AVINASH PRADIP MANIAN
Dye-Surfactant Interactions in Thermosol Dyeing
(Under the direction of J. Nolan Etters)

Thermosol dyeing is a continuous dyeing process for synthetic fibers and their blends. Various auxiliaries are used in thermosol dyeing, including buffers, antimigrants and wetting agents. Non-ionic surfactants are generally used as wetting agents.

It has been reported that some non-ionic surfactants cause a significant change in dye uptake in the thermosol process, the nature of which is the subject of some debate. In this study the nature of the influence that non-ionic surfactants exert on dye fixation in the thermosol process is studied.

It was shown that non-ionic surfactants may act as fixation accelerants in the thermosol process, accelerating the rate of dye dissolution in auxiliary melt, thereby increasing the overall rate of thermo-fixation dyeing. At high surfactant concentrations, dye retention in surfactant may result in surfactants exerting an adverse influence on dye fixation. Dye decomposition in surfactant may also play a significant role in determining the nature of non-ionic surfactant influence in thermo-fixation.

INDEX WORDS: Thermosol Dyeing, Polyester/Cotton Blends, Disperse Dyes, Non-ionic Surfactants, Wetting Agents, Tween® and Triton™ Surfactants.

DYE-SURFACTANT INTERACTIONS IN THERMOSOL DYEING

by

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CHAPTER 1

INTRODUCTION

Synthetic fibers find wide use in the textile industry either by themselves or in blends with natural fibers. Blend fabrics, of synthetic and natural fibers, are commonly used in apparel for reasons such as durability, comfort and easy care properties. The processing of large yardages of fabric is most economically accomplished by continuous processes. Continuous processing of textiles offers the advantages of high production, low staff requirements and low effluent toxicity [1]. Thermosol dyeing is a continuous dyeing process used in dyeing synthetic and blend fabrics, and is used especially for dyeing woven polyester/cotton blends, though with adequate care, the process can be used for dyeing knit goods as well [2-4].

One of the principal reasons for the popularity of the thermosol dyeing process is its production rate. It has been estimated that the output rate of a thermosol-dyeing unit is 30 m/min, which is high compared to the output rate of a jet-dyeing machine, which is 3 m/min. It is also estimated that the capital investment involved in setting up discontinuous dyeing systems is twice as high as that for continuous dyeing systems [5]. Other advantages of thermosol dyeing are: the process requires no carrier (a compound that increases the segmental mobility of the polymer chains in polyester fiber); it exhibits excellent dye utilization; the fabric is processed in open-width form, eliminating the formation of "rope marks" or wrinkles, and the heat setting history of the fabric has little effect on the fabric's dyeability [6].

The Thermosol Process

The principle of thermosol dyeing was demonstrated in 1947, when scientists at DuPont padded nylon and polyester fabrics with dye dispersions, dried them and heated them between two conventional flat irons for 5 seconds at 200°C [7,8]. After the fabrics were washed to remove excess dye, they were found to have been dyed in the shape of the iron. In subsequent mill trials, the process of thermosol dyeing was developed, incorporating new techniques such as using antimigrants (polymers to control dye migration), using infrared heaters for pre-drying, and developing speck-free vat and disperse dye pastes.

The commercial success of thermosol dyeing has been linked to that of polyester/cotton blends. Thermosol dyeing became a fully commercial process in 1958, when rainwear fabrics of polyester/cotton attained a significant share of the market, and enough yardages were processed to make a continuous dyeing process economically viable [8]. With the advent of permanent press finishes in the 1960's, the popularity of polyester/cotton blends grew even more and so did the popularity of the thermosol process as a continuous mode of dyeing.

In the commercial thermosol dyeing process, fabric is padded with liquor containing dye dispersion, dried, and then exposed to dry heat to fix the dye. Heating conditions vary from 5 to 90 seconds at 175-225°C, depending on heat source, fiber type and dye class. A schematic representation of the thermosol dyeing process is shown in Figure 1. Disperse and vat dyes can be used to dye the polyester component of polyester/cotton blends, though disperse dyes are more widely used since vat dyes produce only light to medium shades [9]. Dyeing both fiber components of polyester/cotton blends can be accomplished either in a single bath or a two bath process. Azoic, reactive and sulfur dyes are commonly used for dyeing cellulosic components of polyester/cotton blends [10].

The pad liquor contains the dye and auxiliaries to aid in the dyeing process. The auxiliaries added are wetting

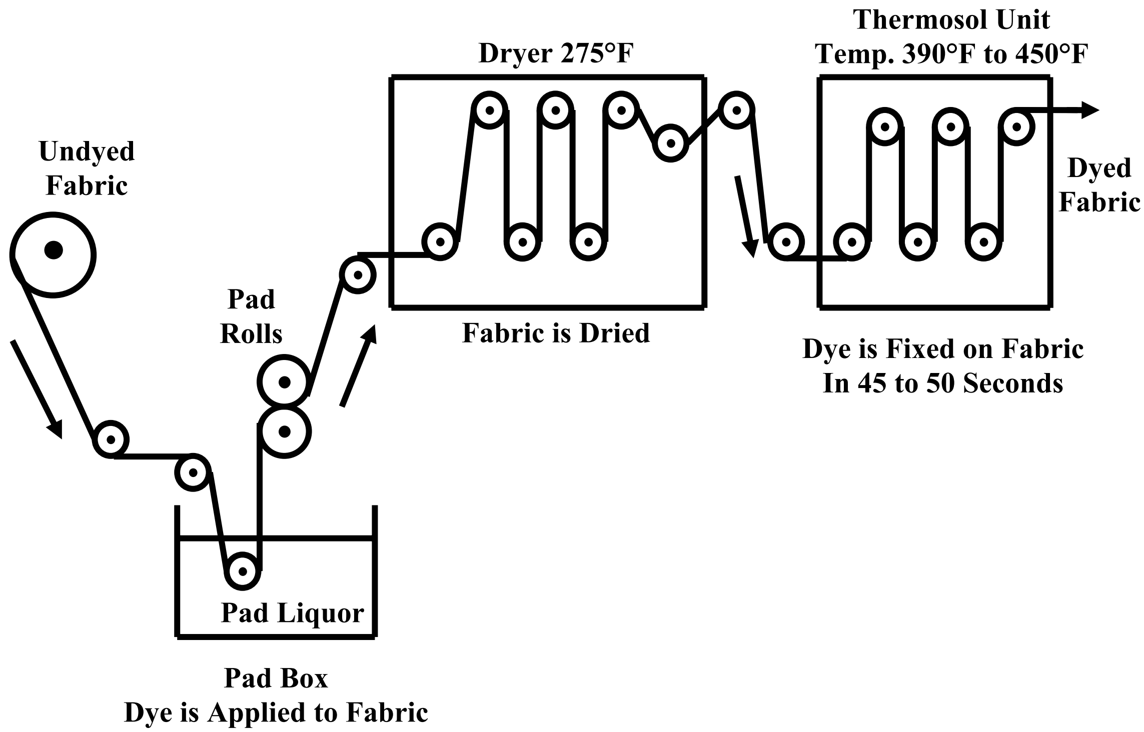


Figure 1. Schematic Representation of the Thermosol Process [8].

agents, pH buffers and migration repressors [3]. The presence of wetting agents ensures that all entrapped air in the fabric is removed and that fabric is uniformly wetted at a quicker rate. The pH of the pad bath, if alkaline, may cause ionization of disperse dyes that are susceptible to dissociation, hence buffers are used to maintain a pH of 4-6 in the pad bath. During the intermediate drying step, disperse dyes tend to exhibit particulate migration, resulting in non-uniform distribution of dye between various areas of the fabric, which leads to less than optimum values of dye fixation in the thermosol process. Migration repressors are agents that prevent particulate migration of disperse dyes during the intermediate drying stage. They are generally polyelectrolytes such as polyacrylic acid, sodium salt of alginic acid or carboxymethyl cellulose, which prevent migration by causing aggregation of disperse dyes within the fiber capillary network [11-14].

Wetting agents, which are generally non-ionic surfactants, appear to influence dye uptake in the thermosol process, though the nature of the influence does not appear to be uniform. Some reports indicate that non-ionic surfactants exhibit a selective restraining action on disperse dyes, that is evident above a certain minimum concentration of the surfactant [19,20]. Other reports maintain that non-ionic surfactants do not exert a detrimental effect on dye uptake [4,17], while some contend that the presence of non-ionic surfactants in the pad bath results in an increase in dye uptake [1].

There appears to be no consensus regarding the influence that non-ionic surfactants exert on dye uptake in the thermosol process. The aim of this study is to investigate the effect that non-ionic surfactants exert on dye uptake in the thermosol process.

Significance of Study

Though the influence of non-ionic surfactants on dye uptake in the thermosol process has been recognized, the issue has scarcely received any attention. It is not clear why this issue has not been investigated at much depth previously. One can speculate that probably dyers circumvented the problem by conducting trials to formulate an optimal combination of dyes and surfactants in pad baths that produced the desired depth of shade in dyeings without a significant increase in concomitant costs. As a result, the issue may not have received any importance, as an empirical solution is possible. Indeed some reports advise dyers to formulate pad baths using such trial and error methods [15,16,18].

Though it is possible to arrive at an optimal pad bath formulation by purely empirical methods, the knowledge of how each constituent functions and interacts with other constituents will be beneficial to the dyer. It is believed that the results of this investigation will assist the dyer in formulating pad baths more efficiently, without wastage of either time or materials.

