The Thermosol Story

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Ladies and gentlemen, I am deeply moved and very appreciative of the honor that you have bestowed upon me by presenting me the OLNEY MEDAL, the most cherished award in the world of textile chemistry.

As a member of the largest department in The Du Pont Co., the textile fibers department, I have been surrounded by company and customer experts in textile dyeing and finishing, and it is the contributions of these men and women that has helped to make the Thermosol development successful. In awarding me this coveted medal, you really honor all who made this accomplishment possible.

Being awarded the OLNEY MEDAL is such a special occasion to me that, rather than present a wholly technical paper, I will cover the trials and tribulations in the development of the Thermosol process from its invention to current prominence as a major dying process used throughout the world. I will place particular emphasis on the Thermosol process, the most outstanding results have been obtained in the application of disperse dyes to polyester fibers in blend fabrics of polyester and cotton.

After a long incubation period, Thermosol became fully commercial in 1958 when sufficient yardage of polyester/cotton blends became available to warrant continuous dying operation. Growth of Thermosol dyeing accelerated in the middle sixties with the introduction of polyester/cotton permanent press fabrics. This growth has continued to the present time with some one billion pounds of fiber annually, mostly polyester/cotton blends, currently being processed by Thermosol in the United States alone.

ABSTRACT

The development of the Du Pont Thermosol process is covered from invention to current prominence as a major dying process used throughout the world. The Thermosol process is a continuous method of dying whereby dye penetration and fixation in the fiber are accomplished with dry heat.

Although many fibers can be dyed with various classes of dyes by this process, the most outstanding results have been obtained in the application of disperse dyes to polyester fibers in blend fabrics of polyester and cotton.

After a long incubation period, Thermosol became fully commercial in 1958 when sufficient yardage of polyester/cotton blends became available to warrant continuous dying operation. Growth of Thermosol dyeing accelerated in the middle sixties with the introduction of polyester/cotton permanent press fabrics. This growth has continued to the present time with some one billion pounds of fiber annually, mostly polyester/cotton blends, currently being processed by Thermosol in the United States alone.

KEY TERMS

Blends
Continuous Dyeing
Cotton
Dyeing
Heat Transfer Printing
Olney Medal Address
Polyester
Thermosol Dyeing

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October of that year. Initial sales in December 1939 were almost exclusively for hosiery. All the nylon produced during World War II, however, went for military uses—parachutes, tires, tents, etc.

Research beyond nylon resulted in the development of two additional fibers—polyacrylonitrile and polyester, the latter being discovered by Winfield and Dixon in England, building on Carothers' work. By 1950, three nylon plants were in operation. Orlon polyacrylonitrile fibers started as continuous filament yarn in 1950 and staple in 1952. The first commercial Dacron polyester plant went into operation in 1953.

Dyeing Research Started

Early in the development of polyester and polyacrylonitrile fibers, it was determined that new dyeing processes, equipment and dyestuffs would be needed to overcome the formidable problems in dyeing these fibers. Their low color sensitivity combined with the close packing of the molecular chains resulted in fibers that were resistant to dyeing by conventional techniques. A team of research scientists were assigned to define and develop new procedures and techniques for attaining practical dyeability of these fibers on a commercial scale. During the early phases of this work, which took place in the late 1940's, before the yarns had been named and commercialized, the polyacrylonitrile fiber was coded Fiber A prior to being named Orlon, and the polyester fiber was coded Fiber V prior to being named Dacron. It was in this challenging atmosphere that I began the task of finding new ways to dye the new fibers.

While it may sometimes be debatable as to whether experience is a hindrance or a help in inventing an unexpected and novel way to do something, it was to my advantage to be a relative newcomer to the field of dye application. It had been firmly accepted through the long history of dying cotton, wool and even the newer fibers like rayon and nylon that conventional dye particles could only penetrate and dye the fiber structure in the presence of a liquid, usually water or its vapor, steam. Dry heat alone without moisture would not do the job.
Lacking sufficient experience to be convinced that this premise was correct and wanting to pursue an inspiration that temperatures well above the 60-120°C conventionally used could be a route to dyeing the new synthetic hydrophobic fibers, I experimented with dry heat.

It was a simple experiment, with dramatic results, that was performed at Du Pont's Technical Laboratory, Chambers Works, Deepwater, N. J., on December 10, 1947, in which fabrics of Fiber A (Orlon) and Fiber V (Dacron) with dye deposited on the fiber surface by padding were placed between two conventional flat irons for 5 sec at 200°C. After washing to remove excess dye, dyed fabric in the shape of an iron was obtained (Fig. 1). And thus the basic principle of the Thermosol process was discovered (1). The dye on the portion of fabric that was not treated between the irons had no affinity for the fiber and was readily washed away. Similar experiments with cotton and wool confirmed that dry heat was not a practical route to dye these fibers.

