A NEW HIGH-VALUE PROCESS FOR DYEING NYLON: AN OVERVIEW

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ABSTRACT

A new process has been developed by Du Pont for the commercial dyeing of nylon yarns, fabrics, garments and carpets. This process, called Infinity*, significantly reduces mill dyeing costs in many applications by shortening dyeing time, increasing dye yields and reducing the need for the chemical retarders and levelers which are often required in conventional dyeing procedures. INFINITY* is more environmentally friendly than conventional dyeing because it requires less dye and chemicals, yields a more completely exhausted dye bath, and in many cases, it uses less total energy and less water. INFINITY* consistently produces more uniform color and deeper shades than conventional dyeing, especially in those applications using critical acid and pre-metallized dyes.

INTRODUCTION

This paper presents an overview of new process technology for dyeing nylon yarns, fabrics, garments, tufted carpets and blends of nylon with other fibers, including Lycra® spandex. The major elements of this technology and its benefits are described here. The next paper in this Section discusses experimental results, and the mechanistic model for this process.

Uniformity of nylon fabrics has been continually improved since Du Pont introduced nylon in 1939. Today, dye uniformity problems are rare in applications that use leveling dyes. However, achieving color uniformity has always been more difficult for enduses which require critical acid and pre-metallized dyes. These typically include automotive fabrics, swimwear, and activewear.

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Uniform, streak-free fabrics are hard to achieve in critical colors because the dyes are sensitive to differences in the physical structure of the nylon fibers themselves. These differences can be introduced at any point from fiber manufacture through textile processing. Furthermore, the fiber structure continues to change throughout the dyeing process as dye bath conditions change. These changes can aggravate differences in dye uptake.

The INFINITY* process exploits the chemical and thermal energy potential of the dye bath to minimize yarn-to-yarn differences and to stabilize fiber structure during dye uptake. The result is a degree of color uniformity previously difficult to obtain, especially in the more critical dyeing applications.

The key features of the INFINITY* process are:

- The process begins with the nylon article in a dyeing machine containing water but no dye. Depending on the type of dyeing machine used, the fabric and/or water are circulated.

- The temperature of the bath is increased to the dyeing temperature, typically 180°F (82°C) to 205°F (96°C). Dyeing under pressure is also practical, if needed.

- A metering pump precisely controls the addition of dye into the isothermal, circulating dye bath. This ensures level dyeing by indirectly, but effectively, controlling exhaust rate.

CONVENTIONAL PROCESSES

Many of the things that dyers do in a conventional dyeing process are designed to cope with changing fabric dyeability as dye bath conditions change. By introducing dye at low temperature, and then slowly heating the bath, the dyer hopes to compensate for the non-uniform and changing accessibility of dye sites.

Temperature holds at pre-determined plateaus compensate for the different rates of uptake of each dye in the dye mixture. Retarders and/or levelers slow the whole process down to achieve color uniformity. For deep shades, the dyer uses more dye and longer dyeing time. An excessive amount of dye may remain in the bath, unused, at the conclusion of the process. Aftertreating with softeners, antistatic agents or fixatives generally requires a fresh bath.

The spent bath, with its unused dye and chemical additives, poses a disposal problem. As if these challenges were not enough, conventional processes can be difficult to replicate because of the sensitivity of dye uptake to critical process conditions.

THE INFINITY* PROCESS

The INFINITY* process begins with the nylon article in a circulating bath which contains no dye. (That is, the bath is infinitely dilute at the beginning of the cycle, and the aim is to end the cycle that way as well.) The temperature of the dye bath is then quickly increased to the dyeing temperature, typically from 180°F to 205°F (82°C to 96°C). The rate of rise is limited only by equipment capability and/or sensitivity of the fabric.

At the dyeing temperature, a metering pump connected to the inlet of the circulation pump is activated (see Figure 1). The metering pump injects a predetermined amount of dye concentrate in a small, even stream. The limited quantity of dye present at any time is rapidly absorbed, minimizing buildup of dye in the bath. The result is uniform dye uptake with greater dye yield, and a highly exhausted dye bath.

Because INFINITY* introduces dye at a precisely controlled rate while the article is ready to absorb it rapidly, the need for retarders and levelers is greatly reduced and sometimes eliminated entirely. In essence, INFINITY* replaces these chemical controls with simple mechanical control.

Mill experience has shown that INFINITY* can produce high quality dyed articles even with significant system failures during the dyeing process (e.g., fabric tangles in jets, pH excursions, etc.). In conventional dyeing, with all the dye in the bath, such mishaps often result in reject fabrics which must be discarded or reworked. But with INFINITY*, very little free dye is present at any time, and the metering pump can be stopped to permit correction of system failures. Then the pump can be restarted to obtain first-quality dyed fabric.

The near-complete exhaust promotes good batch-to-batch shade reproducibility. Moreover, because dye exhaust is so complete, fixatives can often be metered directly into the spent bath. Metering of the fixative keeps concentrations low and minimizes coagulation and deposits. Use of the spent dye bath for aftertreating saves time and water by avoiding the extra rinsing and fresh aftertreating bath.

At the end of the process, the dye bath is cooled and drained. The article can be rinsed and dried in the conventional manner. Figure 2 compares examples of typical dyeing procedures using a conventional method, and the INFINITY* process with "same-bath" aftertreatment. Table 1 shows that the laboratory performance of Nylon/LYCRA® spandex fabrics dyed with INFINITY* matches that of conventionally dyed fabrics.

The finished article dyed with the INFINITY* process exhibits a uniformity of color and depth of shade that is difficult to achieve using conventional methods. For a given amount of dye, the INFINITY* process gives deeper color. This is because of more complete bath exhaust and because it distributes dye more effectively within the fabric. Whereas conventional methods saturate the fiber bundle with dye, INFINITY* preferentially distributes dye to nylon fibers that are located at and near the surface of the fiber bundle. Surprisingly, INFINITY* achieves a more uniform dyed fabric appearance while producing a microscopically non-uniform dye distribution in the fabric. Figure 3 shows microscopic cross-sections of fabrics dyed by conventional methods and by the INFINITY* process. This pattern of dye distribution uniquely identifies articles dyed using the INFINITY* process.

INFINITY* BENEFITS

The cost savings and quality improvements of the INFINITY* dyeing process will vary with dyeing equipment and applications. Nevertheless, most nylon dyeing operations can realize the following benefits to some degree:

- Improved dyed fabric uniformity, quality, and consistency
- Improved process reproducibility, enhancing "product-by-process" control

- Reduced mill cost, due to

  - less dye required to achieve a given shade
  - reduced need for auxiliary chemicals
  - shorter dyeing times
  - use of exhausted dye bath for aftertreatments

- Greater process/product flexibility, due to

  - separate metering of dyes, acid, aftertreatments, etc.
  - greater ease of making dye adds, which if required, can be made without dropping temperature

- Greater environmental "friendliness", due to

  - near-complete dye exhaust
  - fewer auxiliary chemicals in dye effluent
  - reduced water and energy usage

- Increased plant capacity from shorter dyeing times and higher finished fabric yield

SHADE MATCHING

Given the fundamental differences between INFINITY* and conventional dyeing techniques, it is not surprising that INFINITY* requires some modification for developing color shades in the laboratory. To achieve close color reproducibility between laboratory equipment and commercial equipment, the shade matching system should incorporate dye-metering capability. This can be accomplished by using commercially available lab dyers with continuous metering features, or by adding low-cost dye metering units to existing open-system lab dyers.

As a starting point, conventional shade formulations can be adjusted for the INFINITY* process by simply reducing the amount of dye required by a fixed percentage, typically 25% for milling acid and pre-metallized dyes. (This percentage will vary depending on dye type, dye add-on, etc.) Experimentation and experience with the new process will fine-tune the shade matching. Once a shade formulation is established on a commercial dyeing machine, good lot-to-lot reproducibility can be expected because of the superior process control and more complete exhaust afforded by INFINITY*.

KEY PROCESS STEPS

Specific procedures for applying the INFINITY* process will vary among the different types of dyeing equipment and the different types of dyes used. The discussion which follows provides information that is generally applicable to most dyeing operations. It addresses the following steps:

- Scouring
- Heatsetting
- Hydrosetting
- Dyeing
- Aftertreating

Scouring: As in conventional dyeing processes, it is desirable to scour the nylon article before dyeing to remove yarn finishes and other materials which may interfere with dye uptake. Scouring is even more strongly recommended for dyeing elastic warp knit fabrics, particularly for critical dye applications. Scouring articles to be dyed with the INFINITY* process is performed in the same manner as scouring for conventional processes.

Heatsetting: Some warp knit fabrics must be heatset before dyeing to prevent fabric distortions, e.g. "cracks", creases, and edge-curling, which can cause uneven dyeing. Such fabrics should also be heatset before dyeing with the INFINITY* process.

Hydrosetting: Subjecting nylon to steam autoclaving before dyeing can minimize yarn-to-yarn structure differences and thereby improve dye uniformity. This is often done with nylon circular knits. But autoclaving of warp knits or wovens is not practical. INFINITY* allows the dyer to use the heat of the clear dye bath to routinely capture the uniformity advantages of "hydrosetting" without putting the fabric through a separate "hydrosetting" step. Simply exposing the fabric to high temperature in water for just seconds can minimize, or even erase, those residual structure differences in the fabric - before dye is added to the dye machine.

For Type 66 nylon, the clear bath is heated to between 180°F to 205°F (82° to 96°C) or higher, depending on the energy required for the desired dye uniformity. Small scale laboratory tests can quickly identify the preferred hydrosetting temperature. Hydrosetting through INFINITY* has been done at temperatures as high as 270°F (132°C), which is the usual temperature used for steam autoclaving. Hydrosetting occurs in less than two seconds exposure, so the article need be kept at temperature only long enough to ensure uniform energy input. For example, in jet dyeing, where the fabric is generally turned over in less than two minutes, three-to-five minutes at temperature is sufficient for hydrosetting. Dye can generally be metered into the bath without lowering bath temperature.

Dyeing: INFINITY* is a straightforward process in which the article is immersed in a clear circulating bath, the temperature is raised to the dyeing temperature, and the required amount of dye is metered into the bath. Buffers and conventional methods can be used to control pH, or alternately, a pre-acidified dye concentrate can be metered into the bath to provide a programmed pH profile.

The rate at which the dye is metered into the dye bath depends on the article, the dyeing machine, the type of dye used, and the depth of shade required. In most cases, 1% to 3% of the total dye to be used is injected for each revolution of the fabric in the dyeing machine, or each turnover of the dye liquor. Metering at this rate ensures uniform application of the dye concentrate to all portions of the fabric, side-to-side and end-to-end.

These guidelines illustrate how INFINITY* controls the dyeing process mechanically by metering, whereas conventional processes rely on chemicals, rate of temperature rise, and temperature plateaus to control the rate of dye exhaust. Control through metering is more precise and easily reproducible.

For maximum dye yield, conditions in the dye bath should be maintained such that the rate of dye transfer, that is the migration of dye molecules from one dye site to another, is less than 10%. This is inherent with large-molecule acid or pre-metallized dyes, since these do not readily migrate. But for small-molecule leveling dyes, transfer can be held to less than 10% by using some combination of short dyeing time, low bath temperature, and low bath pH.

For applications which use critical acid or pre-metallized dye in combination with a strongly leveling dye, it may be desirable to decrease the pH and/or lower the temperature near the end of the dyeing process to promote the exhaustion of the leveling dye from the bath. In such cases, the acid can be metered into the bath after the dye addition period.

For some applications, an "express" variation of the INFINITY* process can further reduce overall dyeing time. To achieve minimum cycle times, metering of the dye can begin at any time before the dye bath reaches its ultimate temperature, even at the start of the process. This is most successful in less critical applications and generally when all the dyes used are of a similar type (e.g., all milling acid dyes, or all pre-metalized dyes of similar affinities). This "express" procedure can cut another 30 minutes or so from the dye cycle, but the trade-off is that dye yields, and possibly uniformity, may be reduced.

Aftertreating: In many cases, INFINITY* greatly simplifies aftertreating by permitting re-use of the spent dye bath. After the dye metering period is complete, chemicals to enhance colorfastness, softness, or antistatic properties are metered into the same bath. This affords significant savings in time, water, and energy.

SUMMARY

Laboratory and mill trials show that the INFINITY* process offers high potential for improved dyed fabric uniformity and quality, lower mill dyeing costs and greater environmental friendliness. The earliest and greatest realization of that potential will go to dyers most willing to change from the known, conventional dyeing methods to the less known, but higher value, new process. The task ahead is to go through the implementation learning curve to apply this new process to specific equipment, fabric and dye systems. The Du Pont INFINITY* Licensing Program is designed to ease the burden of that implementation effort.

