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ANNUAL PROGRESS REPORT

NATIONAL TEXTILE CENTER

PROJECT TITLE: INDUSTRIAL PLANT TEST: HYDROGEN PEROXIDE-BASED SCOUR/BLEACH PROCESS FOR HOSIERY WITH PREPARATION BATH REUSE

CODE NUMBER: G94TT-2

GOAL STATEMENT: To lay a firm foundation for the plant partner, Chipman-Union Co., to convert its entire sock preparation operations from the current sodium hypochlorite-based process to the developed hydrogen peroxide-based process while tying in direct bath reuse as an integral part of the technology shift, and thus providing a classic Beta Site to ease transfer of the developed technologies to the relevant industry sectors.

ABSTRACT:

REPORT: Through NTC funding in the first two years, the research group has developed a novel hydrogen peroxide-based scour/bleach (HPS/B) process for sock hosiery, and demonstrated on a pilot scale the potential for directly reusing both the HPS/B bath and the subsequent softener finishing bath. The process is designed to replace the current sodium hypochlorite-based scour/bleach (SHCS/B) process for socks dominant in this industry sector. For environmental and effluent reasons, it is imperative that the industry eliminate the chlorine oxidant from the sock preparation process. For example, the SHC has been found to generate undesirable chlorinated organics, e.g., the carcinogen chloroform, in the combined S/B process with the strong oxidant in contact with organics originating from the raw cotton in the sock construction. The SHC process also does not lend itself to land application of pretreated effluent or to direct S/B bath reuse, both goals of the industry and the project's plant partner, the Chipman-Union (C-U) Co. (Bryan-Scott Plant), Greensboro, GA.

In Year 1 of the current project, the process developed at pilot scale (11 lb./run capacity, 12:1 liquor ratio, LR) is being optimized, streamlined to minimize time and materials consumption, and translated to plant-scale, Braun batch preparation equipment (400 lb./run capacity, 8:1 LR, smallest production machine available at C-U (400-600-800 lb./run machines are in the partner plant)). Cost-sharing to the NTC project is being provided in Year 1 only by the a new State of Georgia Traditional Industries Initiative, the **Consortium on Competitiveness for the Apparel, Carpet and Textile Industries (CCACTI)**, at a level of $685,000.

The pilot HPS/B process was initially optimized for attainment of whiteness level only (foot section of sock). Whiteness values (W) using standard CIE color computer equations were in the 81-82 range, compared to current values being attained on the Braun machines with an upgraded SHCS/B process in the 88-90 range. In reviewing the developed formulation and process, staffers at C-U

requested the following optimization steps be taken before plant trials were attempted:

. Raise the W values to approach those attainable in the current process.

. Investigate chemical elimination/reduction possibilities.

. Streamline the total time of the process, e.g., by investigating the elimination of the second rinse step.

A series of pilot scale runs were initiated with the HPS/B process to meet these objectives. Main strategies were:

. **Dramatically Increased Oxidant Concentration** - With the large concentration of organics being generated from the cotton of the socks by the scouring action of the bath, it was theorized that the kinetic chains producing the desired hydroxyl radical (the suspected active agent for cellulose bleaching) from HP were being terminated and/or interfered with by the contaminants in the bath.[1] The general conception is that ferrous ions in the water initiate the chain breakdown reaction of HP, and that the color-producing chromophores in cotton compete for the -OH radical in the system.[2] In turn, for unscoured cotton, the organic impurities present in the S/B bath (pectins, pectates, fatty acids/alcohols, waxes, knitting oils, etc.) will also consume the highly-reactive -OH radical, reducing the statistical probability of the "desired" reaction occurring between the radical and a cotton chromophore in a fixed-concentration environment. Indeed, Cates and coworkers showed that under identical conditions, peroxide consumption was reduced dramatically in standard bleaching of unscoured vs. scoured cotton fibers.[1]

To increase the statistical probability of achieving the desired -OH radical/cotton chromophore reaction by providing an increased supply of the hydroxyl radical, mass of 35% w/w HP included in the formulation was increased 3X (to 1500g on the pilot runs), and post-HP addition to the first rinse bath was eliminated. The average W value increased to 83 as a result. Further studies at lower (1000, 1250g) and higher (2000g) mass HP additions showed that 1500g was indeed optimal for W values with the developed formulation and process.

