotton by polymer forming reagents and surface treatments, but that better and more durable levels of wrinkle resistance could be achieved when the reagents actually penetrated the fibers and reacted with the cellulose. The result was a chemical modification of the cotton fabric by crosslinking. This means that the cellulose molecules, which are long chains, are chemically linked by short molecules to make them more rigid and the fabric wrinkle resistant. The crosslinks between cellulose molecules are analogous to the rungs on a ladder. Fabrics thus treated when smooth will return to smoothness when washed.

Formaldehyde derivatives were commonly used because they are cheap and highly effective as wrinkle proofing agents. Formaldehyde derivatives are effective reagents, except that they are not stable. This means there is a very slow release of formaldehyde



J. David Reid (left), head of the Wash Wear Group

during processing in the mill and during storage of the treated fabric or finished garment. Formaldehyde release raised safety concerns, so over the years SRRC scientists worked to control the amount of formaldehyde released in durable press processes.

Researchers succeeded in reducing the amount of formaldehyde released from about three thousand parts per million to about 250 parts per million. Better preparation of the finishing agents helped lower formaldehyde release, but finding newer and more stable finishing agents proved the best method. The major success in this area came with the introduction of DMDHEU (dimethyloldihydroxyethyleneurea), or more correctly 1, 3-bishydroxymethyl-4,5-dihydroxy-2-imidazolidinone. DMDHEU was first patented by BASF, but SRRC scientists researched capping agents added in the crosslinking process that further lowered the formaldehyde release.

Of course, eliminating formaldehyde altogether became a goal. While some successes were achieved in finding formaldehyde-free reagents, there were problems. The formaldehyde-free reagents are more expensive and many of them cause discoloration. Some have toxicity problems of their own. One safe but relatively expensive reagent, DHDMI [dihydroxydimethylimidazolidinone (1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone)] produced moderate levels of resilience and is used in infants' clothing. Polycarboxylic acids are the most successful of the non-formaldehyde agents, particularly BTCA (butanetetracarboxylic acid). SRRC scientists discovered a series of catalysts to enable these acids to react with cotton fabrics to achieve the crosslinking needed to impart durable press properties. The greater cost of formaldehyde-free agents, however, has limited their commercial adoption.

In addition to safety concerns, there were other problems with finished cotton treated with nitrogenous formaldehyde-based reagents. The main problem was chlorine absorption, which would make cotton garments turn yellow upon washing and lose strength on "touch-up" ironing. Another problem with durable press treatments is strength loss, which is caused mainly by what is called "crosslink embrittlement." The goal in all treatments was to get a balance between smooth appearance and retention of a practical level of strength.

Many approaches were taken to solve these problems. One avenue was to blend cotton with polyester, which produced a stronger fabric but not a stronger crosslinked cotton component. SRRC researchers also explored additives which did not chemically attach to the fibers. One such additive is emulsified polyethylene, which stays on the surface and essentially protects the surface from wear. Polyethylene softens cotton fabric, gives it more strength, and increases abrasion resistance substantially. It is also inexpensive and remains much in use.

Durable press has helped to revive the cotton textile industry. Much of the work in improving durable press, in elucidating crosslinking mechanisms, and in discovering additives to improve fabric performance was done at the Southern Regional Research Center. Imparting wrinkle resistance without losing strength, while at the same time minimizing abrasion, remains the primary research objective for the cotton fabric industry.

Flame Retardant

The initial impetus for research at the SRRC into flame resistant cotton fabrics came from the U.S. Army's Quartermaster Corps, which was seeking fire retardant uniforms. At the same time, people in the cotton industry understood there would be consumer demand for flame retardant textiles if they could be made durable and if the fabrics could overcome the stiffness and roughness that characterized early attempts.

Research at SRRC focused on the chemical modification of cotton by the chemical reaction of flame retardants with the cellulose molecules on the surface and within the cotton fiber. Early work centered on treatments with tetrakis(hydroxymethyl)-phosphonium chloride (THPC), which unfortunately had the disadvantage of a significant loss in fabric strength. To counter this problem, scientists raised the pH of THPC with aqueous sodium hydroxide, creating THPOH [tris(hydroxymethyl)-phosphonium hydroxide]. This process resulted in fabrics which were less stiff and stronger. THPC and THPOH were both treated with bromine compounds and ammonia in an attempt to produce flame retardant fabrics that were light weight and had a good "hand," that is were soft.

Other reagents that were used included APO [tris(aziridinyl) phosphine oxide]. Combinations of APO with THPC and THPOH were tried as well. The combination of APO and THPC proved to be one of the most effective flame retardants because the properties of the fabric remained good. Unfortunately, APO is expensive and toxic, so it could not be used commercially.

SRRC research results in flame retardant cotton and blends are used by the military in various projects to provide U.S. service men and women with the best protective clothing possible. Some of the materials produced were used by NASA in early space flights and by fire departments throughout the country. The many publications by SRRC scientists kept focus on the dangers of performing risky operations at high temperatures without the use of specialized flame retardant fabrics and undoubtedly resulted in the saving of lives and property.

National Historic Chemical Landmark

The American Chemical Society designated the evolution of durable press and flame retardant cotton at the Southern Regional Research Center a National Historic Chemical Landmark on March 24, 2004. The plaque commemorating the event reads:

By the 1950s, synthetic fabrics – often wrinkle resistant and flame retardant – began to overtake cotton as the dominant U.S. textile fiber. To reverse this trend chemists and chemical engineers at the Southern Regional Research Center initiated research to modify cotton chemically. Their efforts in developing agents that crosslinked the cellulose fibers and in establishing crosslinking mechanisms led to improved durable press fabrics. SRRC studies also developed new agents that improved the durability of flame retardant cotton to laundering. These significant advances in the properties of cotton enabled this natural fiber to remain a highly competitive textile.

About the National Historic Chemical Landmarks Program

The American Chemical Society, the world's largest scientific society with more than 159,000 members, has designated landmarks in the history of chemistry for more than a decade. The process begins at the local level. Members identify milestones in their cities or regions, document their importance, and nominate them for landmark designation. An international committee of chemists, chemical engineers, museum curators, and historians evaluates each nomination. For more information, please call the Office of Communications at 202-872-6274 or 800-227-5558, e-mail us at nhclp@acs.org, or visit our web site: www.chemistry.org/landmarks.

A nonprofit organization, the American Chemical Society publishes scientific journals and databases, convenes major research conferences, and provides educational, science policy, and career programs in chemistry. Its main offices are in Washington, DC, and Columbus, Ohio.

Acknowledgments

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Written by Judah Ginsberg

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