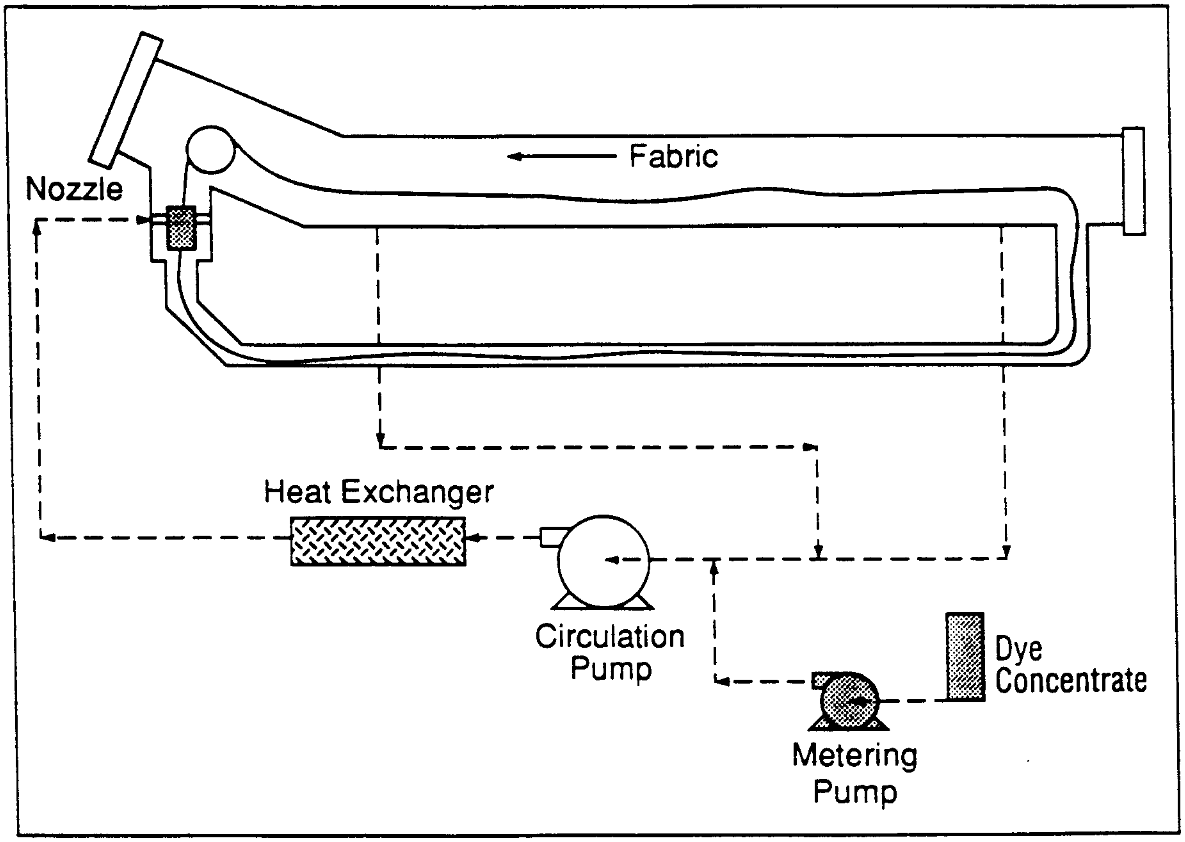

FIG. 1: JET DYER – METERING PUMP INSTALLATION

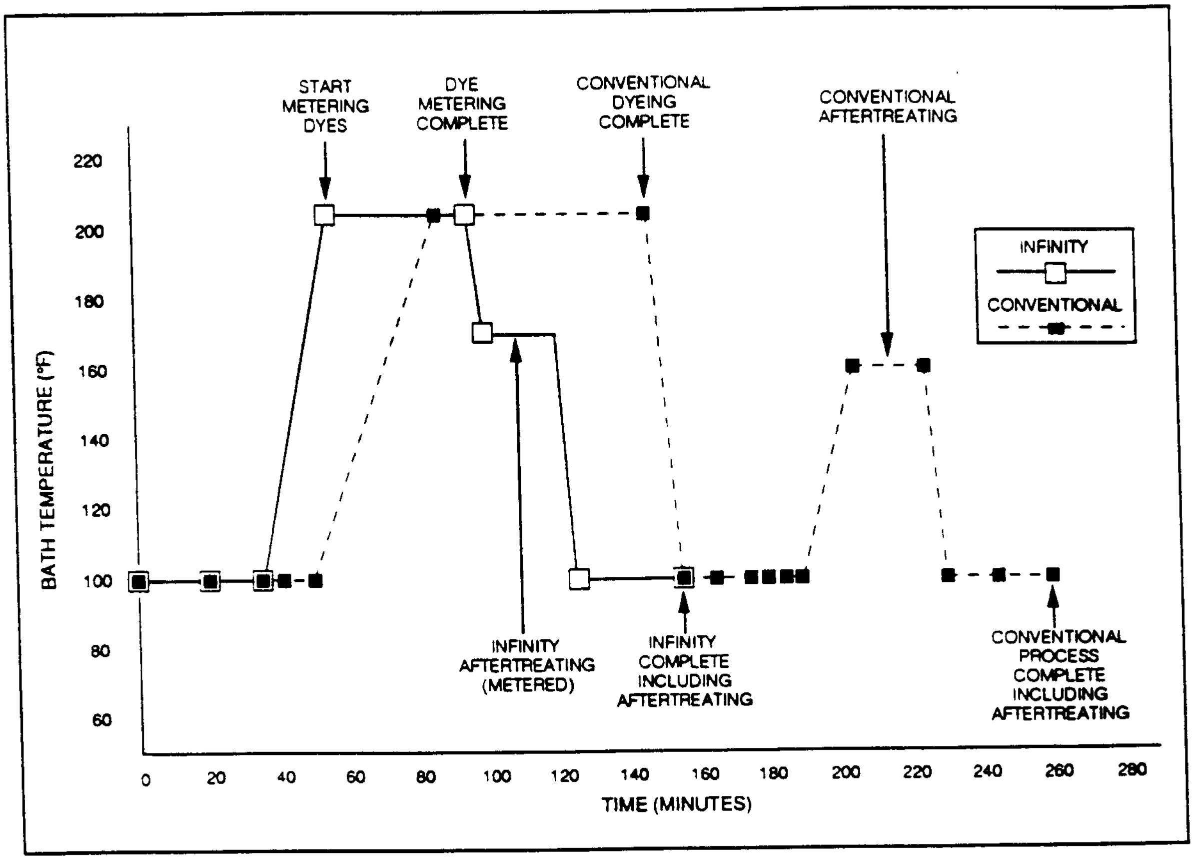

FIG. 2: TYPICAL INFINITY AND CONVENTIONAL DYEING PROCEDURES

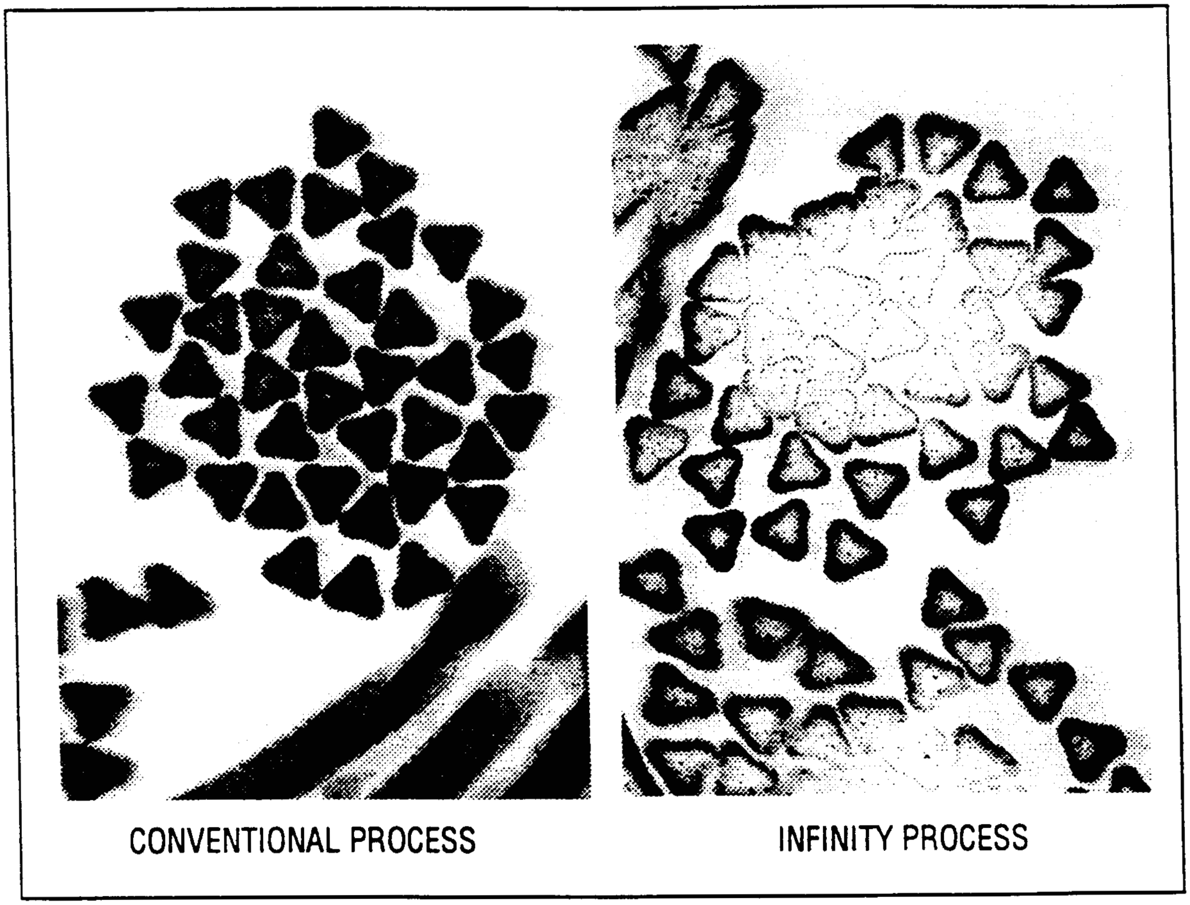

FIG. 3: COMPARISON OF CROSS-SECTIONS OF FIBER BUNDLES

TABLE I: LABORATORY PERFORMANCE (INFINITY VS. CONVENTIONAL DYEING, NYLON LYCRA® SPANDEX FABRICS)

	Dye Class/Shade	INFINITY		Conventional	
Wet Fastness		Shade	Stain	Shade	Stain
2A	Leveling Acid + Milling Acid/ Lime Green	5	5	5	5
3A		5-4	4	5-4	4
4A		5-4	3	5-4	3
3A	Milling/Navy Blue	5	5-4	5	5-4
4A		4	3	4	3
Light Fastness					
10 hours	Milling/Blue	5		5	
20 hours		5		5	
40 hours		5		5	
60 hours		5-4		5-4	
80 hours		5-4		5-4	
10 hours	Leveling Acid/ Yellow – Flavine	3-2		3-2	
20 hours		2		2	
10 hours	Pre-Met/Black	5		5	
20 hours		5		5	
Frosting					
12 cycles	Milling/Blue	5		5	
24 cycles		5		5	
12 cycles	Milling/Navy Blue	5		5	
24 cycles		5		5	
Crocking					
Dry	Milling/Navy Blue	5		5	
Wet		5		5	
Dry	Pre-Met/Black	5-4		5-4	
Wet		5		5	
Abrasion					
Taber	Milling/Navy Blue	5		5	
Taber	Leveling Acid+ Milling Acid/ Lime Green	2		2	

THE FIBER AS AN ENERGY BARRIER
Preparation, Dyeing and Finishing as
Energy Balancing Process

PART II
A NEW HIGH-VALUE PROCESS FOR DYEING NYLON

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INTRODUCTION

This paper reviews the energy history concept (1, 2, 3) and its application to the nylon-water system to develop a better understanding of the factors which influence the dye rate uniformity of nylon. The resulting working hypotheses lead to a novel process for dyeing nylon in a way that helps control and improve dye rate uniformity. This new technology is called the INFINITY* Process, since it approximates dyeing from an infinitely dilute bath.

The following topics are discussed:

- Dye rate uniformity - background
- Dyeing nylon: Why we dye the way we do
- The fiber as an energy barrier
    - Heat history vs. energy history
    - Equilibrium
- The effects of energy...
    - thermal
    - mechanical
    - chemical

  ...on fiber structure and dyeability
- Nylon dye-rate uniformity - the role of fiber energy history

*Du Pont mark for its proprietary dyeing technology.

- Exploiting dye bath energy to control dye rate uniformity
- The INFINITY* Process for dyeing nylon
  - some laboratory results and observations

DYE RATE UNIFORMITY: BACKGROUND

Energy History

The familiar "heat history" concept describes the effects of thermal and mechanical energy on fiber structure. But it does not consider the effects of chemical energy, which are a major factor for the aqueous dyeing of nylon. The term "energy history" is simply a more complete form of the heat history concept (1). It describes the cumulative effects upon fiber structure of exposure to thermal, chemical, and mechanical energy during the fiber's manufacture and textile processing. Each application of energy can cause changes in fiber structure and, therefore in dye rate characteristics. Unfortunately for the dyer, the dye molecule is the most sensitive probe of fiber structure. Critical acid and pre-metallized dyes leave behind, as it were, a full color "picture" of even minor variations of energy history in the form of barre or streaks*.

Previously, it was shown that dye rate uniformity is a direct, uniquely sensitive measure of the uniformity of fiber history (1). Dye rate defects - i.e. streaks or barre - were shown to be caused primarily by differences in accessibility and not by variations in dye sites, per se. Water is a potent source of chemical energy for nylon, which can help to minimize differences in accessibility. These concepts and hypothesis led us to explore ways to better exploit the total energy of the aqueous dyebath to help control the dye rate uniformity of nylon.

DYEING NYLON: WHY DO WE DYE THE WAY WE DO?

Nylon fiber structure changes dramatically with increasing humidity, even at room temperature (2). Structural changes continue when fibers are immersed in

*barre - is generally used when referring to circular knits
streaks - refers to warp knits and wovens

water at increasing temperatures (Figure 1). Dye-fiber interactions also continuously change in complex ways as dye bath conditions change. The dyer is really "shooting at a moving target".

A key concept is that as the fiber transitions approach the rubbery plateau, the polymer behaves like a viscous fluid, which facilitates dye migration and minimizes dye rate differences by minimizing differences in accessibility. However, critical acid and pre-metallized dyes resist migration under practical conditions.

Figure 2 presents a conceptual model of nylon structure during dyeing. Exposure to heat and water causes polymer chains to relax, forming small pores in the fiber. Dye molecules diffuse through the pores and are attracted by ionic sites inside the pore walls. As temperature rises, the number and size of pores increase and the interaction of fiber with the dye changes in a complex way. The temperature dependence of these changes and the rate at which they occur reflect the energy histories of individual fibers, and may differ from yarn to yarn. Even small differences in energy history can cause variations in pore size which result in dye rate differences which produce streaky fabrics.

The dyer, therefore, must deal with at least three critical temperatures in designing his procedures:

- T_g, the glass transition temperature, where there is a gradual increase in porosity with the onset of polymer chain segmental mobility.
- T_d, the dyeing transition temperature, where there is a rapid increase in the rate of dye uptake when average "pore size" just exceeds the size of the dye molecules being applied.
- T, the dyeing temperature.
- $T-T_d$, which helps determine porosity (free volume) during dye uptake.

To slow down and control these complex, changing interactions to consistently produce acceptable dyed fabrics, we have learned to use chemical and thermal energy plus time:

- ph controls
  - buffers
  - acid donors
  - programmed addition of acid
- retarders
- levelers
- rate of rise control
- hold times at predetermined temperature plateaus
- dyes selected for "compatibility"
- combinations of these

The dyer's task clearly is extremely challenging.

THE FIBER AS AN ENERGY BARRIER

The disperse dye capacity of nylon and polyester is sufficiently constant at equilibrium, in spite of non-uniform energy histories, to produce commercially acceptable dye uniformity: i.e., not perfectly uniform, but free from objectionable dye-related streaks/barre (2). The key nylon evidence is this:

> At equilibrium, nylon 6-6 (disperse) dye capacity is approximately constant in spite of differences in chemical composition, crystallinity and orientation! Thus, deep, regular and light acid-dyeable nylon styling-yarns, which have wide range of amine-end groups; acid modified, cationic-dyeable nylon; steam heat-set and unset, low and high draw ratio versions of these yarns all dye to about the same shade in competitive, equilibrium dyeings with Disperse Blue 3! In contrast, these same yarns have markedly different dye uptake in non-equilibrium dyeings with Disperse Blue 3., e.g., dyed for one hour at 25°C., or with a structure sensitive, non-equilibrating dye like Acid Blue 122.

This suggests that dye-rate streaks or barre generally are due to failure to reach equilibrium. Unless all fibers/yarns in a fabric have equivalent energy levels, the system must reach equilibrium to take advantage of this constant dye capacity and eliminate dye-rate differences.

What is equilibrium dyeing? In our hypotheses, equilibrium is defined as follows (3):

- From the fiber point of view - conditions of sufficient energy input for fiber property transitions to approach the rubbery plateau.
- From the point of view of the dye molecule - dye bath conditions which produce good dye transfer.
- At equilibrium, differences in accessibility are minimized or eliminated.

The fiber can be considered as an energy barrier, since the energy history of the fiber must be "overcome" to reach equilibrium. Achieving optimum results in dyeing and finishing, e.g., good dye-uniformity, is a problem in balancing total energy during preparation and dyeing/finishing against the previous energy inputs during fiber manufacturing and textile processing.

THE EFFECTS OF ENERGY INPUTS ON FIBER STRUCTURE AND DYEABILITY

Energy History describes the cumulative effects on fiber structure and dyeability of exposure to energy -- thermal, mechanical and chemical, over time -- during polymer/fiber manufacture and textile processing.

Evidence for the effects of energy on fiber structure and dyeability was described previously (2). A brief summary is in Table (I) which shows that thermal (dry) and mechanical (e.g., tension) energies generally "close" fiber structure and reduce dyeability (i.e, dye rate) while chemical energy (carriers; solvents) "open" fiber structure and increase dyeability. Chemical energy generally has the greatest effects on structure/dyeability. By itself, thermal energy has the least effect. The energy components are interactive in their effects on transitional properties like T_g and T_d (2). This exacerbates the problems in achieving the uniform energy history necessary for good dye rate uniformity.