. **Raise Temperature** - Earlier research had shown that the stripes inherent in ~30% of C-U's sock production (formed by knitting in precolored polyester (disperse dyed) or acrylic (cationic dyed) yarns from various suppliers) occasionally bled and/or transferred color at HPS/B process temperatures >180F. Using the increased peroxide concentration, fresh runs were at 200F on white socks only, i.e., striped socks were eliminated from the load, whereas previously they had been included in equal weights with the white socks. No immediate W improvement was observed with the temperature increase, remaining at 83.

. **Eliminated Epsom Salt** - Magnesium sulfate, or Epsom Salt, is a known stabilizer for HP, complexing the molecule and thus inhibiting the initiation of the chain breakdown cycle by the ferrous ions. With the high concentration of sodium hydroxide (a HP activator) required in the developed HPS/B process formulation to effect the proper scouring of the socks, epsom salt was included in the formulation to work in concert with the normal sodium silicate stabilizer to prevent too-rapid breakdown of the oxidant. The latter can cause excessive degradation of the cellulose in the cotton fiber, resulting in unacceptable strength loss. However, in the runs to date, low peroxide consumptions had been recorded (normally 20-35%) via potassium permanganate titrations. The system was thus theorized to be over-stabilized, with the organics emanating from the cellulose acting as an additional stabilization force with the epsom salt/sodium silicate combination (see earlier discussion).

A pilot run at 200F with 1500g of 35% w/w HP and **no** Epsom Salt gave the highest average W values achieved to date with the pilot HPS/B process, 85 (white socks only, see Table I). Elimination of the chemical from the formulation thus appears possible, simplifying it and reducing overall costs. However, the **percent** of HP consumption did not improve in the run, remaining at a low 22.6% of available.

A second meeting was held with the partner plant staff to review the above results. After visual comparison of the socks produced by the pilot run detailed in the preceding paragraph with those pulled from current plant production, agreement was reached that a whiteness value of 85 was sufficient to meet customer satisfaction. However, the plant staff asked that the research be redirected toward a maximum process temperature of 180F so that **both** total white and striped socks could be manufactured by the same preparation process, despite the fact that only ~30% of current production consists of the latter. This approach was perceived to have several advantages:

. All-white and striped socks are often mixed in the same transparent package of 4-8 pairs. The customer would likely be able to visually detect a whiteness difference between the two classes of socks at the retail level if they were prepared by different processes.

. The SHCS/B process would have to be kept in place for just the striped or for newly-developed insignia socks (those with a logo knitted into the top or foot, again using predyed yarns), and thus chlorine would not be eliminated from the operation. The popularity of striped socks is also very cyclical, and expectations are that the percentage of production devoted to striped socks will increase sometime within the next 3-5 years.

. Due the presence of chlorinated organics in the effluent of the SHCS/B process, that portion of the plant's effluent

remaining on this process would not be suitable for land application after pretreatment, forcing the company to separate and dispose of the two effluent streams in different modes.

. The plant would be forced to operate two different S/B processes, with attendant chemical inventory, supply and space storage problems, as well as presenting opportunities for operator mistakes.

Research is thus continuing on optimizing/streamlining the HPS/B process to achieve an average W value of 85, but at a maximum process temperature of 180F. To date, the run detailed above that yielded socks with an average W value of 85 has been repeated, with the only change a reduction of the maximum hold temperature from 200F to the requested 180F. The W value dropped from 85 to 81, indicating the Epsom Salt deletion will have to be readdressed at the lower hold temperature to determine its role in the reduced value vis-a-vis the delta T.