The influx of imports has hurt the textile processing industry in the USA, leading to a decline in the use of the thermosol process, but thermosol dyeing is also used to dye other substrates such as workwear, home furnishings and industrial fabrics [19], and is used the world over to dye polyester seatbelts [8].

Processing of textiles began and flourished long before any degree of understanding about the science behind it was attained. Hence, in the early ages, textile processing was more an art form than a science. An increased understanding of textile science has helped the industry to design more effective and efficient processes, though even now textile processing may be considered an art form in some measure. It is hoped that the results of this investigation will contribute towards the science behind this art.

Purpose and Objectives

1. To determine if non-ionic surfactants influence dye uptake in the thermosol process.
2. To determine the nature of any influence observed.
3. To determine the mechanism behind any influence of non-ionic surfactants on dye uptake in the thermosol process.

Limitations of Study

1. The study was limited to one substrate, plain woven polyester cotton 50/50 blend. The effect of structural characteristics, such as yarn construction, twist and number, fabric count, fabric weave, fabric weight, and fabric thickness, on the results of the investigation was not considered.
2. The study was limited to three dyes, representative of the nitro, anthraquinonoid and azo chemical classes.
3. Commercial samples of dyes were used in the dyeing experiments. No control was exerted on dye formulation. Hence, the effect of additives, present in commercial dyestuffs, on the results of this experiment was not determined.
4. The non-ionic surfactants in this investigation were commercial samples, used in the form supplied by the manufacturers, without purification.

5. The surfactants used in this study may represent only a small subset of non-ionic surfactants used as wetting agents in commercial thermosol dyeing.

CHAPTER 2

REVIEW OF LITERATURE

To investigate how non-ionic surfactants may influence dye uptake in the thermosol process, one must first understand the mechanism of thermosol dyeing. The general belief is that dye is deposited on the fiber surface and that heat imparted to fabric during thermal fixation causes plasticization of polyester fibers causing the polymers to open up to allow diffusion of dye within the fiber structure, a phenomenon referred to as "solid-solution dyeing" [8,20].

The distribution of dye between fiber types in a polyester/cotton blend at various stages of the thermosol process is as follows: During the padding operation the cotton component takes up most of the liquor, since it is more hydrophilic [6-8,21]. In the dried fabric, the majority of the dye is found on the cotton component, at amounts disproportionate to the relative amount of cotton in the blend. After thermo-fixation the majority of the dye is found in polyester, in excess of amounts found on polyester after the drying operation. To illustrate the description given above, a schematic representation of the typical dye distribution on a 65/35 polyester/cotton blend fabric, at various stages of the thermosol process, is shown in Figure 2.

From the discussion above it is evident that there is dye transfer from cotton to polyester during thermo-fixation, the mechanism of which is relevant to this investigation.

Mechanism of Dye Transfer

The mechanism of dye transfer from cotton to polyester during thermo-fixation has been the subject of much discussion and there are three principal schools of thought regarding this phenomenon. The three mechanisms proposed are labeled as vapor transfer, contact transfer and medium transfer.

Vapor Transfer

According to the vapor transfer mechanism, dye transfer from cotton to polyester fibers occurs through the vapor phase [22-24]. Dye is believed to volatilize at the surfaces of the cellulose and polyester fibers and because of the higher substantivity of polyester for dye vapor, it moves from cotton to polyester, where it is adsorbed [22]. It is believed that dye adsorption occurs from unsaturated vapors and that the rate limiting step in dyeing kinetics

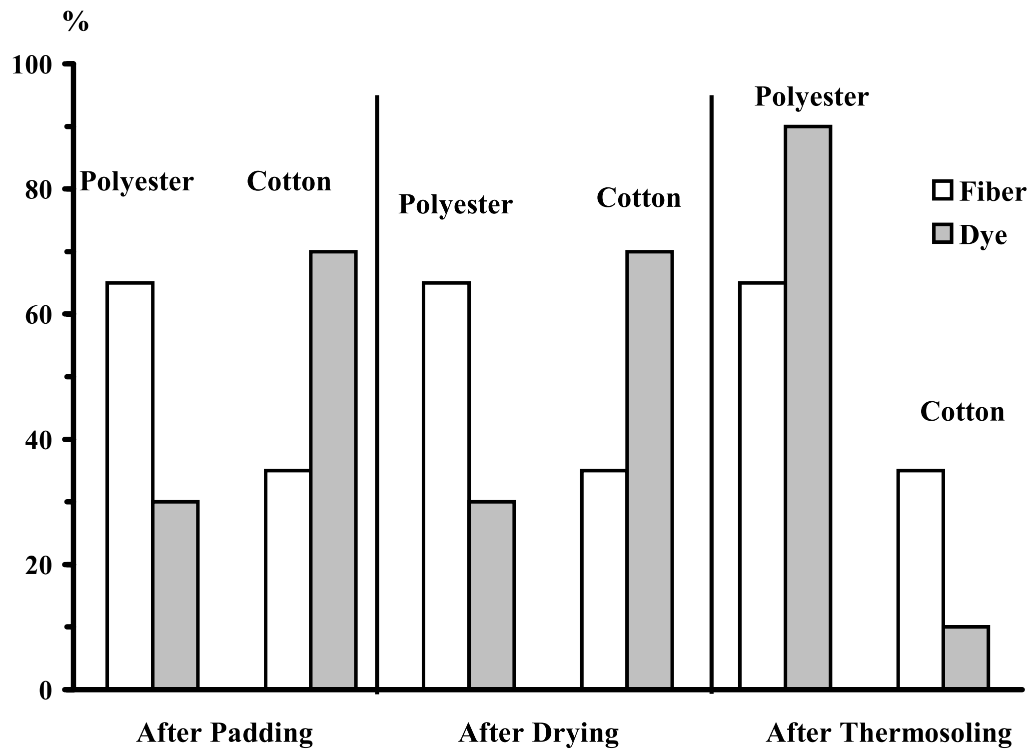


Figure 2. Schematic Representation of Disperse Dye Distribution on 65/35 Polyester/Cotton Fabric at Various Stages of the Thermosol Process [21].

is the rate of volatilization of dye molecules from the fabric surface [23,24].

Contact Transfer

According to the contact transfer mechanism, dye is transferred from cotton to polyester at points where the two fibers are in intimate contact with each other, though the physical form of the dye, during transfer, is unknown [22].

Medium Transfer

According to the medium transfer mechanism, the dyestuff padded onto the fabric dissolves in the melt of auxiliaries that forms and coats the fibers at thermo-fixation temperatures. Dye transfer to polyester is thought to occur from the dye solution in auxiliary melt [1,25]. The rate of dye fixation is thought to be determined by the rate of solution, i.e. the rate of dissolution of dye in the auxiliary melt [25]. Hence, to increase the rate of dyeing, compounds such as hydroxyethylated fats or fatty alcohols are sometimes added to the pad bath [13]. It is believed that these compounds, called as fixation accelerants, accelerate the dissolution of dye in auxiliary melt thereby increasing the overall rate of thermosol dyeing [25].

Some authors are of the view that dye transfer between cotton and polyester occurs by a combination of two or more of the mechanisms described above [26-28]. It is reported that factors such as fabric construction and sublimation tendency of dye are critical in dictating the mechanism of dye transfer between cotton and polyester fibers [27,28]. In spite of the uncertainty about the operative dyeing mechanism in thermosol dyeing, empirical rate equations have been derived and used to characterize dyeing kinetics [13,14,29,30].

Dye-Surfactant Interactions in Aqueous Media

Dye-surfactant interactions have been studied extensively in aqueous systems, in the context of exhaust dyeing processes. In exhaust dyeing, surfactants are used primarily as wetting, dispersing and leveling agents [31]. Surfactants maybe used in place of carrier solvents in polyester dyeing [32], and may also be used in dyeing natural fibers with some disperse dyes [33].

Generally, anionic surfactants are used as dispersing agents, e.g. in commercial disperse dye formulations. Micelles of anionic surfactants carry a negative charge on the surface and therefore are soluble in water. Non-ionic disperse dyes are dispersed by being preferentially solubilized in the micelle hydrocarbon core [34]. The micelles are believed to constantly open and close (i.e. re-form); thereby permitting dye molecules to come in contact with the fiber surface and diffuse into the fiber structure.

The leveling action of surfactants is made possible by one of two mechanisms [35-37]:

1. Surfactant molecules interact with dye molecules forming dye-surfactant complexes.
2. Surfactant molecules compete with dyes for available sites on the fiber.

Various forces govern interaction between dye and surfactant molecules. Coulombic forces operate between ionic dye and surfactant molecules, and take primacy over other forces. Non-coulombic hydrophobic forces, such as van der Waal's forces also exert a significant effect on dye-surfactant interactions, though these forces do not exceed coulombic forces [38-41]. The strength of hydrophobic interactions between dye and surfactant molecules depends on the alkyl chain length of surfactant and counter-ions present in the system [38]. Thus, increase in hydrophobicity of either dye or surfactant increases the propensity of dye-surfactant complex formation and the binding energy but if both dye and surfactant molecules possess identical charge, dye-surfactant interaction does not occur [40,41].