THE ROLE OF WATER

For nylon, but not for polyester, water provides a large amount of chemical energy which substitutes for some of the thermal energy which would otherwise be required to dye nylon. Water, functioning as a carrier, causes changes in fiber properties which would require as much as 100°C of added (dry) thermal energy (2)! This suggests that aqueous dyeing of nylon at the boil is equivalent to dyeing polyester at up to 200°C (392°F) - 100°C thermal energy plus 100°C from the chemical energy of water. This is why nylon dyes so easily in water, and why procedures for nylon are generally designed to slow down the rate of dye uptake. In contrast, most polyesters require pressure dyeing systems or addition of carriers, i.e., chemical energy to speed up the dyeing process.

How can we exploit the chemical and thermal energy potential of the aqueous system to improve nylon dye rate uniformity?

NYLON DYE-RATE UNIFORMITY - THE ROLE OF ENERGY HISTORY: Td

Background

We previously used the responses to diagnostic dye tests (appendix I; ref. 1) of texturing-induced dye-rate variations - barre - to monitor the effects of water/steam on nylon dye-rate uniformity (2). Circular knit fabrics containing two types of barre were used as model systems to study variations in energy history and energy inputs during preparation and dyeing:

- crimper-tube barre, CTB, induced during stuffer-box texturing
- false-twist barre, FTB, induced during false twist texturing.

Results of diagnostic dyeings indicated that:

- equilibrium disperse or acid dyeings (diagnostic procedures 2 and 3, Appendix I) eliminated CTB and FTB
- non-equilibrium disperse or acid dyeings (diagnostic 1 and 4) brought out CTB and FTB

- steam autoclaving at 132°C (270°F), a routine commercial procedure for nylon circular knits, lowers T_d (C.I. Acid Blue 122) 10 to 15°C and:
    - eliminates CTB (diagnostic procedure 4, Appendix I)
    - does not eliminate FTB, but makes it easy to eliminate FTB with subsequent retarder/leveler pretreatment technology (diagnostic procedure 4-B, Appendix I)

- nylon undergoes reversible and irreversible changes on pretreatment with water at increasing temperatures as evidenced by stepwise reductions in barre as well as by changes in dye wet-fastness before vs. after hydrosetting (2).

The difference between CTB and FTB in response to steam autoclaving appears to be due to the higher energy history from false twist texturing which "triggers" permanent setting. These results and observations led to the hypothesis that keeping total energy during dyeing above the energy history from textile processing/fiber manufacturing should minimize or eliminate dye rate barre/streaks in nylon fabrics. The key appears to be control of T_d, since the lower T_d during dyeing, the easier it becomes for the dye-fiber system to approach equilibrium and the uniformity benefits of constant dye capacity by minimizing variations in dye-site accessibility, i.e. "porosity" or T_d.

The key evidence is summarized in Table II. Pretreatment of CTB fabrics with water at increasing temperatures gave a stepwise reduction in barre. This suggests a range of fiber transition temperatures - T_d differences - caused by energy variations during texturing. CTB was also markedly reduced, without pre-treatment, by adding dye above a critical 70°C (158°F) structural transition identified in diagnostic dyeings (2). This result indicates that the structural changes at 70°C minimized accessibility differences since the dye used, C.I. Acid Blue 122 exhibits low transfer, even at higher dyeing temperatures. Further, samples pretreated at 70°C, then dyed via conventional, low temperature addition of dye to the bath, still showed severe barre.

EFFECT OF HYDROSETTING ON DYE RATE UNIFORMITY

The working hypotheses derived from these results pose the question of how we can translate these leads to, eg, nylon automotive fabrics. These fabrics are not autoclaved in normal mill processing. However, many of these fabrics are jet-dyed, so hot water pretreatment before dyeing at autoclaving temperatures is possible. Hydrosetting occurs in less than two seconds exposure. Therefore, fabrics need only be pretreated long enough to ensure uniform energy history, typically three to five minutes in jets with fabric turnover rates of less than three minutes. After hydrosetting, the bath is cooled and the fabric is dyed by a conventional procedure.

Laboratory tests confirmed that hydrosetting can dramatically improve uniformity of automotive nylon fabrics dyed with Acid Blue 122 (diagnostic 4) and with a critical pre-metallized dye formulation (Table III). However, this approach has limited commercial potential because of the increased cycle time required to heat-up to hydrosetting conditions and then to cool the bath for dyeing. Again, the question: how can we exploit this lead for use of dye bath energy to help control nylon dye rate uniformity?

These results, observations and questions led us to reconsider some generally accepted rules, especially those dictating low initial bath temperatures and slow rates of temperature rise to avoid uneven dye strike and to ensure shade levelness with high affinity, low transfer dyes. Many nylon fibers hydroset at 80 to 90°C (180 to 188°F). Therefore, a sample of the same warp knit automotive fabric was pretreated at hydrosetting conditions (93°C, 200°F) for five minutes in a blank bath. Dye was then applied in an isothermal dyeing at 93°C (200°F) by metering a dye-concentrate solution of Acid Blue 122 (diagnostic 4 conditions) into the circulating bath over 40 minutes. The dyed fabric showed the hoped for, dramatic uniformity improvement vs. the conventionally dyed control (diagnostic 4). In addition, there was an unexpected, remarkable (105%) increase in dye yield!

The same fabric then was dyed with a critical pre-metalized formula via this isothermal, metered dye addition process. The dye uniformity was, again, dramatically improved with a substantial (34%) increase in dye yield vs. the conventionally dyed control. These results are summarized in Table IV.

Repeated experiments with a variety of 100% nylon fabrics and nylon/Lycra® spandex containing fabrics confirmed and extended these results/conclusions: dyeing from a dilute, isothermal bath above T_d improves fabric dye rate uniformity and increases dye yields vs. conventionally dyed controls (4).

THE INFINITY* PROCESS AND PRODUCT ARE UNIQUE

THE PROCESS

Since, initially, dye is applied from an infinitely dilute bath, we named this the INFINITY* Process. Although some of the individual components of the INFINITY* Process have been used before (5, 6, 7) the INFINITY* Process combines them in a unique way (8) for dyeing nylon from a dilute, isothermal bath, above Td, which gives a number of high-value benefits:

- improved dye-rate uniformity
- increased dye-yield
- shorter cycle times
- reduced chemical
- cleaner effluents
- potential for increased product by process control

THE PRODUCT

Photomicroscopy and ultra-violet microspectrophotometry (9) of yarns from INFINITY* samples showed, unexpectedly, that the product is randomly and microscopically non-uniform; in essence it is a "micro heather" which is visually uniform:

- radial cross-sections show that individual fibers are asymmetrically ring dyed, with some filaments having little or no dye

* longitudinal scans of filaments show random along-end patterns of dye/no-dye with four "fingerprint" characteristics identified by scans across fiber cross-sections:

    a) undyed
    b) one-sided dyeing
    c) asymmetric broad ring-dyeing
    d) uniform, broad ring-dyeing

Slow and high-speed U.V. microscopy, longitudinal scans and cross section scans showing these "fingerprint" characteristics of INFINITY* product are in Appendix II (9).

The unique dye distribution appears to be primarily responsible for the increased dye yields. The more complete bath exhaust generally achieved also contributes.

Fabrics are macroscopically - ie, visually - very uniform, with key performance responses fully equivalent to controls, even in laboratory abrasion/frosting tests and in napped and sheared automotive fabrics. These good results may be explained in part because the exceptional toughness of nylon minimizes fiber wear-off during abrasion testing. This minimizes shade change and frosting. Further, the completely random, longitudinal variations of dye described above suggest that, where fibers are abraded, dyed and un-dyed segments are always in a random mix. This would also minimize shade changes and frosting.

This good color fastness in abrasion tests is surprising, since the literature suggests that ring dyeing can lead to color loss/change ("frosting") from abrasion. Merian and Lerch (10) in a discussion of level dyeing problems with disperse dyes on polyester and other synthetic fibers, schematically illustrate various types of ring-dyed yarns which can be found in practice. Fabrics dyed under conditions which produce non-uniform ring-dyeings, where some fibers are dyed while others are undyed generally are unlevel and have poor resistance to color-loss by abrasion. On the other hand, samples where all the individual filaments are uniformly ring dyed have good color fastness to abrasion. They conclude: "We must therefore discard the idea that ring dyeings are always undesirable". Recently, Doran (11), reviewing the low temperature dyeing of wool with acid milling and 2:1 metal-complex dyes, showed that ring dyed samples can have acceptable end-use performance properties.

Therefore, the INFINITY* fabrics which are uniformly dyed; i.e., visually level/uniform, in spite of microscopic, highly random and non-uniform ring dyeing, appear to be another example showing that ring dyeings are not inherently undesirable and, in fact, can provide high value benefits.

MECHANISM OF DYE UPTAKE DURING THE INFINITY PROCESS

The unique, asymmetrically ring-dyed fibers from INFINITY* samples suggest that dye distribution is controlled by diffusional boundary layer kinetics characteristic of conditions which produce high partion coefficients (12):

- Finite, dilute bath
- Restricted dye content in the liquor: metering
- High temperature: above Td
- High rates of dye uptake
  - fiber surfaces rapidly deplete dye from liquor interface
- high affinity dye-types: low transfer
- dyeing conditions, especially pH, which minimize transfer

These conditions would produce the observed non-uniform dye uptake since the most accessible fibers and regions within a yarn bundle or fabric would dye preferentially. There would be less dye on the less accessible fibers/regions and dye yield would increase because more dye is where it can be seen. Results to date strongly support the hypothesis that the INFINITY* Process is primarily controlled by boundary layer kinetics since it "works" best-in terms of increased dye yields - with:

- high affinity, non migrating dyes like pre-metallized and milling - acid dyes
- conditions which minimize transfer like low pH, relatively low temperature and short times

- less to no yield increases with low affinity leveling dyes and/or conditions which increase migration

THE DIFFUSIONAL BOUNDARY LAYER AND THE INFINITY PROCESS AND PRODUCT

The diffusional boundary layer is a concentration gradient which develops during dyeing between the dye solution adjacent to the substrate and the rest of the bath. Mc Gregor, Peters, Etters, and others have studied the effects of stirring and liquor flow rates on the mass transfer rate of dye from the bath to the substrate (13, 14, 15, 6). A dimensionless parameter, L, describes the transfer rate of dye between the bath and the substrate:

$$L=(D_s/D_f K)(r/b)$$

where:

- D_s is the diffusion coefficient of the dye in solution
- D_f is the diffusion coefficient of the dye in the fiber
- K is the equilibrium distribution coefficient for the dye-fiber system
- r is the fiber radius
- b is the thickness of the diffusional boundary layer

In conventional dyeing procedures, conditions are generally selected which tend to drive L towards ∞. Thus, the dyer strives for good mixing; e.g., by high turnover rates of fabrics and/or the dye liquor. Good liquor flow minimizes the boundary layer and increases the rate of dye transfer from the liquor to the substrate. The dyer also selects dyes, auxiliaries and time/temperature/pH conditions which slow down dye strike-rates and/or maximize transfer, as far as the end-use requirements for, e.g., wetfastness, will permit. These selections determine the value of the $(D_s/D_f K)$ parameter, which characterizes the sensitivity of the dye-fiber system to liquor flow effects. The dyer strives for high values of this parameter: the results are to drive L towards ∞.

In contrast, optimum conditions for the INFINITY* Process and Product drive L towards O! It appears likely that the distribution coefficient K is the primary control factor to ensure low values of L in the INFINITY* Process (12). The necessary high values of K can be produced by use of low pH, and by restricting time and temperature (to minimize dye desorbtion/transfer). In addition, McGregor (13) showed that, at pH 3.3 and 73.8°C with C.I. Acid Red 13 and a nylon 6-6 fabric, K could be increased by a factor of 100 by reducing dye concentration from 58 ppm to 0.52 ppm. Therefore, the controlled, low dyebath concentrations used to ensure levelness in the INFINITY* Process also work to increase K and drive L towards 0. Under conditions where fibers can accept dye more rapidly than the dye liquor can provide it, the dyebath concentration at the fiber surfaces will approach zero and K can be as high as 2.4×10^5 (7,10).

McGregor points out that the maximum possible rate of dyeing is determined by the boundary layer and the solution dye concentration (13). The rate of supply of dye to the fiber surfaces is independent of the diffusion coefficient in the fiber. This minimizes sensitivity to structural differences between fibers and may contribute to improved dye uniformity. However, these conditions also maximize the non-uniformity of dye distribution within and between filaments. Therefore, achieving level dyeings will be critically dependent on adequate flow and circulation in a uniform manner to all fabric surfaces.

ACHIEVING LEVEL DYEINGS WITH THE INFINITY PROCESS

Since the boundary layer and dye diffusion rates in the liquor are fixed under constant dyeing conditions, control of the dyebath concentration has a powerful influence on levelness.

Results of many experiments showed that for good levelness with the INFINITY* Process, two factors are essential:

- The dye concentrate solution must be thoroughly mixed with bath liquor <u>before</u> the diluted dye solution impinges on the fabric. The rate of mixing should be an order of magnitude faster than the rate of dye uptake (16):

    - this is easily accomplished by connecting the metering pump through the inlet of the machine circulating pump. A schematic of a laboratory - jet modified for metered dye addition appears in Figure 4.

- The rate of dye-concentrate addition must be the primary control over the rate of dye uptake. Results show that, in most cases, this is accomplished by adjusting the rate of addition so that between about 1.0% and about 3.0% of the total dye is added per machine turnover cycle. This rate of addition will vary depending on the fabric structure (e.g., tightly vs. loosely constructed), the affinity of the dyes being used, the liquor flow characteristics of the dyeing machine and the dyeing conditions (e.g., temperature, pH, auxiliaries, liquor ratio). Lower rates of addition are useful for low percent dye-on-fiber applications of high affinity dyes. This provides a sufficient number of machine cycles for adequate averaging to produce level dye uptake.

  Pale shades with high affinity dyes are difficult to dye levelly in conventional procedures. Generally, conditions are set so that about 2% of the total dye exhausts per machine cycle, (6, 17). Therefore, the adjustment of addition rates in the INFINITY* Process is readily understandable, since INFINITY* uses the rate of addition of dye under conditions of rapid dye uptake as the primary control of dye exhaust.

OPTIMIZED CONDITIONS FOR INFINITY

In-depth laboratory and small-scale mill tests showed that INFINITY* gave consistent, reproducible results with critical pre-metallized shades on automotive nylon fabrics. This likely is because the dyes all have similar, high affinities and, most importantly, fiber structure/ porosity/free volume is essentially constant because of the isothermal process. In short, the INFINITY* Process minimizes or eliminates some of the major variables the dyer has to control: the "moving target" has been slowed down or even stopped!

So-called critical "fashion" colors often require the use of combinations of rate incompatible dyes, namely high affinity, non migrating colors, like; e.g., C.I. Acid Violet 48 and low affinity, migrating dyes like C.I. Acid Red 52 ("Rhodamine"). To study the effects of dye bath variables on dye uptake and dye yield, we used

Violet 48 as a model of a high affinity dye and Acid Blue 45 as a model of a low affinity dye.

The results (Tables V and VI) show:

- dye yield increases up to 49% with Violet 48
  - determined by dye affinity/migration
  - confirmed by matching controls with less dye
- conditions which increase dye yield with Acid Blue 45.
- interactive effects of
  - pH
  - temperature
  - time at temperature
- high vs. low affinity dyes require different pH and temperature conditions, as they do in conventional procedures.