Engineering plans for modification of the 400 lb. Braun machine that will be used for the scale-up of the HPS/B process have been completed in conjunction with the plant staff, and a location has been isolated in the facility for placement of the necessary two holding tanks for reuse of both the S/B and softener finishing bath. Suitable holding tanks were not available in C-U's equipment inventory, so the specifications are being circulated to the textile/carpet network in the state with the help of the Georgia Textile Manufacturers Association to determine if a loan or purchase of used tanks can be arranged. Tentative engineering plans for conversion of the entire plant to the developed process have also been developed in conjunction with the plant staff.

During the first year of work on this project, a competing technology has been made public that is providing a benchmark opportunity to the batch HPS/B process for hosiery preparation. Surry Chemical Co. has been working for the past two years with Texchine Corp., the U.S. representative for the Bowe-Passat Continuous Batch Bleach Tunnel (Model Ultratandem 45) of Germany, to develop a semicontinuous, HP-based process for preparation of socks. The combined GIT/C-U research team has visited a demonstration trial site for the continuous process at the Fruit of the Loom Co. hosiery plant in Star, NC. The exact Surry chemical formulation is proprietary at this stage, but rapport was established with the Surry team in hopes of developing a more-open partnership in the sock preparation area in the future. The Surry process operates at 200F in the S/B chamber, and can only accommodate all-white socks as a result (see earlier discussions on stripes bleeding and transferring color at temperatures >180F). All-white socks brought back from the Surry trials gave average W values of ~82.

The remainder of the current year's research on this project will be devoted to:

. Completing chemical/time consumption optimizations for the HPS/B process on pilot scale while achieving W values of ~85.

. Conducting a 5-cycle reuse series on the fully-optimized HPS/B process (S/B **and** finish baths), again on pilot scale.

. Transferring the final process to the 400 lb. Braun machine at C-U. The major translation challenge will be successfully converting the formulation from a 12:1 LR at the pilot scale to 8:1 at the commercial scale.

. In consecutive 10-cycle plant run sequences of each of the sock types (solid white, polyester stripe, acrylic stripe), demonstrate the viability of directly reusing both the HPS/B and softener baths without adversely impacting product quality.

. Perform cost/benefit analyses for full plant implementation of the process (with **and** without bath reuse).

Year 2 of this technology transfer effort, projected to begin on March 1, 1995, will be devoted to assisting C-U in implementing the developed technologies plant wide, with ultimate tie-in to land application of the plant's pretreated effluent. In preparation for the final step, the company has installed a $150,000 pretreatment pond and purchased 25 acres of young pine trees to provide a land application site adjacent to the plant.

REFERENCES:

1. A. M. M. Taher and D. M. Cates, **Text. Chem. Color.**, 7, 220 (1975); W. G. Steinmiller and D. M. Cates, **Ibid**, 8, 14 (1976).

2. N. Sukumar and M. L. Gulrajani, **Text. Res. J.**, 55(6), 367 (1985); **Ibid**, 57(2), 105 (1987).

TABLE 1

MOD. TEXTECH PROCESS-RESULTS OF WHITENESS TESTS

RUN #	DESCRIPTION OF RUN	WHITENESS VALUE(W AD)	WHITENESS VALUE(BEST)	TYPE OF SOCKS
TT 92	1500g peroxide in scour 560g in rinse	82	83	A (AD)
TT 93	Same as TT 92	83	83	W,A,P(AD)
TT 94	1500g peroxide, none in rinse	83	83	W,A (AD)
TT 95	1500g peroxide, Uvitex in 1st rinse	81	81	W,A (AD)
TT 96	1500g peroxide, Uvitex in scour bath	82	82	W,A (AD)
TT 97	2000g peroxide	82	83	A (AD)
TT 98	1000g peroxide	77	77	W,P (AD)
TT 99	1250g peroxide	78	81	A (AD)
TT 100	1250g peroxide-repeat	79	81	P (AD)
TT 101	1500g peroxide, 200 F	83	84	W (AD-A)
TT 102	1500g peroxide, no epsom salt, 200 F	85	85	W (AD)
TT 103	1500g peroxide, no epsom salt, 180 F	81	84	A (AD)