The nature of dye-surfactant complexes and their morphology is unclear. Some conclusions about the nature of anionic dye - non-ionic surfactant complexes are as follows [36,43]:

1. Free and bound dye molecules exist in equilibrium with each other.
2. Bound dye molecules may exist in two forms -
   - Surfactant molecules attached to dye anion.
   - Dye molecules solubilized in surfactant micelles.
3. Dye solubilization results from the following interactions -
   - Hydrophilic: The dye is included into the polyoxyethylene exterior of micelles.
   - Hydrophobic: The dye is incorporated into the hydrophobic core of surfactant micelles.
4. In non-ionic surfactants with the same hydrophobic group, as the ethylene oxide chain length decreases, its tendency to micellize increases and as dye hydrophobicity decreases, its solubilization tendency decreases.

5. Surfactants that have a high micellization tendency, characterized by short ethylene oxide chains, tend to promote dye diffusion within fibers.
6. There is no direct correlation between surfactant Critical Micelle Concentration (CMC) and stability of dye-surfactant complexes.

Dye solubility and the CMC of the dye liquor play a major role in dye uptake when non-ionic surfactants are used in the dyebath [43,44]. Addition of surfactant in concentrations below dye liquor CMC is found to influence neither rate of exhaustion nor dye uptake. If surfactants are added at concentrations greater than dye liquor CMC, both rate of exhaustion and dye uptake are found to decrease [43]. In a study on the effect of non-ionic surfactants in high-temperature (HT) polyester dyeing with disperse dyes, the dyeing process was examined microscopically and the following observations were reported [44]:

1. Dye deposition occurred on fiber in the temperature range between 60°C and 80°C, corresponding with high dye exhaustion.
2. The dye liquor turned cloudy at temperatures above 80°C (i.e. above the cloud point of the dye liquor),

and dye deposition on fiber was accompanied by the formation of visible colorless droplets.

3. Dissolution of dye from liquor into surfactant droplets occurred at about 85°C, coloring the surfactant droplets. Dye deposits fell away from the fiber surface, corresponding with a decrease in dye uptake.
4. With increase in temperature to about 100°C, dyed droplets accumulated near the fiber in a dynamic process with deposited droplets moving away from the fiber, and other droplets settling on the fiber.
5. At a temperature of 110°C, the dyed droplets began to spread on the fiber forming a discontinuous film-like covering on the fiber surface.
6. At temperatures between 120°C and 130°C, fibers were dyed from either the surfactant droplets or surfactant film.

Figure 3 is a schematic representation of the observations described above and numbers in the illustration correspond to the steps listed above.

In the experiment discussed above, the temperature at which surfactant droplets were formed corresponded with the dye liquor cloud point. Aqueous non-ionic surfactant solutions, at concentrations greater than surfactant CMC,

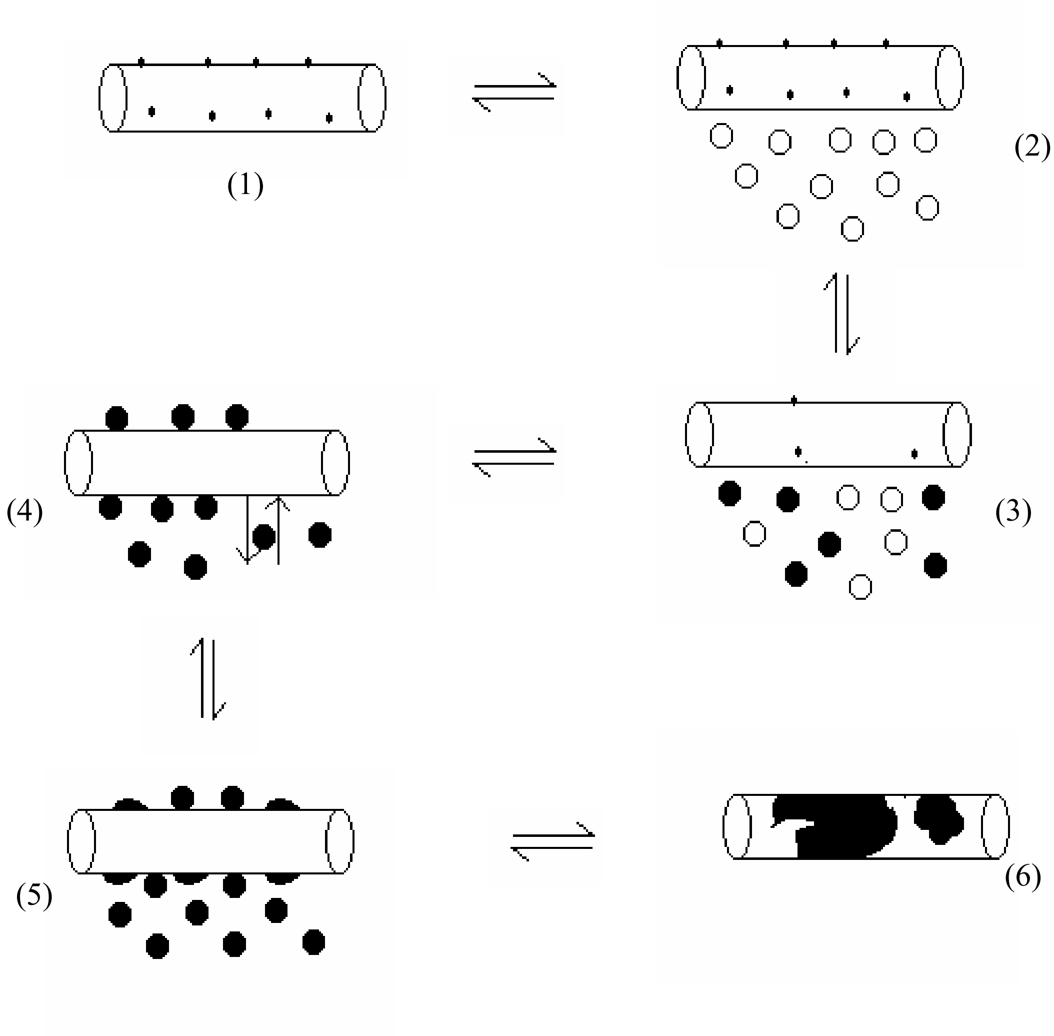


Figure 3. Schematic Representation of Dye-Surfactant Interaction in Polyester High-Temperature Dyeing [44].

turn turbid upon heating, at temperatures that are product specific. The temperature at which turbidity first becomes apparent is called the cloud point of the surfactant [45]. Cloud points change with addition of dyestuffs and other auxiliaries, and no effect on total disperse dye solubility is observed with increasing surfactant concentration above cloud point temperatures [44]. Multi-phase systems develop in surfactant solutions at temperatures above cloud point, consisting of an aqueous phase with monomolecularly dissolved surfactant molecules and a few micelles, and a surfactant phase low in water content. Due to high dye solubility in surfactant, the largest part of dye is present in the surfactant phase.

By altering the cloud point of dye liquor, either by using different non-ionic surfactants or by adding an anionic surfactant, disperse dye solubilization could be altered. Additions of anionic surfactant in amounts just necessary to increase the cloud point produced no significant change in dye solubilization, but addition of excess anionic surfactant resulted in decreased dye solubilization and increased dye uptake. Increased dye solubilization favors dye retention in liquor and as dye solubilization increases, its effect on dyeing becomes more pronounced. Increased particle size due to dye solubilization could be also be responsible for reduced dye uptake, but the solvation effect of non-ionic surfactants on dye particles is favored as the reason for decrease in dye uptake [44].

Thus, decreased rate of dyeing and reduced dye uptake were attributed to dye retention in liquor due to increased dye solubilization in surfactant micelles that are formed above dye liquor CMC. Reduction in dye uptake was found to be directly proportional to increasing surfactant concentration and increasing dye solubility. No evidence of surfactant diffusion into fibers was detected.

Similar observations regarding decrease in dye uptake due to non-ionic surfactants in HT polyester dyeing have been reported elsewhere [46,47]. The reasons cited for decrease in dye uptake include dye aggregation due to cloud point formation and also non-ionic surfactant induced dye crystallization. The retardation effect of non-ionic surfactants on dyeing was reported to be highly dye-specific [47].

In apparent contradiction to the reports mentioned above, some authors believe that non-ionic surfactants increase the rate of dyeing of disperse dyes at temperatures below normal boiling point, though the mode of action is not elaborated [48]. Even so, they maintain that dye uptake is detrimentally affected at temperatures above surfactant cloud point and hence recommend the use of products with high cloud point temperatures.

Dye-surfactant interactions have been reported to occur at surfactant concentrations below its CMC [49]. In some cases, surfactants have been found to associate with themselves far below CMC concentrations, leading to formation of surfactant dimers. It is thought that dimerization is favored by reduced interfacial energy, and expanded chain length but and is disfavored by repulsion of head charges (in case of ionic surfactants). Dyes too are thought to aggregate in a stepwise manner, i.e. formation of dimers, followed by trimers, polymers and finally colloidal particles. The propensity of dyes to aggregate is believed to depend on the balance between the hydrophobic and hydrophilic tendencies of the dye. If a surfactant is added to dye dispersion or solution, at sub-micellar concentrations, both surfactant monomers and dye aggregates may interact forming mixed aggregates, far below the surfactant CMC. Once the CMC of the surfactant is reached or surpassed, it is thought that dye molecules are incorporated into surfactant micelles.

Polyester fabric was treated with non-ionic surfactant solutions to try and alter its wicking and absorbency properties [50]. A Langmuir type adsorption of non-ionic surfactants onto polyester fiber surfaces was observed with the adsorption plateau occurring at surfactant CMC. Surfactant adsorption onto polyester rendered the fibers more hydrophilic. It was observed that the surface properties of polyester fibers could be changed and made more hydrophilic by the application of a topical finish resulting in a marked effect on water retention and solution retention values of the fibers. Similar effects were not observed when the fibers were left unchanged and non-ionic surfactants were used to lower the surface tension of water.