These results indicate that, as in conventional procedures, applications of mixtures of rate incompatible dyes requires attention to the details of dyeing conditions to produce consistently acceptable results.

Effects of INFINITY* Dyeing Temperature on Dye-Rate Uniformity

To determine whether the temperature at which dye is metered affects dye rate uniformity, we dyed the automotive fabric used previously at a range of temperatures with the same pre-metallized dye formula. The results (Table VII) clearly show that dye uniformity improves in a stepwise manner as the dye metering temperature is increased from 66°C (150°F) to 71°C (160°F) to 77°C (170°F) to 93°C (200°F). These results are similar to the previously described, stepwise improvements in the uniformity of CTB fabrics with increasing pretreatment temperatures (Table II). The hypothesis that a range of fiber transition temperatures are involved in such stepwise changes could also help to explain the effects of INFINITY* dyeing temperature on uniformity.

A schematic represenatation of this hypothesis (Fig. 3) depicts two yarns of different energy histories. In the INFINITY* process, dye is usually introduced at 82°C (180°F) or higher, after the fiber structure transitions have been completed. The fiber structure stabilizes and energy history differences are minimized before dyeing begins. In contrast, in conventional procedures, all the dye is present at the start of the process and during the various fiber structure changes as the bath heats up. Differences in the rates of uptake between the two yarns result in dye content differences which can cause streaky fabrics.

Dyeing Conditions and the Use of Dyeing Auxiliaries

The auxiliaries the dyer uses with conventional procedures can also be used advantageously in the INFINITY* process to help control dye-fiber interactions. However, less auxiliary is generally needed with INFINITY*, particularly when applying formulations of dyes with similar affinities in equipment, like jets, which provides good liquor flow and fabric movement. High liquor flow rates reduce the boundary layer and help to provide uniform dye transport to the substrate surfaces, on average.

When applying rate incompatible mixtures of dyes, like, e.g. C.I. Acid Violet 48 and C.I. Acid Red 52 (Rhodamine), auxiliaries can be useful for INFINITY* dyeing, as they are for conventional procedures These combinations are difficult to apply by conventional procedures. Because of the large difference in affinity between these dyes, boundary layer effects can result in the phenomenon known as "shade fractionation": i.e., areas of the substrate predominantly absorb one component or the other, but not the desired mixture.

Under the low pH conditions required for reasonable exhaust of the Rhodamine component, e.g, pH 4.0, Violet 48 has such high affinity that it rapidly strikes accessible surfaces. The boundary layer is preferentially depleted of Violet 48, which, consequently is non-uniformity distributed. Rhodamine has a much lower affinity and migrates readily. Therefore, it has a more uniform uptake. As a result, portions of the fabric can vary from a deep violet, with an excess of violet 48 to a bright pink, where there is less of the violet component.

Tests showed that the addition to the bath of small amounts of amphoteric/cationic auxiliaries markedly reduced or eliminated shade fractionation with violet 48/ Rhodamine and other rate incompatible formulations. Such auxiliaries are useful for applying mixtures of low and high affinity dyes in conventional procedures, as well as for INFINITY* dyeings where boundary layer effects can be more pronounced.

CONCLUSIONS

With INFINITY*, buffers can be used to set the bath at a predetermined pH level to achieve good levelness and good exhaust, under the conditions of application. Results show that with formulations of dyes with similar, high affinities like, e.g., pre-metallized automotive shades, excellent reproducibility is provided by buffering the bath to a pH of about 6.0. The fiber structure, i.e., porosity/free volume, is constant under isothermal conditions. Metering, the primary control for rate of exhaust is precise and reproducible. Given a reasonably constant liquor ratio and in a given dyeing machine, temperature and pH are the remaining variables for control of dye-fiber interaction. These can likewise be precisely measured and controlled.

Therefore, with appropriate control of temperature, pH and metering, it appears likely that with experience, INFINITY* should provide improved product by process control since the major variables which influence dye-fiber interactions are either constant or can be precisely measured and controlled.

PROGRAM

The INFINITY* Process appears to be rooted in the same fundamental principles as those operating in conventional procedures. Therefore, work is planned to build from established theory and experience to more broadly develop and apply this new way of dyeing nylon.

ACKNOWLEDGEMENTS

Many of our colleagues contributed valuable suggestions during this work. We express our appreciation to all of them. We especially thank J.L. Chang, H.A. Davis and R.F. Hampton for their photomicroscopy studies and suggestions. Special thanks are due to Prof. R. Mc Gregor for his insight, suggestions, guidance and stimulating discussions.

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TABLE I: Effects of Energy on Fiber Structure and Dyeability

What Does Thermal Energy Do to Fiber Structure?

Up to approximately 180°C, crystallinity increases because number of "small" crystals increases.

From approximately 180°C and up, crystallinity increases because small crystals reform into fewer but much larger, more stable, higher-melting crystals.

- Hearle
- Dumbleton, Bell, Murayama
- Valk, et al.
- Statton
- etc.

What Does Tension Do to Fiber Structure?

In general, tension decreases fiber porosity.

Combined with heat, these effects become permanent through formation of crystals.

- Classic work by Statton

Crystals, in effect "cross link", stabilize fiber structure.

What Does Chemical Energy Do to Fiber Structure?

In general, solvents/carriers increase fiber porosity.

Where applied in combination with heat and tension, the effects of chemical energy on fiber structure are orders of magnitude greater than those of thermal energy alone.

What Is the Fiber Structure "Doing" In Response to Energy Input?

The polymer chains are moving to a more stable, lower energy, more "comfortable" equilibrium configuration.

In essence, fibers are relieving themselves of variations in thermal/mechanical/chemical energy input during fiber manufacture and textile processing.

Key: at equilibrium, dye capacity is constant.

TABLE II: Effect of Water Pretreatment Temperature on Crimper Tube Barré

Pretreatment Conditions

Temperature (C)	Time (Min)	Temperature of Dye Addition (C)	Barré Rating**
—	—	27	1.0
98	30	27	4.6
104	30	27	5.2
116	30	27	5.8
116	60	27	5.6
129	30	27	8.2
—	—	71	7.6

* All samples dyed by the Diagnostic Test 4: C.I. Acid Blue 122 at pH 5.0. Fabrics are knit (full Fashioned) from 70-34 nylon, stuffer box crimped.

** Scale: 10 = no barré; 6.0 = slight, commercially acceptable barré; 1.0 = severe barré

TABLE III: Effect of Hydrosettting on Fabric Dye Rate Uniformity

Fabric: Warp knit containing 50-17 round nylon yarns

Dye Procedure	Uniformity Rating*
Diagnostic 4	2.0
Diagnostic 4-B	7.5
Control: Pre-met shade	2.0
Hydroset at 270°F (132°C)	
Pre-met shade control procedure	7.0

* Rated against Du Pont Computer Generated Uniformity Standards:

10.0 = No Streaks
6.0 = Commercially Acceptable
1.0 = Severe Streaks

TABLE IV: Effect of INFINITY Process on Fabric Dye Rate Uniformity

Fabric: Warp knit containing 50-17 round nylon yarns (50-gram samples in each test)

Dye Procedure	**Uniformity Rating***
Diagnostic 4	2.0
Diagnostic 4-B	7.5
Control: Pre-met shade	2.0
INFINITY:	
C.I. acid blue 122	8.0
Pre-met shade metered at 93°C	7.5

* Rated against Du Pont Computer Generated Uniformity Standards:
- 10.0 = No Streaks
- 6.0 = Commercially Acceptable
- 1.0 = Severe Streaks

TABLE V: Effect of Dyeing Conditions on Dye Yield

C.I. Acid Violet 48

pH	Temperature °F	Time at Temperature	% Dye Yield Increase
4	180	15	41
4	180	45	34
4	205	15	49
4	205	45	46
6	180	15	4
6	205	15	13
6	205	45	9

TABLE VI: Concentrations of C. I. Acid Blue 45 During Conventional (Control) and INFINITY Dyeing Processes

Conventional Process: pH 4.5

Sample	Temperature °C/°F	Time (Minutes) After Reaching 60°C/140°F	Concentration in Bath; Parts per Million
1	27/80		42
2	30/86		50
3	35/95		47
4	40/104		44
5	45/113		41
6	50/122		36
7	55/131		32
8	60/140		29
9		5	16
10		10	13
11		15	7
12		20	3
13		25	2
14		30	1

INFINITY Process: pH 4.5, 60°C (140°F)

Sample	ML of Dye Concentrate Added	Time (Minutes) After All Dye Added	Concentration in Bath; Parts per Million
1	25		0.4
2	50		1.1
3	75		1.6
4	100		2.1
5	125		1.9
6	150		3.1
7	175		4.3
8	200		4.1
9		5	2.9
10		10	1.6
11		15	1.1
12		20	0.7
13		25	0.5
14		30	0.4

TABLE VII: Effect of INFINITY Dyeing Temperature on Dye Rate Uniformity of Warp Knit Automotive Fabric

Warp knit containing 50 - 17 round nylon yarns

Dye Metering Temperature	Metering Time	Uniformity Rating*
Control-dyed at 107°C (225°F) - all dye added at start of cycle: 31°C (80°F)	—	3.0
66°C (150°F)	80 minutes	1.0
71°C (160°F)	80 minutes	2.5
77°C (170°F)	80 minutes	5.0
93°C (200°F)	80 minutes	7.0

* Rated against Du Pont Computer Generated Uniformity Standards:
- 10.0 = No Streaks
- 6.0 = Commercially Acceptable
- 1.0 = Severe Streaks