The Thermosol Process

The Thermosol process is a relatively simple procedure (Fig. 2). It is a continuous process in which the fabric is padded with a dispersion of dye, dried and exposed to heat via an air oven, hot rolls, infrared unit or tenter frame to develop the dye (2). The conditions for Thermosol treatment vary from 5 to 90 sec at 175-225°C depending on heat source, fiber type and dye class compared to 1 hr or more at considerably lower temperatures for conventional batch dye processes in aqueous baths. The mechanism of Thermosol dyeing has been the subject of speculation and study over the years. It is the general consensus that heat opens up the polymer structure like a plasticizer and makes the fiber more permeable to the dye molecules, which then diffuse from the surface to the interior of the fiber, dissolving in the fiber. Dye fixation is dependent on molecular size and shape, volatility and solubility of the dyes in the fiber (3).

The name Thermosol was coined within Du Pont as a designation for this "heat soluble" process. Nonionic dyes—a grouping that includes disperse dyes, vat dye pigments, azoic pigments or any other coloring matter without pronounced ionic properties—can penetrate and dye any thermoplastic fiber in which they are soluble (4).

Generally, dye suitability increases as molecular weight and/or bulkiness decreases because smaller dye molecules diffuse between the molecular chains more easily than larger dye molecules. The rate of diffusion is quite rapid with most disperse dyes, and the dyeing time depends upon the rate at which the fibers are heated. As a comparison, if a padded fabric is heated between two flat irons, the fabric is dyed in a matter of 5 to 10 sec, while it would take 45 to 90 sec in a hot air oven at 205°C where the heat transfer is less efficient.

Although many fibers can be dyed with various classes of dyes by this procedure, the most outstanding results have been obtained in the application of disperse dyes to polyester fibers in blend fabrics of polyester and cotton. In this situation, dye is deposited on both fibers during padding. Upon Thermosol treatment, not only does the dye on the polyester diffuse and dissolve in the polyester fiber but the majority of the dye on the cotton sublimes from the cotton to the polyester where it diffuses and dissolves in the polyester fiber.

For example, when dyeing a 65/35 blend of polyester and cotton, the theoretical amount of dye that is fixed on the polyester would be expected to be 65%

The mechanism of Thermosol dyeing process heat treatment of padded polyester fabric between two flat irons.
Thermosol. These two dyes were dye nylon or acetate fibers from a disperse medium violet shade on Dacron by Thermosol application simultaneously from a dispersion in an aqueous bath, gave a bright yellow on Dacron by Thermosol dye, Celanthrene Fast Yellow GL (on the left), which normally was used to dye nylon or acetate fibers from a dispersion in an aqueous bath, gave a medium violet shade on Dacron by Thermosol. The violet vat dye, Ponsol Red Violet RRNX (Anthraquinone Vat Violet 1) (on the right), which normally was used to dye cotton by reduction and oxidation from an aqueous bath, gave a rust-orange mixture shade. Dye formulations using mixtures of vat and disperse dyes on the same fiber were heretofore not feasible.

**Development Activity**

For approximately ten years after the Thermosol process was announced in June 1949 and made available to the trade on a royalty-free basis, there were no major commercial applications. In one sense, the Thermosol process was developed and demonstrated in mill trials long before its time. During this period, however, there was considerable activity in both laboratory and mill trials to develop additional information regarding the commercial feasibility, relative cost and performance of this continuous procedure versus conventional batch methods. Alternate types of equipment for obtaining the required heat for Thermosoling were investigated. These included contact roller type ovens heated by gas, electricity, hot air or heat transferring liquids, superheated steam, tenter frames, infrared ovens, high frequency dielectric heating and molten metal baths. Based on present technology, Thermosoling is best carried out on semi-contact air heated rolls which typically operate at about 80 yd/min with about 30 sec dwell time.

A large number of dyes of the various dye classes were screened to establish affinity and fastness properties for Thermosol dyeing of various fiber substrates. In early studies, the two-iron procedure was used since it was rapid and easy to perform. Work was also undertaken to develop and synthesize new dyes tailored specifically for Thermosol dyeing. From these programs evolved recommendations for preferred dyes and Thermosol application procedures. The first summary of recommended dyes and process was published in the original announcement of the Thermosol process in Du Pont's **Dyes and Chemicals Technical Bulletin** in 1949. A new series of disperse dyes of the Latyl type were developed for use in the Thermosol process. These included dyes having high resistance to sublimation with maximum fastness for Thermosol application to durable press fabrics. To obtain successful Thermosol dyeings, it is necessary that the fabric be properly prepared prior to dyeing. This includes removal of residual oils and dirt and making the fabric absorbent. Properly prepared fabrics exhibit excellent appearance, penetration and fastness properties.