Dye-Surfactant Interactions in Thermosol Dyeing

Interactions between dye and surfactant under relatively moisture-free conditions, which prevail in the thermo-fixation step of thermosol dyeing, have not received the same degree of attention that dye-surfactant interactions in aqueous media have.

In a study on the effect of non-ionic surfactants in thermosol dyeing, it was concluded that non-ionic surfactants cause a decrease in dye uptake [51]. It is believed that a dye-surfactant complex is formed causing a decrease in dye surface area, which acts hinders dye vaporization leading to decrease in dye uptake. Other authors have also expressed a similar view [16].

Hildebrand and Marschner [1] report that non-ionic surfactants enhance dye uptake in thermosol dyeing. They believe that auxiliary agents, including non-ionic surfactants, liquefy at temperatures of 180°-230°C and coat the fiber surface as a homogenous film. Disperse dyes dissolve in auxiliary melt and are present at higher concentrations at the fiber surface, resulting in a higher gradient for dye diffusion as compared to the situation where auxiliary agents are absent. In the authors' opinion dissolution of dye in liquefied auxiliary melt prevents the formation of localized excess concentrations of dye on the fiber surface that are a hindrance to dye uptake in the thermosol process.

In a different study, it was observed that non-ionic surfactants accelerate the rate of dyeing and intensify dye fixation in disperse dyeing of polyester by superheated steam or hot air [52]. The behavior of disperse dye in non-ionic surfactant containing a little water was related to the amount of water. The rate of dye diffusion in fiber and its partition coefficient increased with the amount of water, with a concurrent decrease in solubility of dye in surfactant.

Fox et al. [16] attribute any increase in dye uptake in thermosol dyeing, upon addition of wetting agents, to an increase in pick up from the pad bath. They stipulated that well-prepared and absorbent fabrics do not show increased pick up upon addition of wetting agents to the pad bath, instead the pick up is usually lower. Hence, they stated, any improvement in dye pickup from pad bath could be traced back to deficiencies in preparatory processing. Working on this premise, Etters [15] advised the inclusion of polyacrylamide in the pad bath, as it would assist under-prepared fabrics to achieve pick up values. Polyacrylamide, it was stated, functions by changing the pad liquor rheology, and its inclusion would result in more of the pad liquor being dragged along with the fabric.

Summary

Dye-surfactant interactions in aqueous media and their influence on dye uptake in exhaust dyeing procedures have been studied extensively and are well characterized. Dye fixation in the thermosol process occurs under relatively moisture-free conditions as compared to exhaust dyeing, and dye-surfactant interactions under these conditions have received little attention. Among published reports on the topic, there appears a lack of consensus regarding the nature of dye-surfactant interactions in thermosol dyeing and the effect that they exert on dye uptake in the thermosol process. In order to better characterize the thermosol dyeing process, it is important to understand the influence that non-ionic surfactants exert on dye uptake in the thermosol process.

CHAPTER 2

MATERIALS AND METHODS

Materials

Fabrics

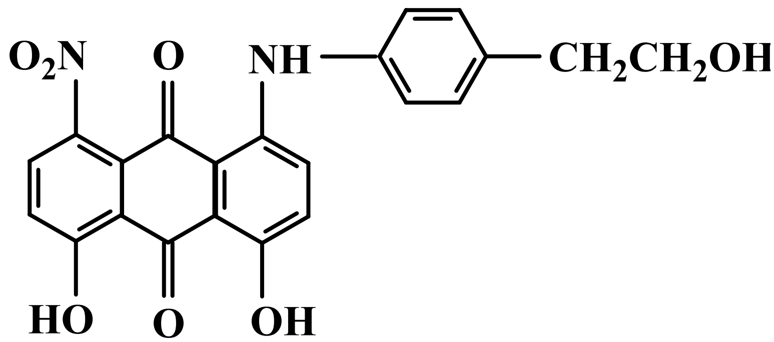
The fabrics used in this investigation are listed below. All fabrics were used as they were supplied, without scouring or cleaning.

1. Polyester/Cotton 50/50 Print Cloth, Bleached, Style #7426, Testfabrics, Inc.
2. Bleached Cotton, Print Cloth, Style # 400, Testfabrics, Inc.
3. Polyester Taffeta, Style # 738, Testfabrics, Inc.

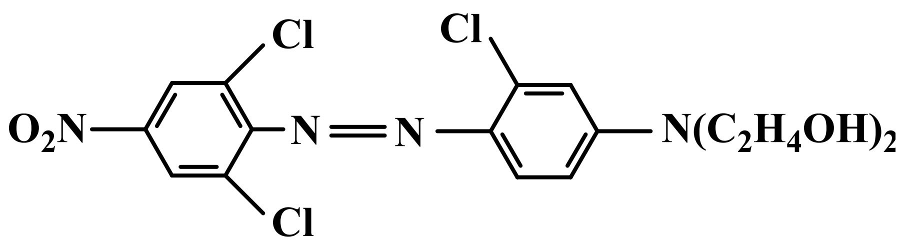
Dyes

The dyes used in this investigation are listed below and their chemical structures are given in Figure 4. Commercial samples of these dyes, as supplied by the manufacturer, were used in the dyeing experiments.

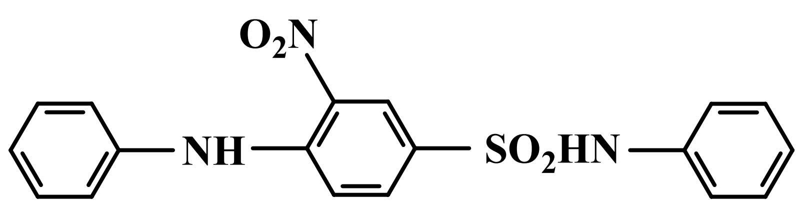
1. C.I. Disperse Blue 27 (Terasil Blue GLF) - Ciba Specialty Chemicals.
2. C.I. Disperse Brown 1 (Terasil Brown P-3R) - Ciba Specialty Chemicals.



C.I. Disperse Blue 27



C.I. Disperse Brown 1



C.I. Disperse Yellow 42

Figure 4. Chemical Structures of Dyes used in this Investigation.

3. C.I. Disperse Yellow 42 (Terasil Yellow GWL) - Ciba Specialty Chemicals.

Antimigrant

The antimigrant used in this investigation is a concentrated sodium alginate based compound, Antimigrant C-45, supplied by Yorkshire Pat-Chem, Inc. The antimigrant was used as supplied by the manufacturer.

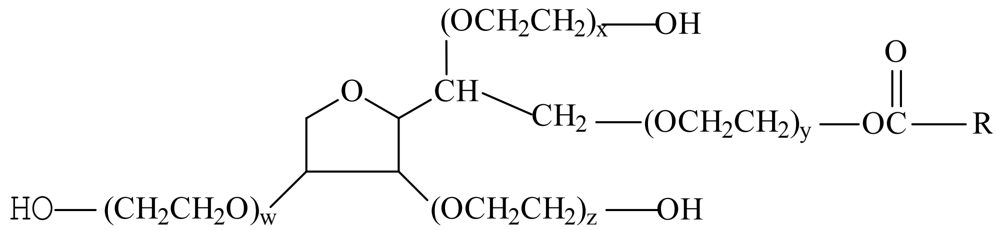
Surfactants

The surfactants used in this investigation are listed below and their chemical structures are shown in Figures 5 and 6. The surfactants were used as supplied by the manufacturers.

1. Tween® 20 - Uniqema
2. Tween® 40 - Uniqema
3. Triton™ X-100 - Union Carbide
4. Triton™ X-102 - Union Carbide
5. Triton™ X-305 (70% Actives) - Union Carbide

Thermofixation Apparatus

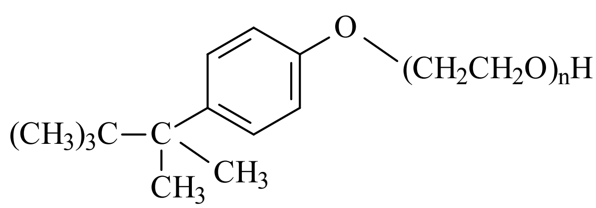
A Roaches Contact Heat Test Unit was used for thermofixation of padded samples. The instrument, Figure 7, consists of two hot plates each of which can be heated up to 450°F independent of the other, with an error margin of ± 2°F. In this investigation, both hot plates were heated to the desired fixation temperature. The instrument



W+X+Y+Z = % EO Groups in esterified Polyoxyethylene

Surfactant	**R**	**% EO Groups in Esterified Polyoxythelene**
Tween® 20	$-C_{11}H_{23}$	20%
Tween® 40	$-C_{16}H_{33}$	20%

Figure 5. Chemical Structure of Tween® Surfactants [53, 54].



Surfactant	**n (Number of EO Groups)**
Triton™ X-100	9-10
Triton™ X-102	12-13
Triton™ X-305	30

Figure 6. Chemical Structure of Triton™ Surfactants [53-55].