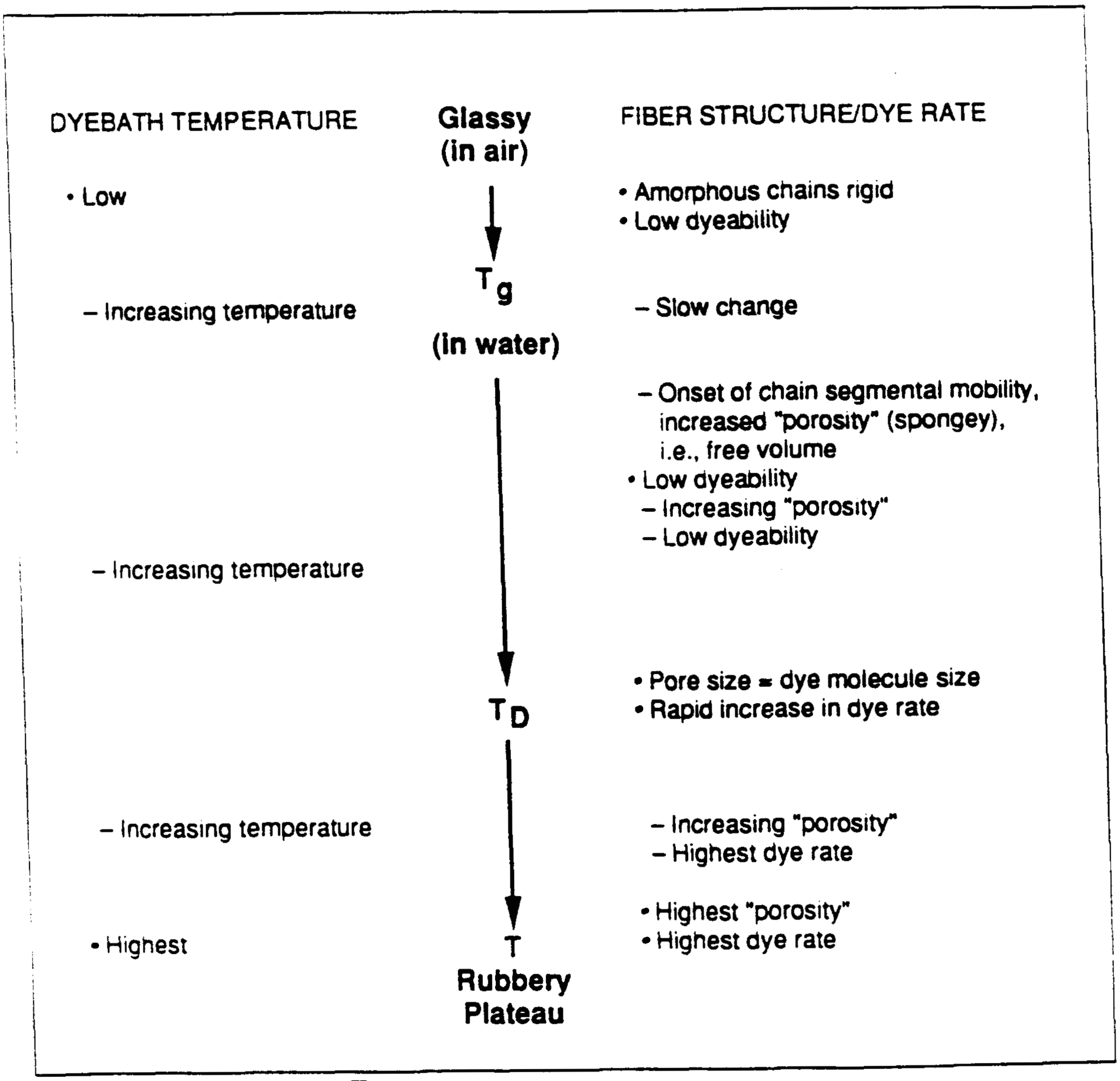


FIG. 1: Fiber Transition Temperatures

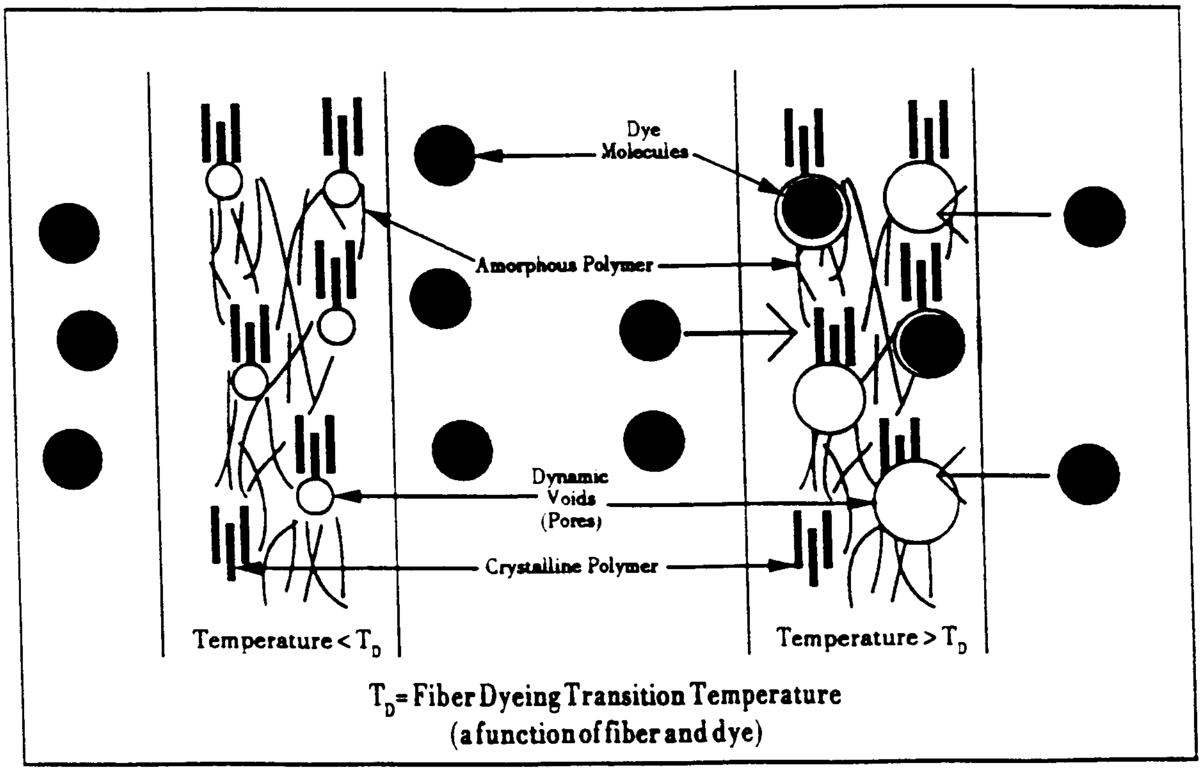


FIG. 2: Model of Fiber Dyeability at Low and High Temperatures

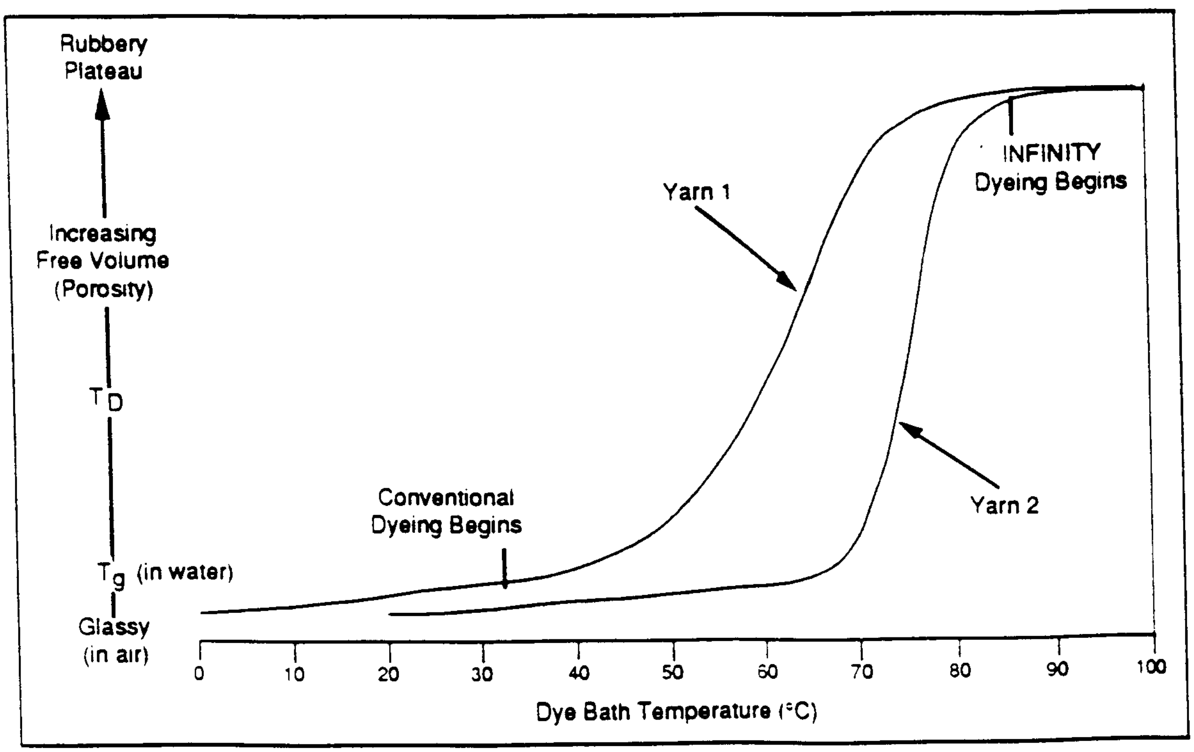


FIG. 3: Effect of Dye Bath Temperature on Fiber Structure

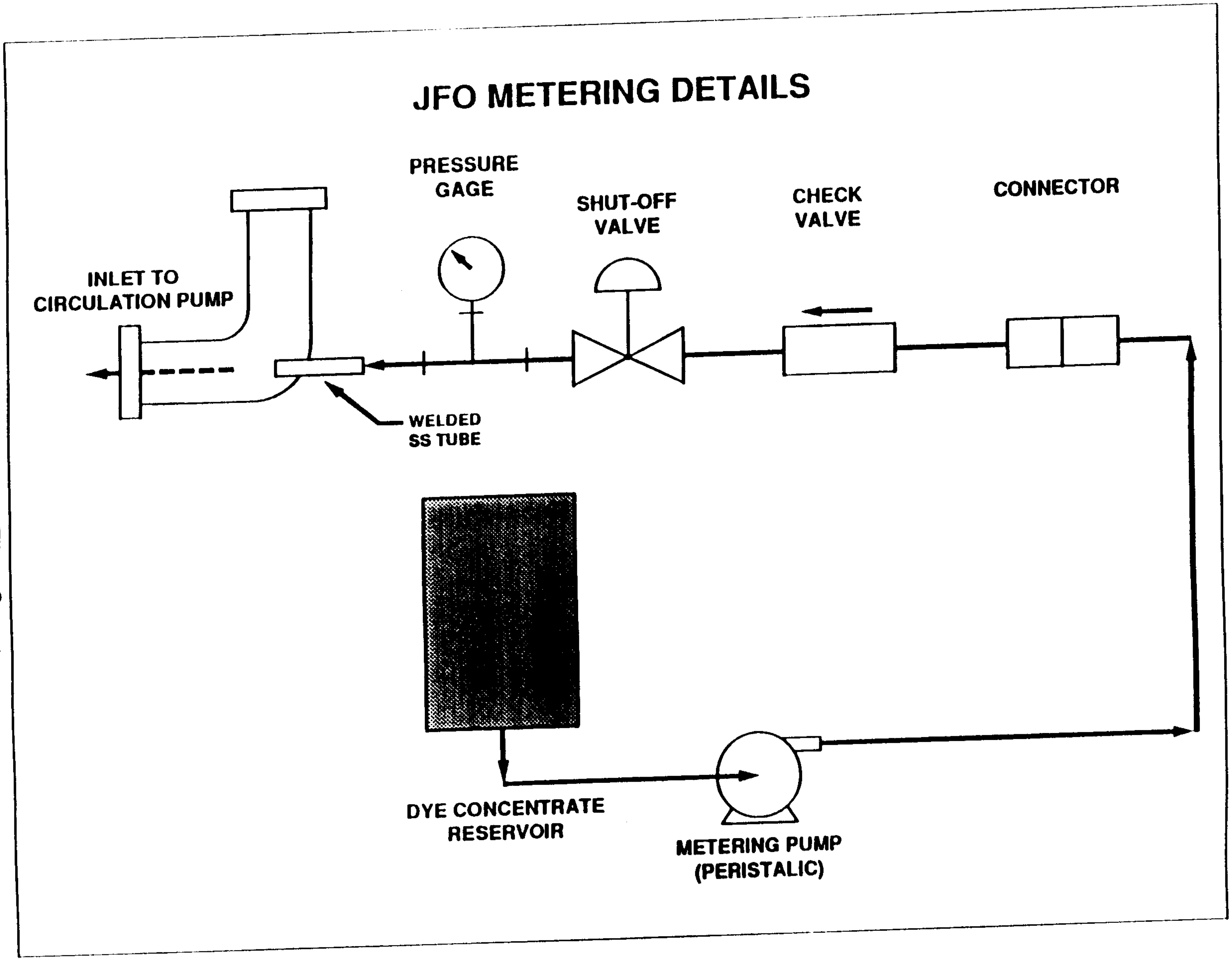


FIG. 4: Effect of Dye Bath Temperature on Fiber Structure

APPENDIX 1

General Principles

- No DYE Will Cover Physical/Optical Differences
- Disperse Dyes
  - Cover Amine End Differences (Equilibrium)
  - Cover Most Rate Differences (Equilibrium)
- Level Dyeing Acid Dyes
  - Cover Most Rate Differences (Equilibrium)
  - Amine End Sensitive (Equilibrium)
- Structure/Rate Sensitive Acid, Direct and Premetalized Dyes
  - Very Structure (TD) Sensitive (Non-Equilibrium)
  - Relatively Insensitive to Amine Ends (Non-Equilibrium)

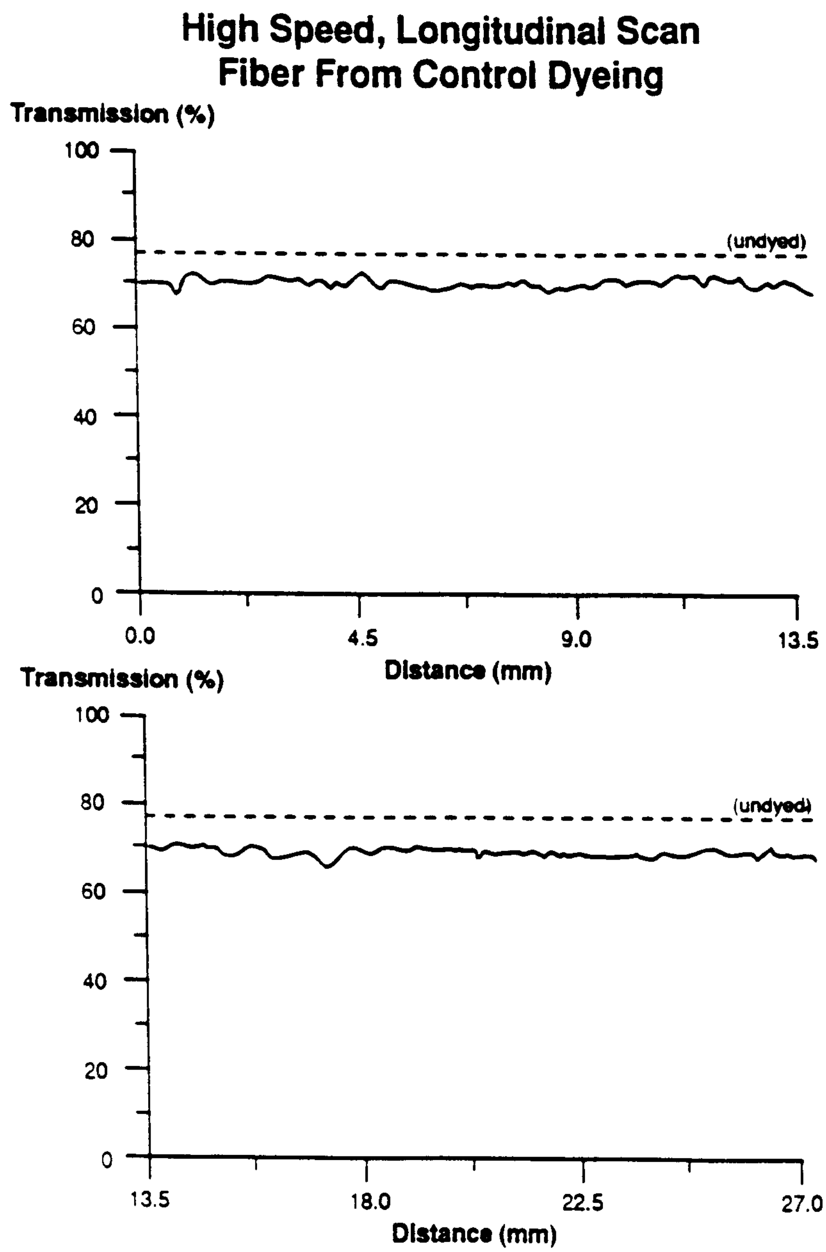
Diagnostic Dyeing (Nylon)*

NO.	PROCEDURE	STREAK TYPES
5	Mock Dye White	Configuration**
2	Disperse (Blue 3) Equilibrium	Configuration**
3	Small Ionic (Blue 45) Equilibrium	Configuration + Dye Sites
1	Disperse (Blue 3) Non-equilibrium	Configuration + Dye Rate
4	Large Ionic (Blue 122) Non-equilibrium PH 5	Configuration + Dye Rate + Dye Sites + (Slight)
4A	Large Ionic (Blue 122) Non-equilibrium Typical Trade Procedure pH 6	Configuration + Dye Rate + Dye Sites (Slight)
4B	Large Ionic (Blue 122) Alkanol® ND Pretreatment	Skin vs. Core
8	Large Ionic Direct (Blue 86)	Configuration + Dye Rate + Dye Sites

* Specific Procedures Developed for Conventional Textile Yarns.

** Opacity Streaks (E.G., Denier, Bulk) More Intense in Diagnostic 5. Luster Streaks (E.G., Cross-Section, Voids, Surface Smoothness) More Intense in Diagnostic 2

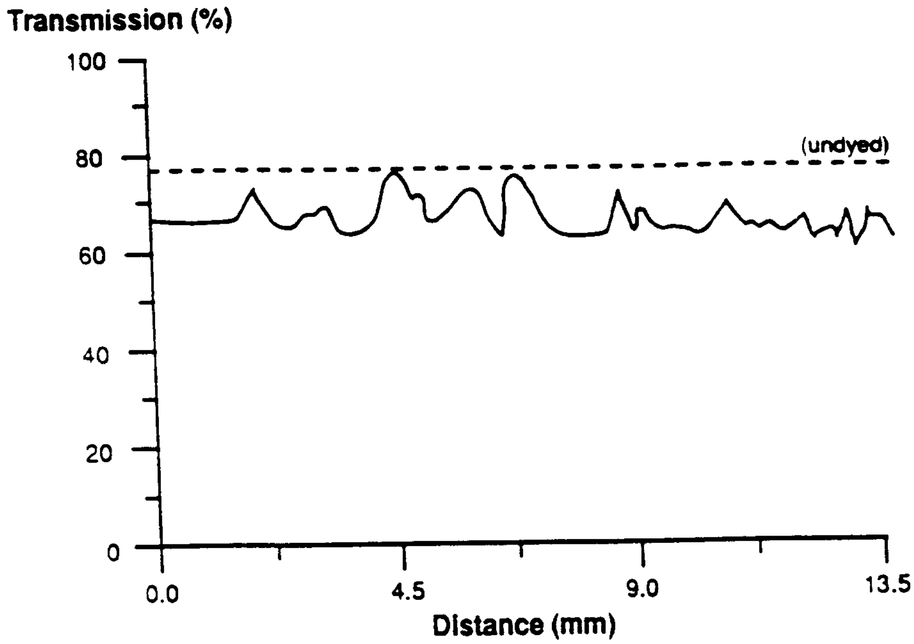
APPENDIX 2

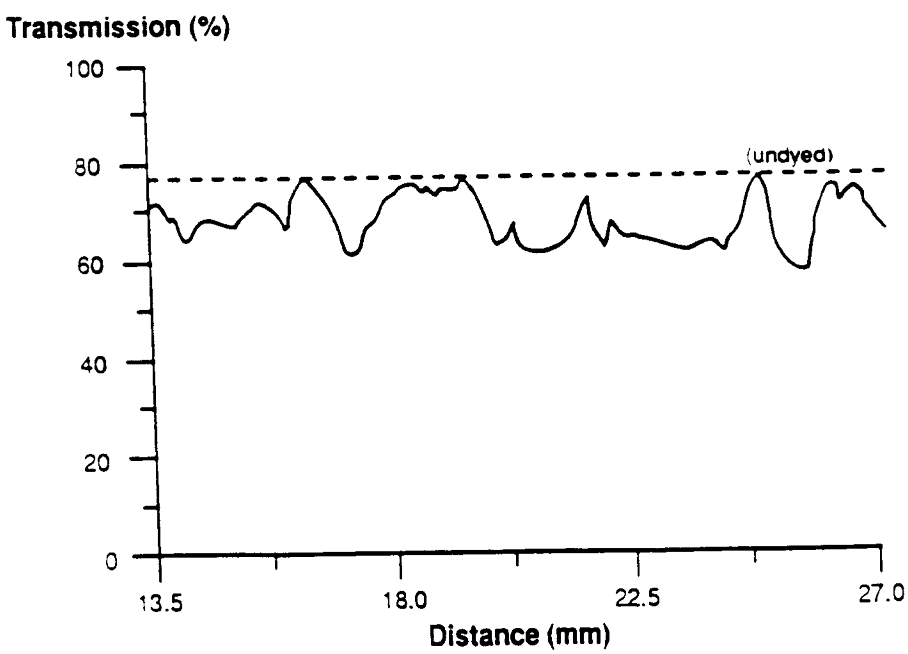


High speed, long distance scan, along a longitudinally viewed control fiber (Control: 2% C.I.A.B.-122; 0.5% DA) note uniformity of dye uptake.