The advantages of the Thermosol process are (1) it is a continuous process, therefore large yardages can be dyed more economically than by batch procedures; (2) dye utilization is excellent; (3) no carrier is required, consequently the chances of spotting and the adverse influence of some carriers on lightfastness are eliminated; (4) fabric is processed in open width, eliminating rope marks; (5) dyeability is not affected by previous heat setting; and (6) energy consumption is lower than batch procedures primarily because of shorter cycles, lower bath-to-fabric ratios, and energy recovery devices. Potential to reduce energy costs and their wetfastness and lightfastness properties in general are very good on this fiber.

An illustration of the successful coloration of Dacron polyester fiber with a vat dye by the Thermosol process is shown in a reproduction from the original Thermosol report issued in 1949 (Fig. 3). Cotton was conventionally dyed with Sulfanthrene Pink FF (C.I. Vat Red 1) for 1 hr at 140°F (60°C) in an aqueous bath. Dacron was only stained after dyeing 1 hr at the boil in an aqueous bath while Thermosol dry heat dyeing for 30 sec at 430°F (about 220°C) produced a brilliant pink shade.

A second illustration from this same report demonstrated the compatibility of mixing dyes from different classes by the Thermosol process to Dacron polyester fiber (Fig. 4). The yellow disperse dye, Celanthrene Fast Yellow GL (on the left), which normally was used to dye nylon or acetate fibers from a dispersion in an aqueous bath, gave a bright yellow on Dacron by Thermosol. The violet vat dye, Ponsol Red Violet RRNX Paste (Anthraquinone Vat Violet 1) (on the right), which normally was used to dye cotton by reduction and oxidation from an aqueous bath, gave a rust-orange mixture shade. Dye formulations using mixtures of vat and disperse dyes on the same fiber were heretofore not feasible.

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further during Thermosol processing lie primarily in attaining more efficient drying both before and after thermosoling as 78% of the total energy is consumed in the two drying operations. The Thermosol step consumes only 5% of the total energy of the process.

Initial Thermosol mill trials were conducted in 1949-1950 on fabrics of filament and spun Dacron polyester and nylon fibers. The author and Robert P. S. Black, also of Du Pont, are shown in Fig. 5 observing one of these early mill trials with the Thermosol process. Problems that were encountered and resolved during the development period included (1) techniques for controlling migration through the use of pad bath additives and infrared predrying; (2) development of speck-free vat dye and disperse dye pastes; and (3) chemical finishing techniques for durable press, water and oil repellent finishes, etc.

Of historical interest is a photograph of the original Thermosol mill dyed fabric of spun Dacron polyester fiber with Acetamine Rubine B processed at Hellwig Dyeing Corp., Philadelphia, Pa., in 1949 (Fig. 6).

Through the co-operative efforts of mill personnel and Du Pont technicians, it was determined that the Thermosol process was entirely practical and could be operated on available mill equipment. The only deterrent was that there were insufficient yardages of fabrics containing polyester fiber to make the operation economically attractive. An added incentive to use a continuous dye process for Dacron polyester fiber was the emergence of polyester/cotton blends in the late 1950's. Fabric development and market studies showed that an economical continuous process for these blends was a "must" if Dacron polyester fibers were to penetrate the huge cotton market (4).

The tools to accomplish this goal were available—the Thermosol method for dyeing polyester with disperse dyes and the pad-steam process for dyeing the cotton portion of the blend with vat dyes. Nevertheless, applications research and engineering studies were needed to bring about the unification of the two processes in the smooth running operations of today. This was a joint effort of the dyeing and finishing industry and dyes and chemicals manufacturers. Thermosol dyeing became a fully commercial process in 1958 when rainwear fabrics of 65/35 Dacron/cotton attained a significant share of the market and the number of yards required in a given shade was sufficient to warrant continuous operation (5). The fiber blend business had become big business and was growing rapidly.

**Commercial Growth**

Significant increase in demand for polyester/cotton blends and for Thermosol dyeing occurred in the middle 1960's with the advent of permanent press finishes. This revolutionary wash-wear concept significantly reduced the chore of ironing in the home and was in great demand by the consumer. It is not surprising that the number of Thermosol dye ranges in the United States, processing some 20 million yards each year, more than doubled from 1963 to 1966 — increasing from 26 to 55 full size ranges (2). Similarly, polyester/cotton broadwoven production increased from some 430 million yards in 1963 to 1050 million yards in 1966 (Fig. 7). This growth has continued into the 1970's reaching 2000 million yards in 1972 and 2700 million yards in 1977 (11).