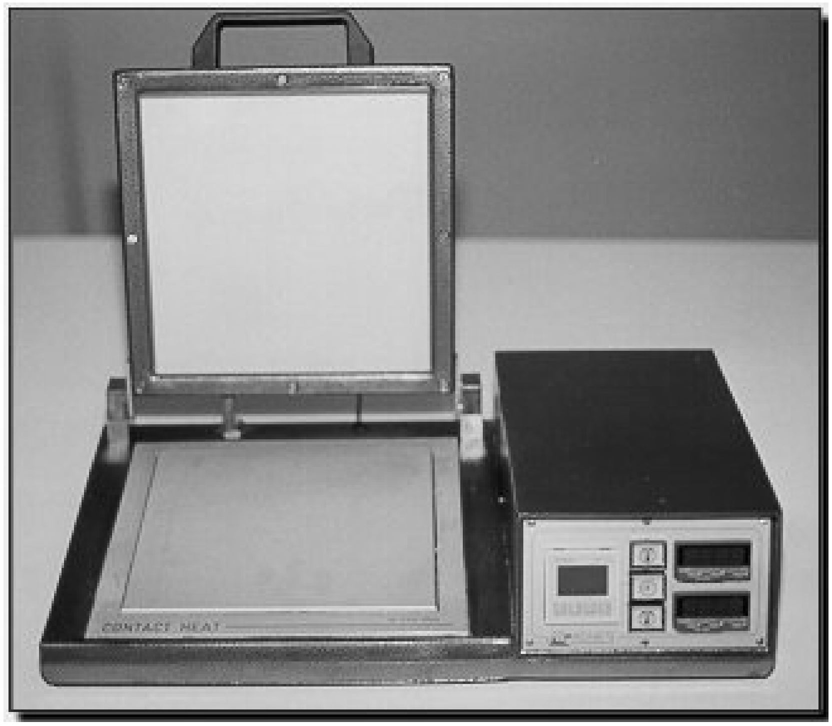


Figure 7. Photograph of Thermo-fixation Apparatus [56].

also contains a timer by which duration of fixation can be controlled.

Padder

A Roaches Model BVHP Vertical Padder was used for all padding operations. The nip pressure was maintained at 450 kPa.

Spectrophotometer

A Jasco V-570 UV-VIS Spectrophotometer was used for all spectrophotometric measurements.

Reagents

The following reagents were used without further purification.

1. N,N'-Dimethylformamide (DMF) – Spectrophotometric grade, J.T. Baker
2. Methanol - HPLC Grade, Fischer Scientific
3. Acetic Acid - Glacial, J.T. Baker

Methods

Critical Micelle Concentration (CMC) of Surfactants

The critical micelle concentrations (CMC) of surfactants used in this investigation were determined by measuring the apparent surface tension values of surfactant solutions in deionized water, at concentrations ranging from 1×10^{-4} g/L to 10 g/L, and plotting them against the logarithm (to the base 10) of surfactant concentration (wt%). The surface tension method is commonly used for determining surfactant CMC values [57].

All surface tension measurements were carried out on a Fisher Autotensiomat, operating on the du Nuoy platinum ring principle according to the method described in ASTM D 1331-89 [58], except that apparent surface tension values were used. The specifications used in the procedure are as follows.

- Solution Temperature: 25°C
- Elevator Speed: 0.05 in./min
- Chart Speed: 2 cm/min
- Pin input: 1 mV

Dye Isolation

C.I. Disperse Yellow 42 was obtained in press-cake form from Ciba Specialty Chemicals. The press-cake was dried at 60°C until a constant weight of solids was obtained. The dried press-cake was used as "isolated dye" in all solubilization experiments.

Press-cake forms of C.I. Disperse Blue 27 and C.I. Disperse Brown 1 could not be obtained, hence dyes were isolated from commercial samples. The isolation process began with a Soxhlet extraction of the commercial dyes in methanol. The filtrate obtained from the extraction process was then heated to boil off excess solvent until a viscous paste remained. Deionized water was added to the viscous paste, causing the pure dye to precipitate, and this mixture was stirred at room temperature for 60±5 min. The mixture was then filtered through two layers of Whatman Filter paper No. 1. The residue was washed repeatedly with deionized water until the washings were colorless. The residue was then dried until a constant weight of solids was obtained, and used as "isolated dye" in dye solubilization experiments.

Dye Solubilization

Aqueous solutions of each surfactant were prepared, in concentrations ranging from below CMC levels to above CMC levels. To 100 mL of these solutions, 0.2 g of isolated dye was added. The dye-surfactant mixtures were then gently stirred in a shaker bath at a temperature of 25°C, until the surfactant liquor was saturated with the dye. It was determined that 16 hrs were required for dye saturation of all surfactant liquors except for solutions of Tween® 40, which required 45 hours.

The dye-surfactant mixtures were then centrifuged, and the amount of dye solubilized in the surfactant liquor was determined by measuring the electronic absorbance spectra of the supernatant solutions in the spectrophotometer. Plots of supernatant solutions absorbance, at wavelengths of maximum absorbance, against surfactant concentration were used to determine changes in dye solubilization with changes in surfactant concentration.

Thermal Fixation

Polyester/Cotton fabric strips (20 X 5 cm) were padded from pad liquors containing dye, antimigrant and surfactant. The formulation of the pad liquors is described in Table 1. Acetic acid (56%) was added to all pad formulations to adjust the liquor pH to 5.5 - 6.0.

In all, 21 pad liquors were prepared, each differing in surfactant and its concentration in the liquor. Control samples were obtained by padding fabric strips from liquors that contained all other components except surfactant. Three fabric strips were padded from each pad formulation and all fabric strips were then line-dried overnight.

Each padded sample, after being dried, was cut into four pieces of which one was retained without thermal fixation, to serve as the "unfixed" sample. The three pieces that remained were then subjected to thermal fixation, each at one of three temperatures listed in Table 2. The thermo-fixation apparatus was calibrated in the Fahrenheit scale and hence fixation temperatures are reported in Fahrenheit units. The duration of thermal fixation at each instance was 15 seconds.

Table 1. Pad Bath Formulations

Component	Concentration (g/L)
Dye	10.0
Antimigrant	20.0
Surfactant:	
Tween® 20	0.01, 0.1, 0.5, 1.0
Tween® 40	0.5, 1.0, 5.0, 10.0
Triton™ X-100	0.01, 0.1, 0.5, 1.0
Triton™ X-102	0.01, 0.1, 0.5, 1.0
Triton™ X-305	0.01, 0.25, 0.5, 1.0

Table 2. Fixation Temperatures

Dye	Fixation Temperatures (°F)
C.I. Disperse Blue 27	375, 400, 425
C.I. Disperse Brown 1	350, 375, 400
C.I. Disperse Yellow 42	350, 375, 400

Dye Fixation Measurement

Dye fixation was estimated by one of two methods:

Indirect Method:

Dye fixation was estimated from the difference between the amount of dye in the sample after padding, i.e. the amount of dye in the control sample, and the amount of dye that remained unfixed, on the sample surface, after the thermal fixation process. The control and thermo-fixed samples were subjected to dye extraction by solvent at room temperature for 60 min. The following equation was used to calculate percent dye fixation:

$$C_P = \left(\frac{C_T - C_U}{C_T}\right) X100 \qquad \text{Equation 1}$$

Where:

C_P = Percent dye fixed on the sample

C_T = Dye content of unfixed (control) sample, g of Dye/100 g of Fabric

C_U = Surface (unfixed) dye content of sample after thermal fixation, g of Dye/100 g of Fabric

Direct Method:

Dye fixation was estimated from the amount of dye fixed in the sample expressed as a percentage of the amount of dye padded onto the fabric in the padding operation, i.e. the amount of dye in the control sample. The padded samples that were subjected to thermal fixation were soaped in a solution of 2 g/L Triton™ X-100 at 60°C for 30 min, rinsed in deionized water, and then dried. The soaped and dried samples were then subjected to dye extraction in solvent at 120°C for 3 min. Dye extractions from control (unfixed) samples were carried out by the method described in the previous section. The following equation was used to calculate percent fixation:

$$C_P = \left(\frac{C_F}{C_T}\right) X100 \qquad \text{Equation 2}$$

Where:

C_P = Percent dye fixed on the sample

C_T = Dye content of unfixed (control) sample, g of Dye/100 g of Fabric

C_F = Dye content of sample after thermal fixation and rinsing, g of Dye/100 g of Fabric

<u>Solvent</u>:

A mixture of N,N'-Dimethylformamide (DMF) and deionized water, at a volume ratio of 80:20, was used as the solvent to extract dye from polyester/cotton blends. The pH of the mixture was adjusted to 6.5 - 7.0 with acetic acid (56%). DMF is used to extract unfixed surface dye from dyed samples at room temperature [59,60]. If the dyed fabric contains dye dispersants or pad-bath thickeners on its surface then water is added to DMF to remove water-soluble dyeing auxiliaries and electrolytes from the fiber along with the unfixed surface dye, and to suppress light scattering and reduce aggregation [61]. There may be a change in solvent pH upon heating due to tautomerism and hydrogen bonding that may interfere with the absorbance spectra of the dye solution in DMF and hence an acid is added to the solvent to stabilize its pH.

The amount of dye extracted from dyed or padded fabric was determined quantitatively in the spectrophotometer, using a calibration curve constructed for each dye over a range of isolated dye concentrations in solvent. The wavelength at which absorbance of dye extracts were measured was the wavelength of maximum absorbance for the dye in solvent. The wavelengths of maximum absorbance for C.I. Disperse Blue 27, C.I. Disperse Brown 1 and C.I. Disperse Yellow 42 in DMF-Water (80:20) were 609, 454 and 419 nm, respectively.