APPENDIX 2

High Speed, Longitudinal Scan
Fiber From "Infinity" Dyeing

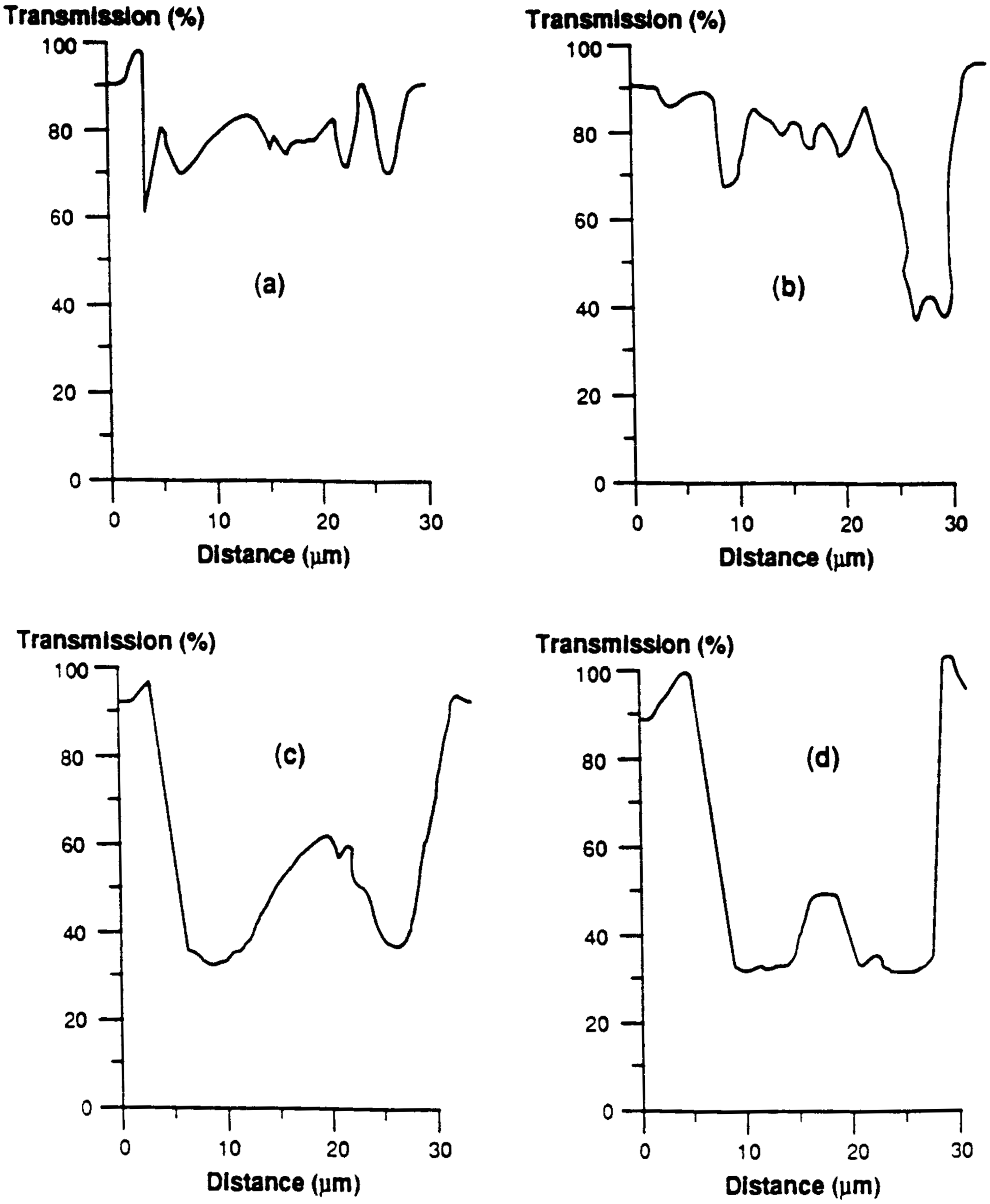




High speed, long distance scan, along a longitudinally viewed fiber
(IP; 2% C.I.A.B.-122; 0.5% DA) note periodicity of alternating undyed/dyed sections

APPENDIX 2

Slow Speed Scans Across Fiber Cross Sections "Infinity" Process



(IP; 2% C.I.A.B. – 122): (a) undyed (b) one-sided dyeing (c) asymmetric broad ring-dyeing (d) uniform, broad ring-dyeing

A New High-Value Process for Dyeing Nylon

2

DU PONT INFINITY

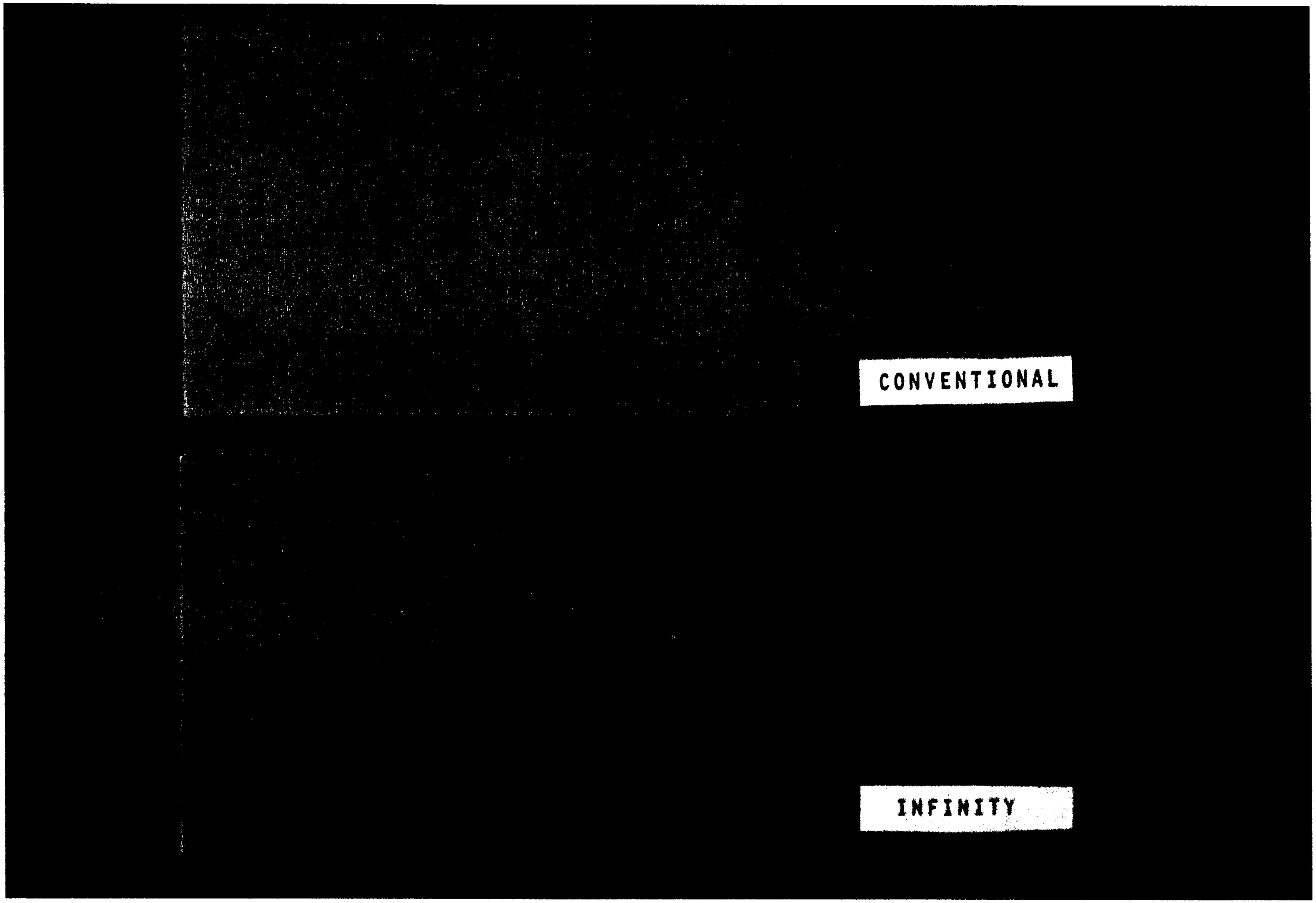
Today's Presentation

First, an Overview:

- Benefits
- Technology
- Process

Then,

- Mechanism
- Laboratory Results



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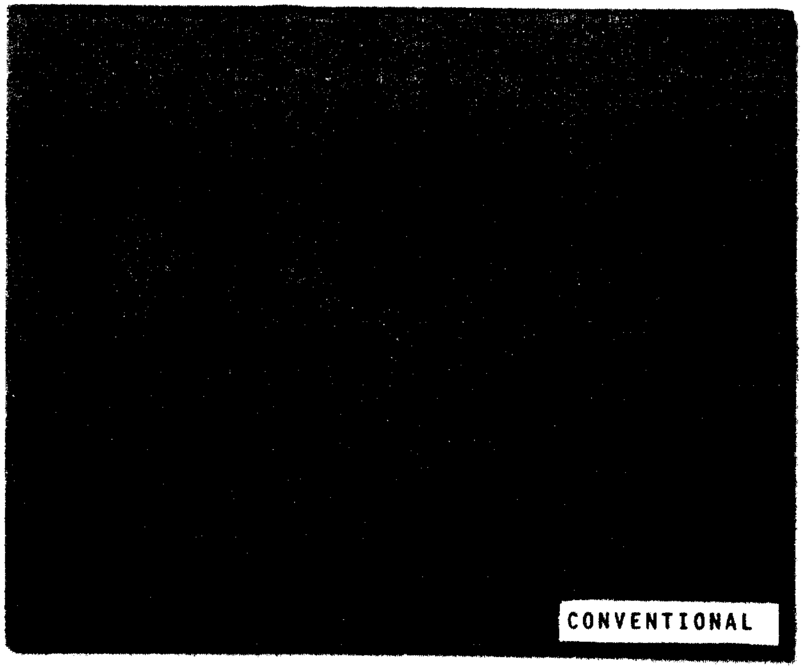
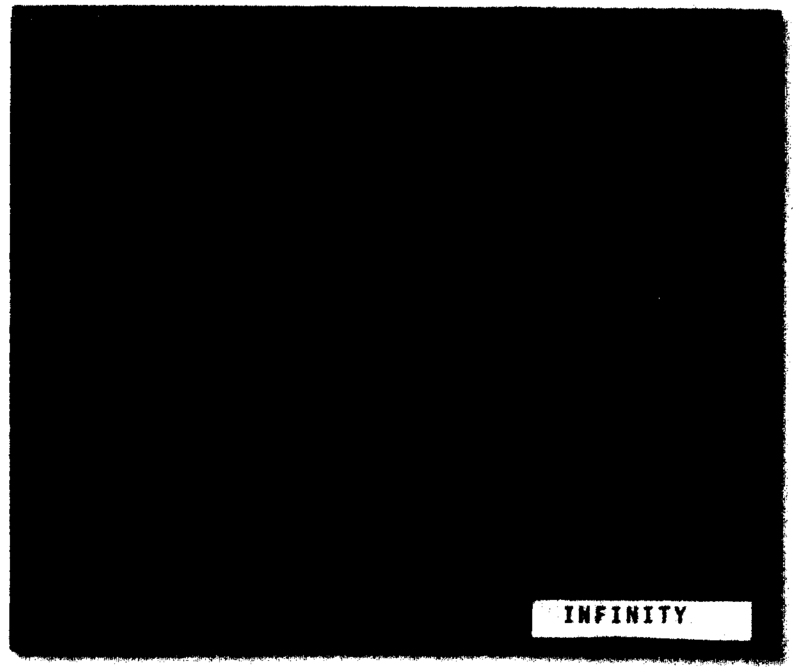

CONVENTIONAL


INFINITY

CONVENTIONAL

INFINITY

Conventional Nylon Dyeing Process

- Fabric, Water, Dyes, Chemicals Are in the Dye Machine
- Dye Bath is Heated Slowly
- "Holds" Are Often Used to Improve Levelness
- Fabric and/or Bath Are Circulated at the Dyeing Temperature

Infinity Process

- Water and Fabric Are in the Dye Machine --- with No Dyes
- Water and Fabric Are Heated Rapidly to the Dyeing Temperature
- Dye is Added to the Bath

Key Process Elements:

1. Heating Fabric in Water <u>Before</u> Adding Dye

   - Improves Fabric Uniformity

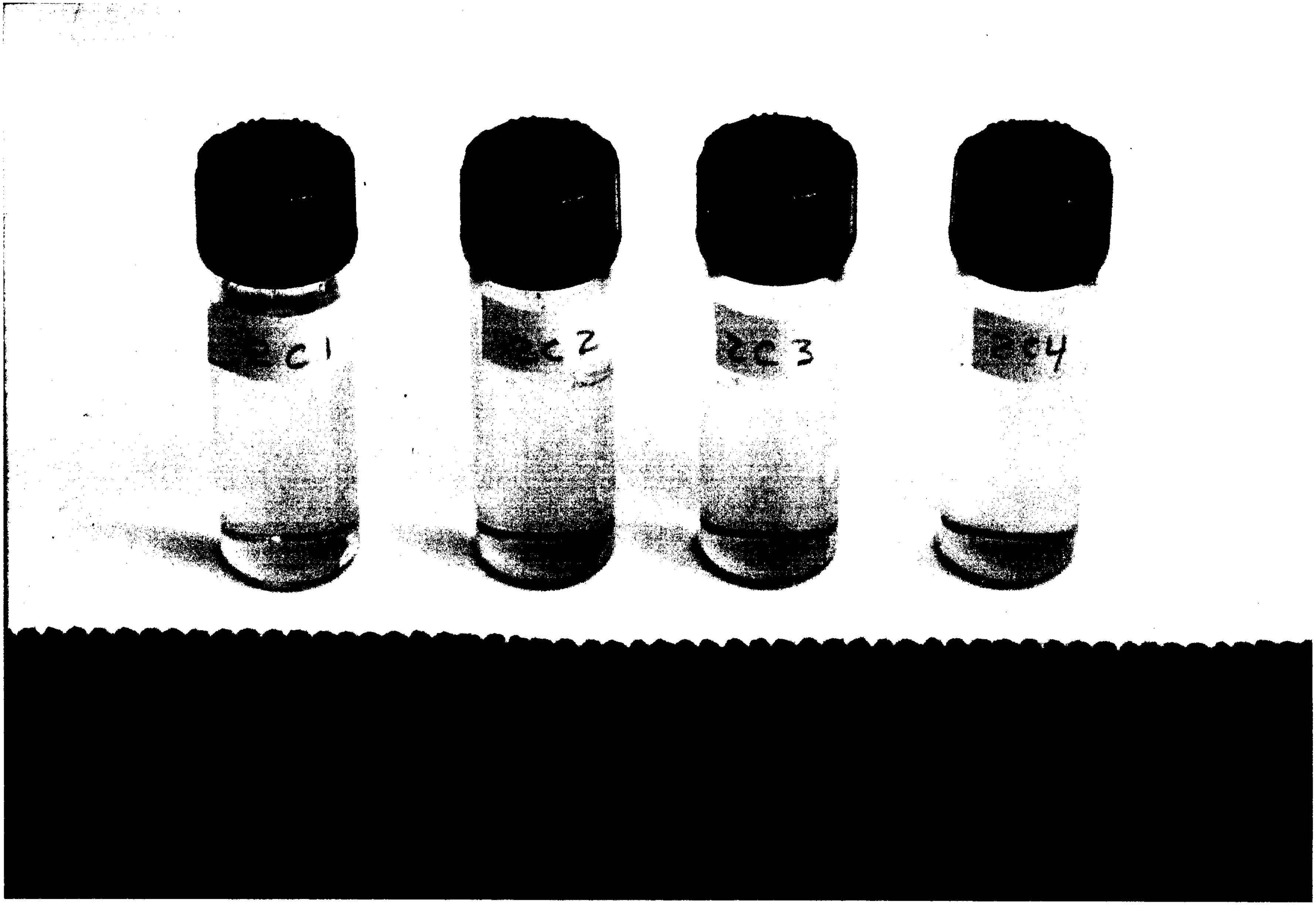
   - Reduces Dye Rate Differences Between Yarns