Many of the permanent press garments produced today are made from polyester/cotton blends and a high percentage of polyester/cotton permanent press garments are dyed by the Thermosol process. The growth of the Thermosol process therefore parallels the growth curve of polyester/cotton. Approximately one billion pounds of fiber, mostly polyester/cotton blends, are currently being processed by Ther-

![Fig. 5. Joseph W. Gibson Jr. (left) and R. P. S. Black are shown conducting an early Thermosol mill trial.](image)

![Fig. 6. Original Thermosol mill dyed polyester fabric with Acetamine Rubine B.](image)

![Fig. 7. Polyester/cotton broadwoven greige fabric production in the United States. (Source: U.S. Department of Commerce, Bureau of the Census, MQ-22T)](image)
mosol annually in the U.S. Fig. 8 shows the pounds of fiber dyed by the leading dye methods for apparel and home fabrics in the U.S. for 1976 (12). Continuous Thermosol processing has a decided edge over the two leading batch dyeing methods: package and atmospheric beck dye processes. The number of full size Thermosol ranges in the U.S. is currently estimated at 90, with 12 additional modified Thermosol units in operation.

While this presentation has covered the development of the Thermosol process in the U.S., there has been extensive research and development work throughout the world on the Thermosol process over the last 30 years. The number of modified Thermosol ranges outside the U.S. is estimated at between 75 and 100.

The success of Thermosol has been closely allied to the success of polyester/cotton permanent press fabrics. The interaction between these two functions and the driving force for use of polyester in the polyester/cotton blend is expounded in a paper by Donald P. Hallada, Du Pont (13), as follows. "The permanent press fabrics and garments composed of a blend of polyster and cotton, heavily treated with resin, are generally made using polyester rather than nylon. While it is true that the polyester would add incrementally to the wash-wear properties of the fabric, fabrics containing nylon performed essentially as well. Clearly, the overwhelming use of polyester in preference to nylon has evolved for other reasons. Cost and ease of textile processing favour polyester, but the most compelling driving force is the availability of an economical, high speed dyeing process—Thermosol—which makes possible the volume production of polyester containing fabrics. This vapour phase application of disperse dyes gives excellent wetfastness on polyester, but is of no practical value on nylon because of the poor washfastness of disperse dyes on the polyamide fibre. Since no other attrac-

Fig. 8. Leading dye methods for apparel and home fabrics in the United States, 1976.

Fig. 9. Novel two-sided heat transfer printed fabric developed in early Thermosol studies.

tive continuous dyeing process is available for nylon containing fabrics, polyester dominates this end use."

Heat Transfer

Finally, I want to briefly discuss the early Thermosol work relative to heat transfer printing. It was discovered that novel dyeing and printing effects could be obtained by applying sublimable dyes to a substrate having no affinity for the dye and transferring with high heat (173-220°C) to hydrophobic fibers having affinity for the dye. A sample from the original work with this concept is shown in Fig. 9. It is a fabric of filament Dacron polyester fiber which is colored differently on front and back by heat treating the undyed Dacron fabric between two differently colored substrates having no affinity for the dye.

The first description of this process was published in 1951 (4). This paper stated: "On heating a printed substrate in contact with undyed Dacron polyester fiber, a surprisingly sharp transfer of the print to the Dacron was obtained." The paper concluded, "While the above 'heat-transfer' process has been developed only on a laboratory basis without practical mill experience, the opportunity to study its practical application with any interested dyer or finisher is welcomed."

No one responded to this offer (15)—and we concentrated all research and development resources on the basic Thermosol process.

The commercialization of this concept, which is the heat transfer printing process as it is carried out today, was begun in Europe about 1958 by Mr. Noel DePlasse (16), who was director of the dyeing department of a large textile complex in Northeastern France. Working with two other firms who jointly formed Sublistatic Corp., the process was marketed in 1968. By 1972, this firm had paper printing plants operating in France, Belgium, Puerto Rico and Japan. By 1976, some 165 million yards were being heat transfer printed in the U.S. with growth expected to reach 700 million yards by 1983. Worldwide, transfer print production was 900 million square yards in 1976 and has been forecast to reach 2100 million square yards by 1980 (17).

In conclusion, the Du Pont Thermosol process, after a long infancy, has grown up and, from all indications, is here to stay. It is a relatively simple continuous process in which large yardages can be dyed more economically than by batch procedures. The potential for continued growth is high primarily due to a major problem facing the world today—the increasing costs of energy, water and labor, factors which favor continued conversion from batch to continuous processing.

References