Dye fixation for the yellow dye, C.I. Disperse Yellow 42, was estimated by the indirect method, because the absorbance spectrum of the yellow dye in solvent was observed to change when the solvent was heated. Dye fixation for the other two dyes, C.I. Disperse Blue 27 and C.I. Disperse Brown 1, was estimated by the direct method.

Dye Vaporization Measurement

The extent of dye vaporization under conditions of thermal fixation was measured by the following method: Strips of cotton fabric (20 X 5 cm) were padded using pad liquors with the same formulations that were used to pad polyester/cotton strips, and then dried. A sandwich was prepared by stapling together a layer of padded cotton strip, two layers of untreated cotton fabric and a layer of untreated polyester fabric, in that order. The untreated cotton strips in the middle had 5/8 in. holes punched out from their center and were aligned so that the polyester was directly exposed to the padded cotton through the holes. There was no physical contact between the polyester and the padded cotton. Three sandwiches of this type were prepared from each padded cotton strip, and each sandwich was then subjected to thermal fixation for 30 seconds in the Roaches Contact Heat test Unit at the temperatures listed in Table 2. A schematic representation of the experimental procedure is given in Figure 8.

Thermal fixation of these sandwiches resulted in the dyeing of polyester only in the area directly exposed to the padded cotton strip. Since the absence of physical contact between padded cotton and polyester was ensured,

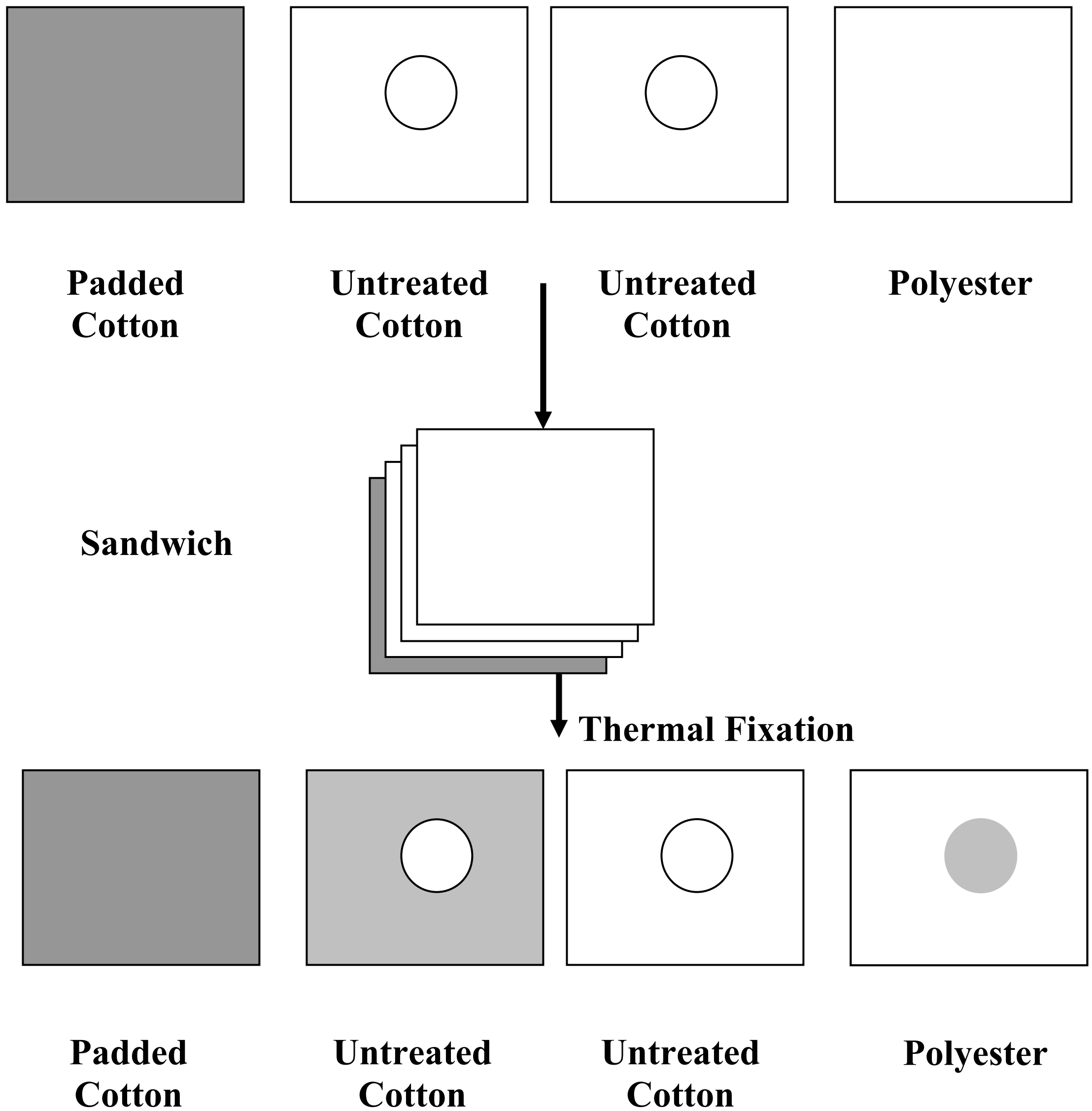


Figure 8. Schematic Representation of Experiment for Measuring Extent of Dye Vaporization.

the dyeing of polyester could be attributed to vapor transfer of dye from padded cotton to polyester. The intensity of color that resulted on polyester could then be used as a measure of the vaporization tendency of the dye.

In this experiment the amount of dye transfer to polyester was very little, making it difficult to conduct a quantitative estimation of dye content by solvent extraction of dye. With small amounts of dye, the process of dye extraction in solvent may result in either a partial or complete destruction of dye leading to erroneous results. Many test methods for colorfastness, such as those for testing colorfastness to heat [62,63], laundering [64] and sublimation [65], make use of visual evaluations to arrive at dye fastness ratings. In these test methods, fastness ratings are assigned after comparing the color intensity of test samples with a standard, called the gray scale. In this experiment a visual comparison of color intensity, between dyed polyester samples, was conducted to qualitatively estimate the effect of surfactants and their concentrations in pad bath on the tendency of dyes to vaporize.

A similar method is reported in literature to evaluate the vaporization tendency of dye [66]. In this method a tin can is used as vaporization vessel, with dye placed on the base and a polyester film placed in the cover as a liner. This assembly is then heated in an oven at the desired temperature for the desired time and the dye absorbed in the polyester film is used as an indicator of the vaporization tendency of the dye. It was reported that the height of the can did not affect the color absorbed in the film, but the time period of heating appeared to affect the color absorbed in polyester film for some dyes.

Dye Decomposition

The influence of surfactant on dye decomposition was evaluated as follows: 0.0010–0.0020 g of isolated dye was dissolved in approximately 20 mL of surfactant at room temperature. A part of each dye solution in surfactant was retained without further treatment and the remainder was heated for 60 minutes at 98-100°C in a water bath and then allowed to cool to room temperature. The part of dye solution that was not heated served as the control. The absorbance spectra of both the control and heated dye solutions were measured in the spectrophotometer.

The area under the curve of an electronic absorbance spectrum may be used as a quantitative measure of the amount of absorbing species in solution. The absorbance spectra of the control and heated dye solutions were compared to evaluate dye decomposition in surfactant. More specifically, the areas under the absorbance curves, over a specific wavelength range, were compared. The following equation was used to calculate dye decomposition in surfactant:

$$D = \left(\frac{A_C - A_H}{A_C}\right) X100 \qquad \text{Equation 3}$$

Where:

D = Dye decomposition, %.

A_C = Area under absorbance curve of control dye solution, over a specific wavelength range.

A_H = Area under absorbance curve of heated dye solution, over the wavelength range used in A_C.

Statistical Analyses

All statistical analyses were carried out, at a 0.05 level of significance, using the statistical software SAS®. To simplify the SAS® program, numerical codes were used to denote surfactant type, surfactant concentration and fixation temperature. The numerical codes used in the statistical analyses are listed in Table 3.

Table 3. Numerical Codes Used in Statistical Analyses.

Factor			
Surfactant Type	**Surfactant Concentration (g/L)**	**Fixation Temperature (°C)**	**Code**
Tween® 20	0	350/375*	1
Tween® 40	0.01	375/400*	2
Triton™ X-100	0.1	400/425*	3
Triton™ X-102	0.25		4
Triton™ X-305	0.5		5
	1.0		6
	5.0		7
	10.0		8

* Fixation temperatures used for C.I. Disperse Blue 27

CHAPTER 4

RESULTS AND DISCUSSION

Critical Micelle Concentration of Surfactants

The change in surface tension of surfactant solutions with change in surfactant concentration is plotted in Figure 9. The experimental values plotted are the mean values of observations from three repetitive experiments.

The surface tension values decrease with increasing surfactant concentration up to a certain point beyond which increasing surfactant concentration does not bring about any change in surface tension. The surfactant concentration at which the surface tension values of surfactant solutions begin to assume a constant value is the critical micelle concentration of the surfactant. The CMC values of the surfactants, as evaluated in this investigation, are listed in Table 4.