Key Process Elements:

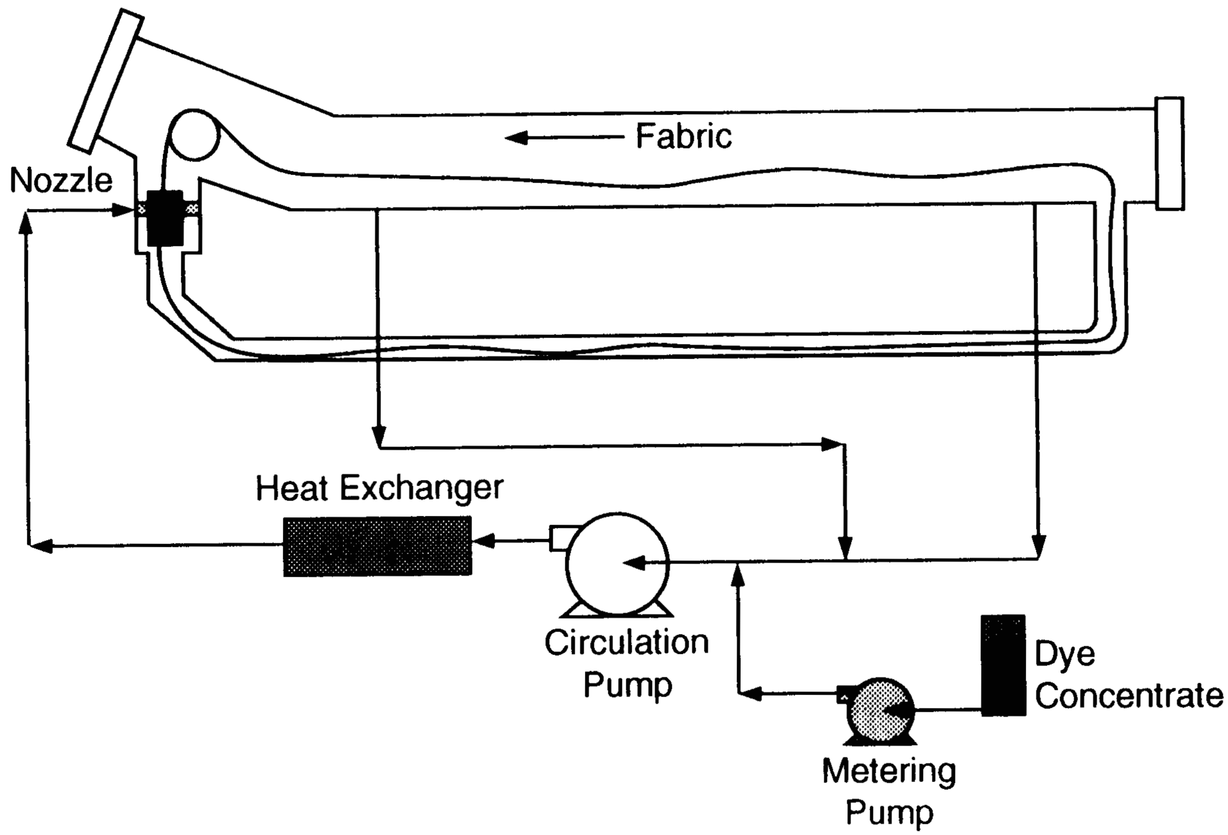
2. Metering Dye Concentrate to the Bath Over 40 to 60 Minutes Provides Level Dyeing

   - Meter 2 to 3% of the Dye Per Fabric or Bath Revolution

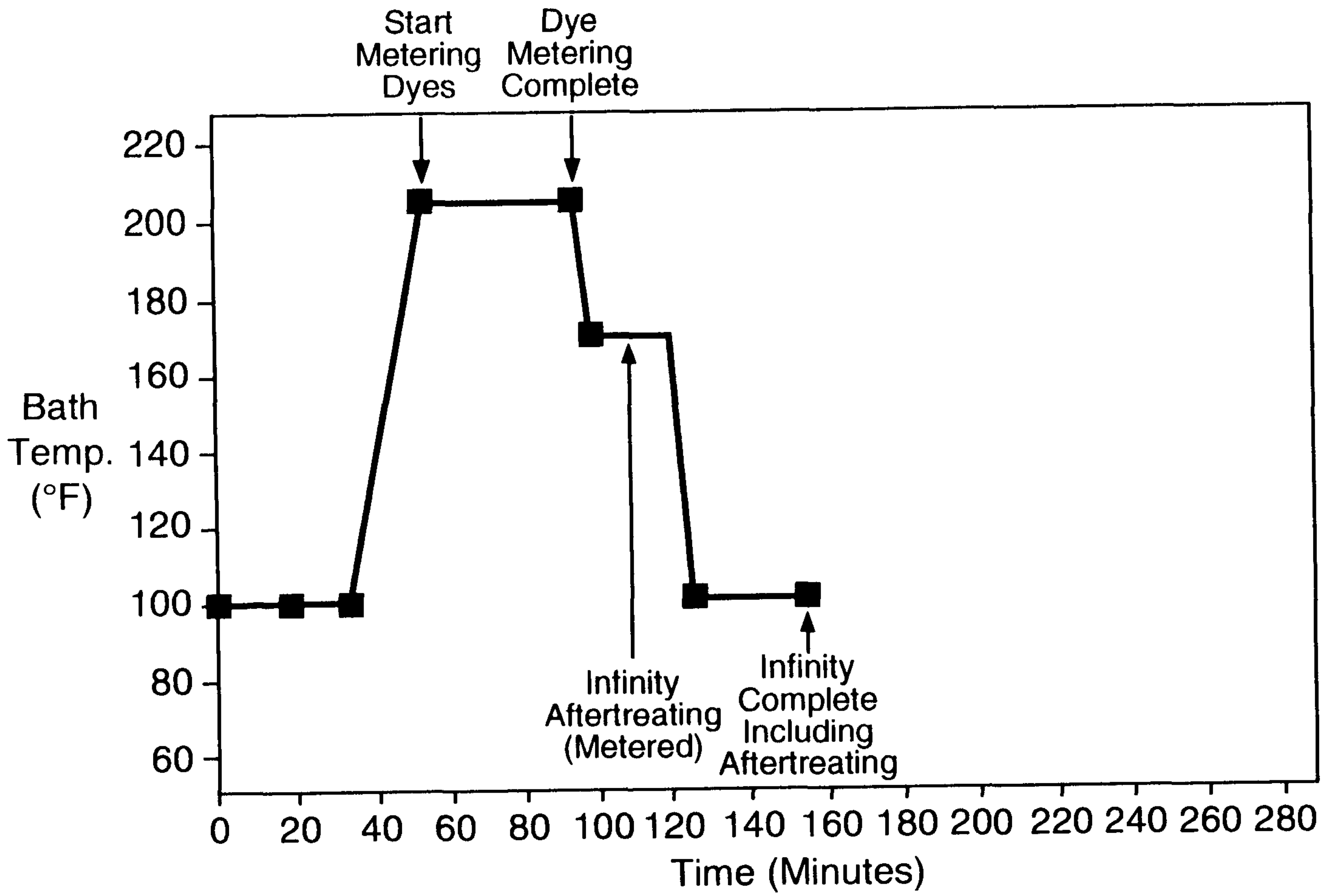

1C2
1C4



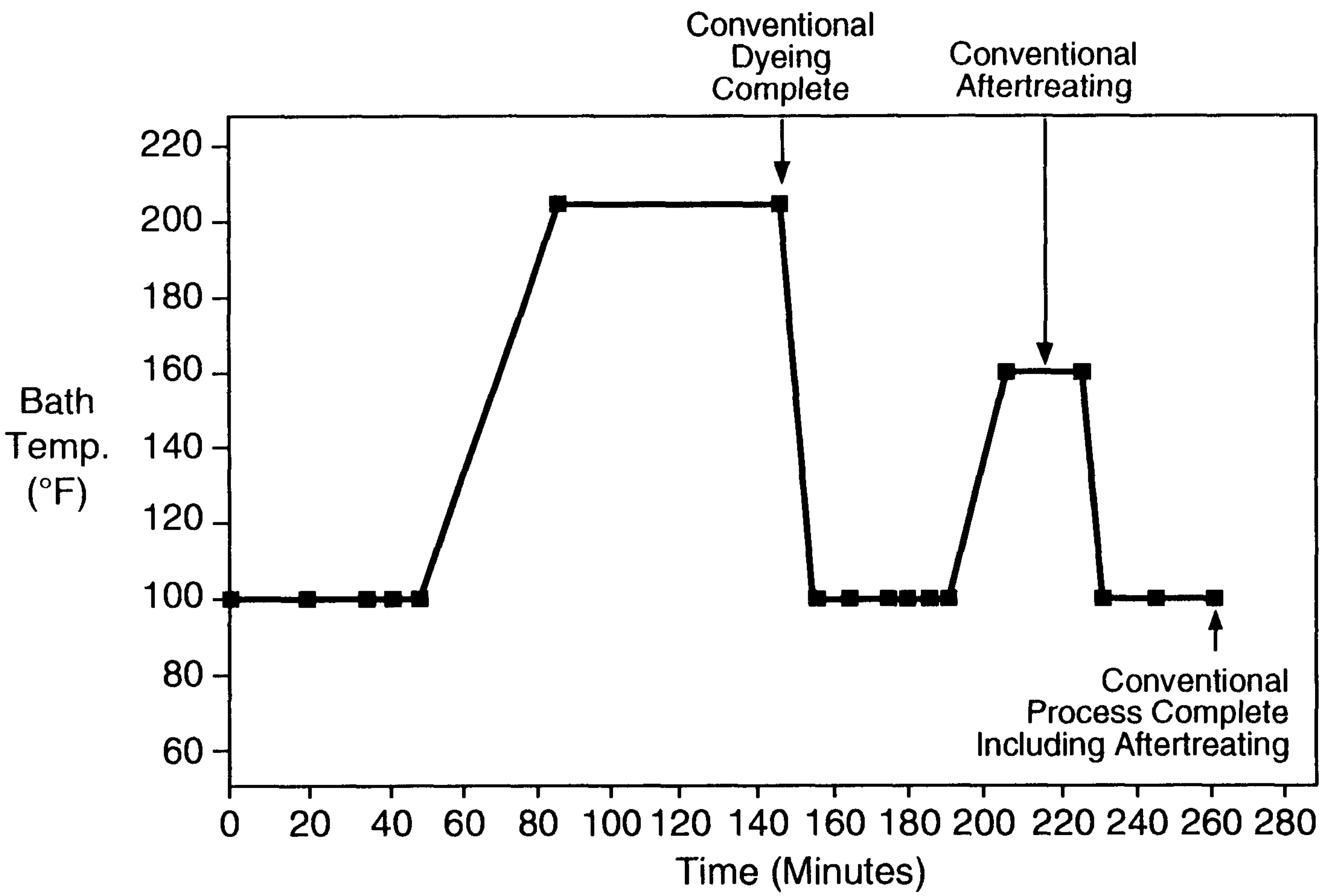
Jet Dyer with Metering Pump Installation