Dye Solubilization

Solubilization maybe defined as "a particular mode of bringing into solution substances that are otherwise insoluble in a given medium, involving the previous presence of a colloidal solution whose particles take up

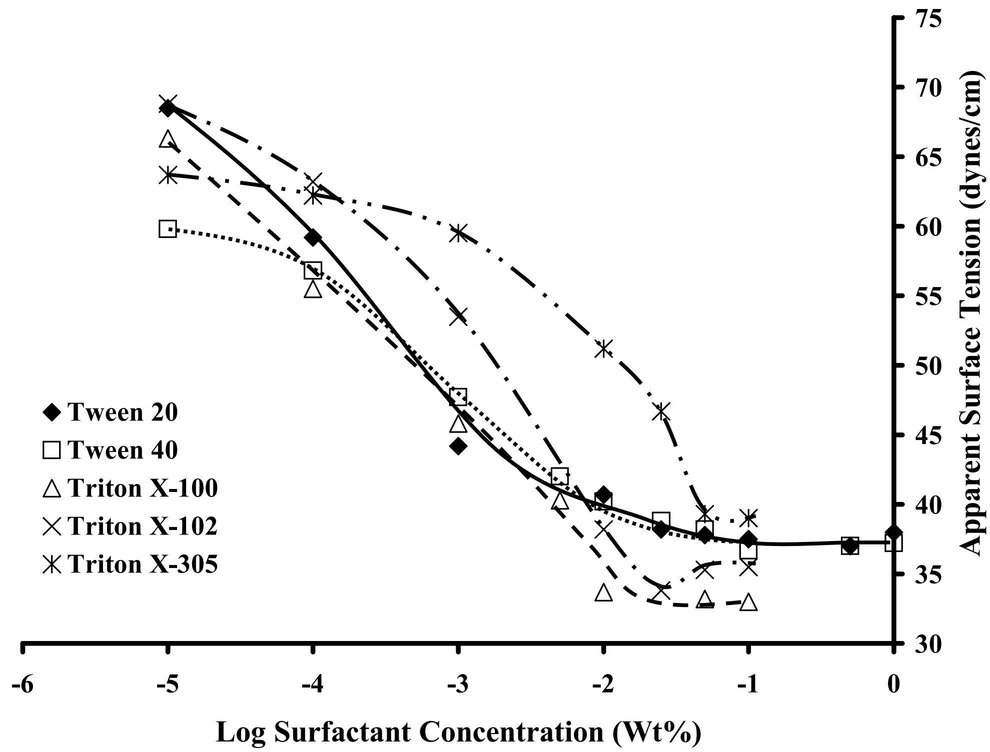


Figure 9. Change in Surface Tension of Surfactant Solutions with Change in Surfactant Concentration.

Table 4. Critical Micelle Concentrations of Surfactants.

Surfactant	**CMC (g/L)**
Tween® 20	0.25
Tween® 40	1.00
Triton™ X-100	0.10
Triton™ X-102	0.25
Triton™ X-305	0.50

and incorporate within and upon themselves the otherwise insoluble material" [67]. The effect of surfactant concentration on dye solubilization is shown in Figures 10-14.

The electronic absorbance spectra of dye solutions changed with increasing surfactant concentration. The wavelength of maximum absorbance (λ_{max}) was observed to change until a particular surfactant concentration was reached and beyond that it did not change. The nature of change in λ_{max} was different for the three dyes; increase in λ_{max} in case of blue and yellow dye solutions and a decrease in λ_{max} in brown dye solutions. The change in absorbance spectra of dye can be attributed to change in the immediate environment of dye molecules, from a polar medium to a non-polar medium, as they get solubilized. Dye solubilization in Triton™ X-305 did not bring about a significant change in λ_{max} in the electronic absorbance spectra of the dye solutions.

Upon examining the dye solubilization curves, the general trend observed is that with increasing surfactant concentration, dye solubilization increases rapidly at first, followed by a more gradual increase until the CMC of

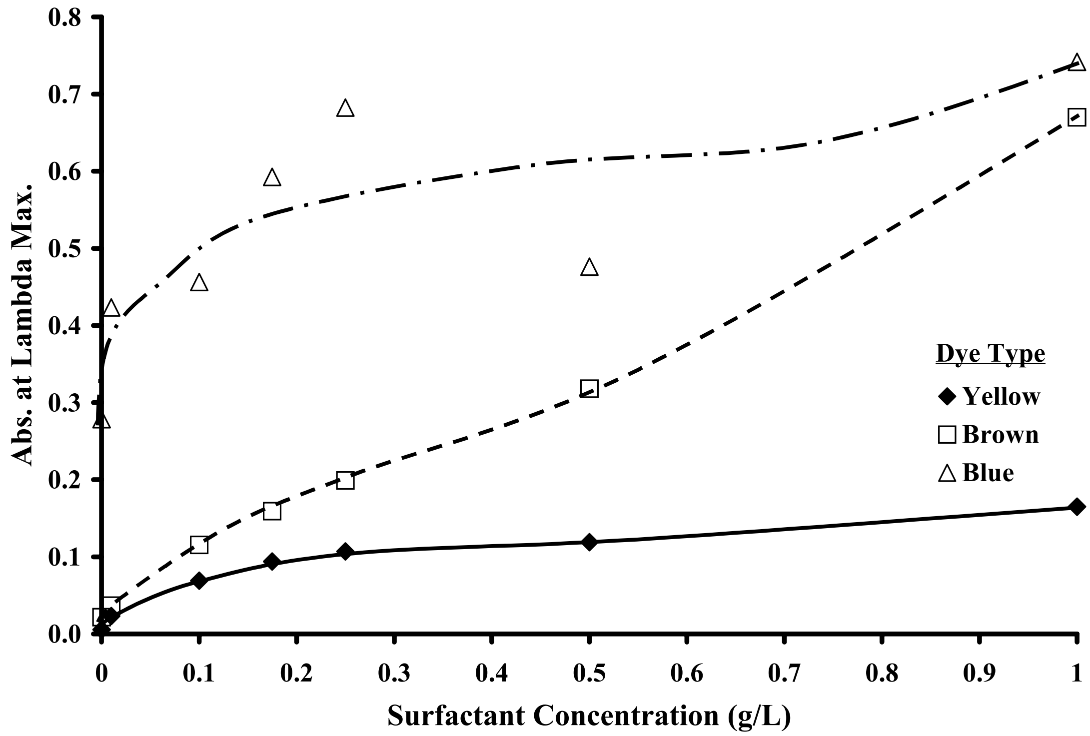


Figure 10. Dye Solubilization in Tween® 20.

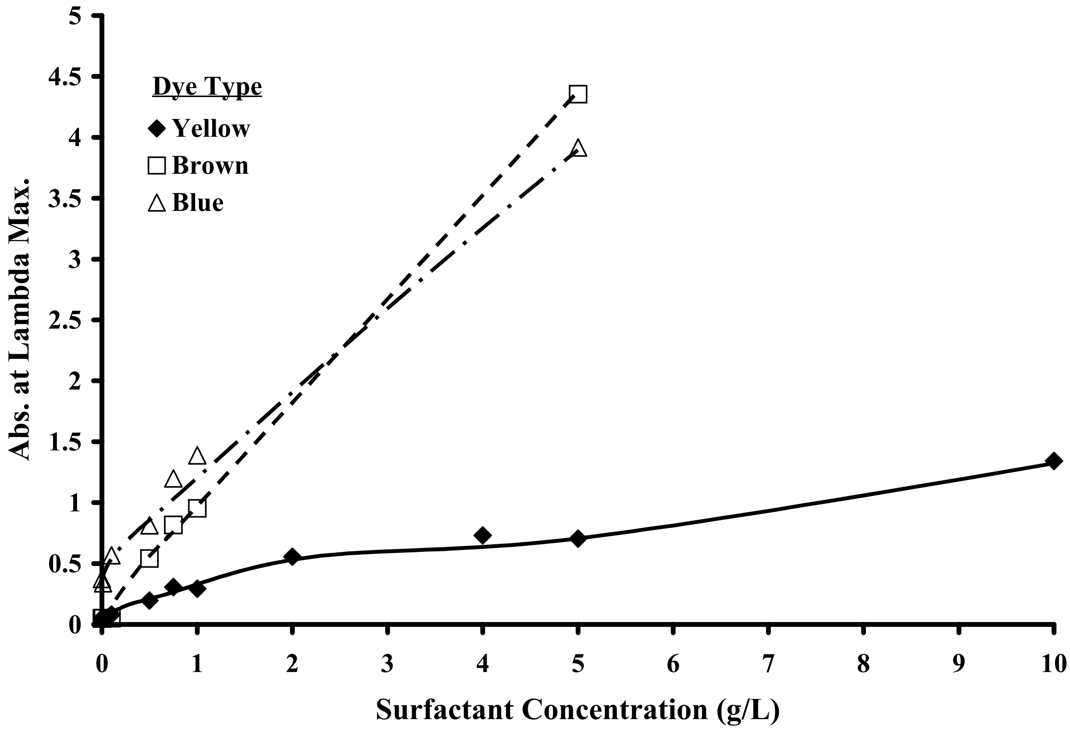


Figure 11. Dye Solubilization in Tween® 40.