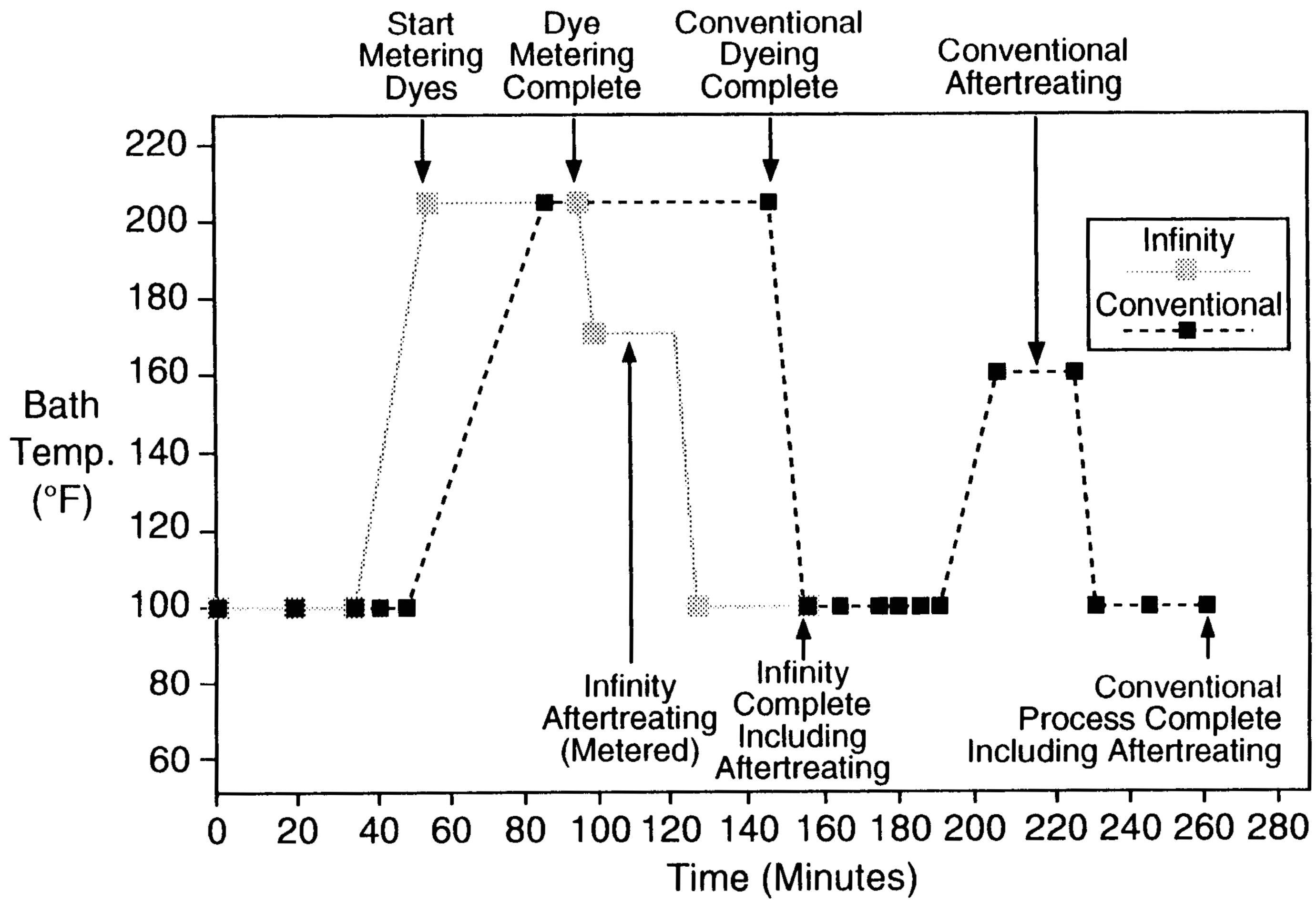
Infinity Process



Conventional Process



Comparison of Infinity vs. Conventional Processes



Aftertreating in the Spent Dye Bath

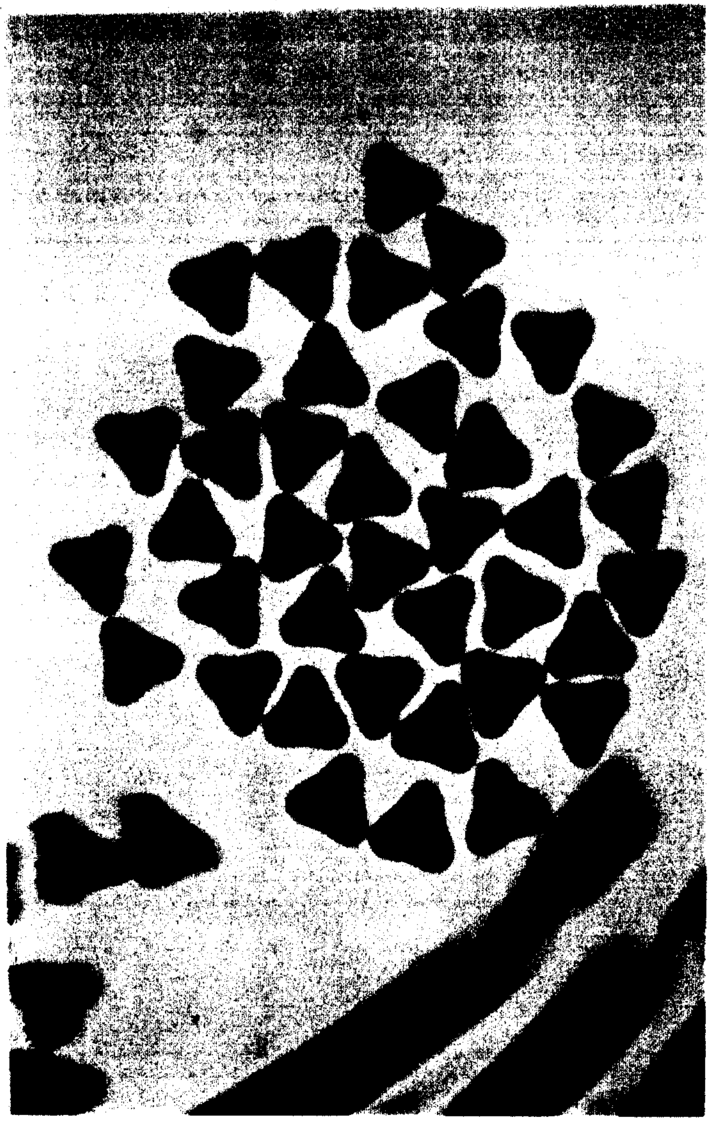
- Less Dyes and Chemicals in the Spent Bath
- Excellent Bath Exhaust
- Meter the Aftertreatment

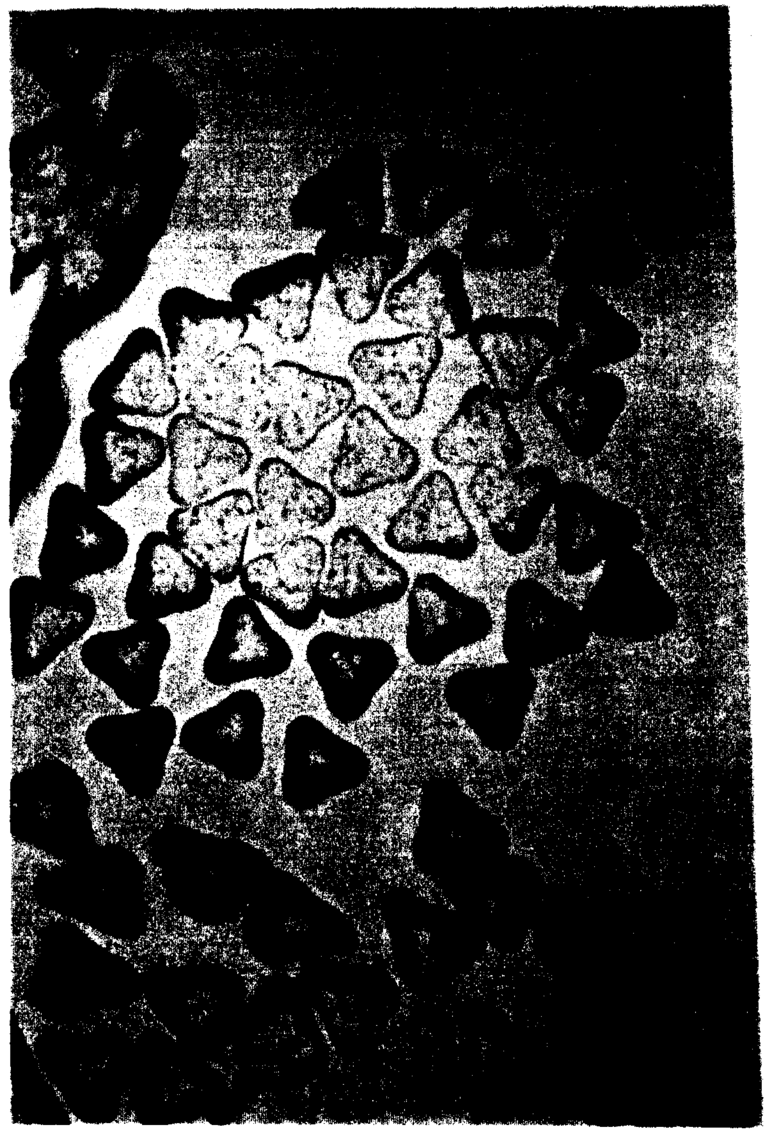
Process Development Status

- Proven in Lab and Semi-Works Trials on Broad Range of Nylon Materials
- Now in Mill Proveout and Scale-Up

Increased Dye Yield

- Higher Exhaust
- More Effective Dye Distribution



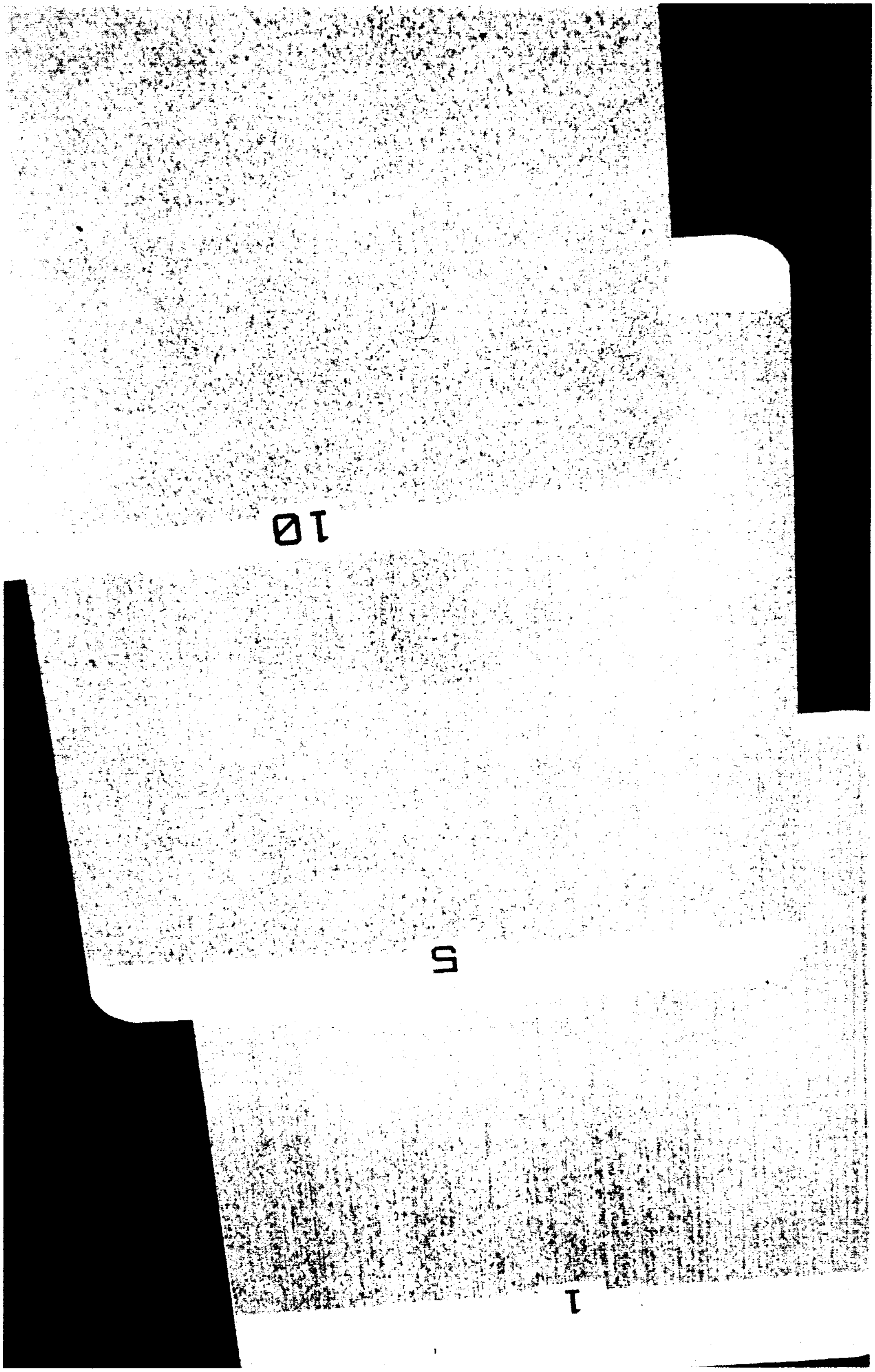


Equivalent Fabric Properties and Performance

- Wetfastness
- Lightfastness
- Wet and Dry Crocking
- Frosting
- Taber Abrasion

Unique Characteristics of Infinity Product

- Superior Uniformity
- Asymmetric Ring Dyeing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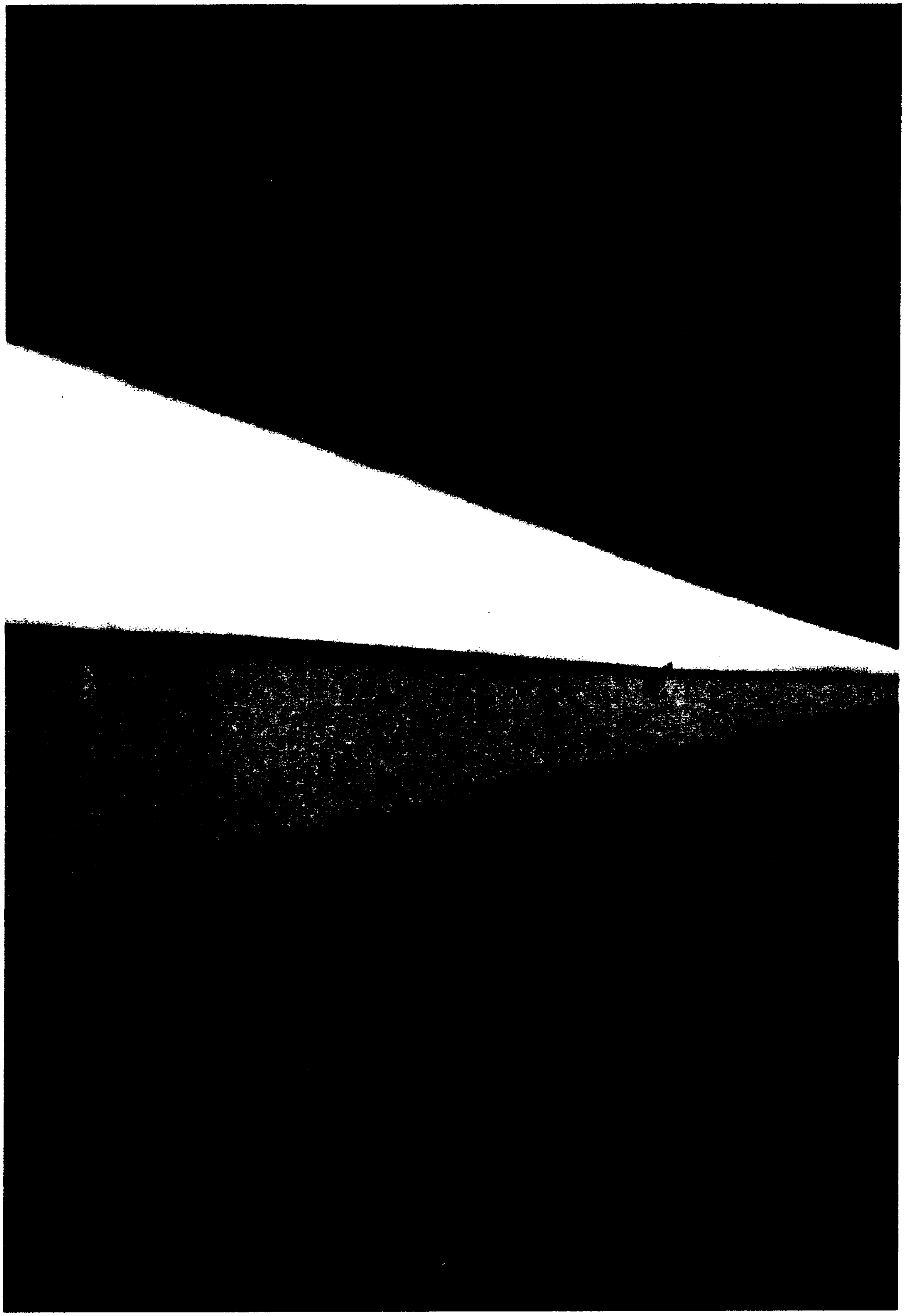

Uniformity Improvement
Swimwear Fabrics

- Average Uniformity Increased ~1 Unit
- Variance Dropped 50%

Recap of Expected Benefits

- Improved Uniformity, Quality, Consistency
- "Product-By-Process" Potential
- Reduced Mill Cost
- Shorter Dye Cycle
- More Environmentally Friendly

Summary

- Exciting Technology
- A New Tool for an Age-Old Task
- Fundamentals Are Sound
- Opportunity to Lower Cost and Add Value