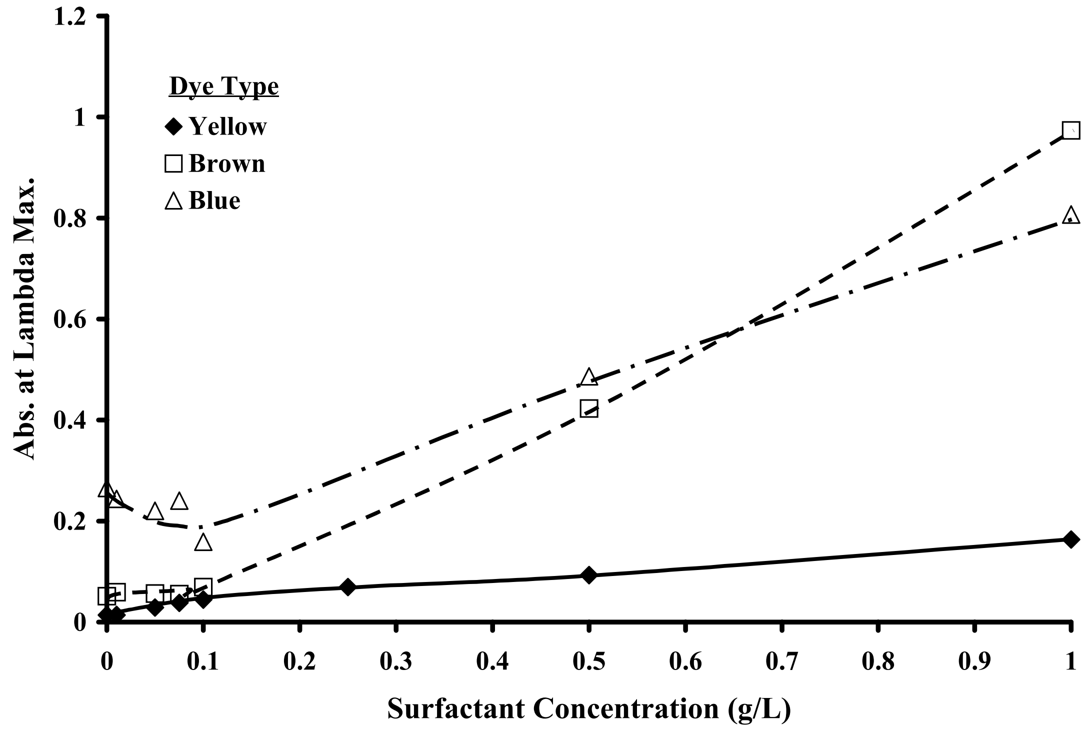


Figure 12. Dye Solubilization in Triton™ X-100.

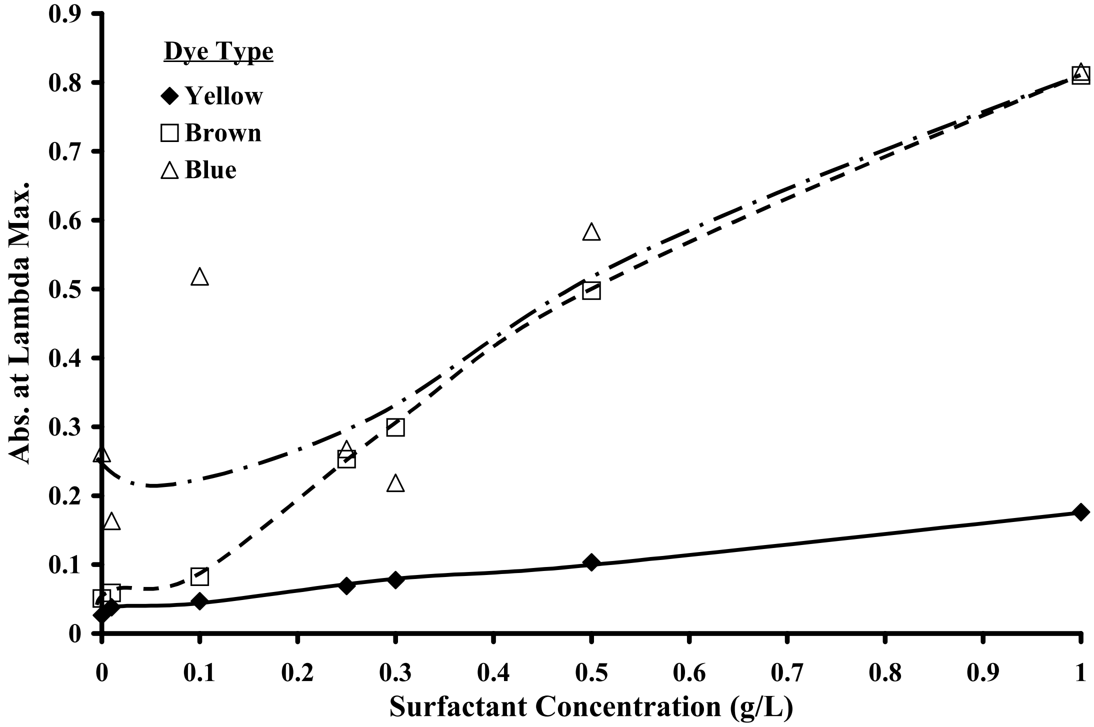


Figure 13. Dye Solubilization in Triton™ X-102.

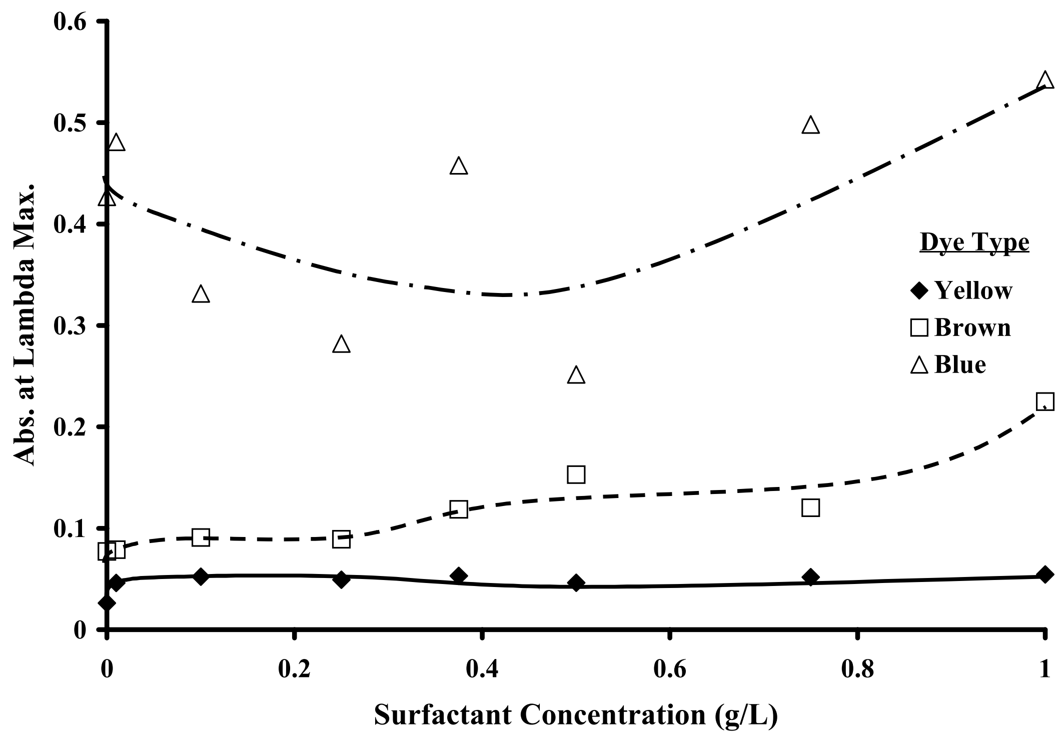


Figure 14. Dye Solubilization in Triton™ X-305.

the surfactant (as determined by surface tension measurements) is reached. Beyond surfactant CMC, dye solubilization continues to increase with increasing surfactant concentration but at a rate that is lower than that at surfactant concentrations below CMC.

Dye solubilization at surfactant concentrations below surfactant CMC maybe attributed to pre-micellar solubilization and that above surfactant CMC to micellar solubilization of dye. Pre-micellar solubilization has been attributed to dye aggregation and also aggregation of dye and surfactant molecules at pre-micellar surfactant concentration [49]. It is believed that once the surfactant concentration closely approaches or surpasses its CMC the dye is eventually incorporated into micelles.

Among the three dyes used in this investigation the yellow dye, C.I. Disperse Yellow 42, exhibited the least degree of solubilization in all surfactants. The degrees of solubilization of the blue and brown dyes were comparable to each other. The solubilization data may be indicative of the hydrophobic nature of the dyes. On comparing the chemical structures of the three dyes, given in Figure 4, it can be seen that the blue and brown dye molecules are bulkier and contain a larger hydrophobic component as compared to yellow dye molecules. Hence, the yellow dye is likely to be the least hydrophobic among the three dyes studied and this may be the reason for its lower degree of solubilization by surfactants.

At low concentrations all surfactants exhibited similar degrees of dye solubilization but with increase in surfactant concentration differences in dye solubilization between surfactant types became evident. In general, at higher concentrations, Triton™ X-305 exhibited the lowest degree of dye solubilization in comparison with other surfactants, which can be attributed to its high degree of ethoxylation, and Tween® 40 exhibited the highest degree of dye solubilization, which is consonant with the larger length of its hydrophobic segment.

In case of C.I. Disperse Blue 27, at high surfactant concentrations, Tween® 40 exhibited most solubilization while solubilization in the other surfactants was comparable. In case of C.I. Disperse Brown 1, at high surfactant concentrations, Triton™ X-305 exhibited least solubilization, while solubilization in other surfactants was similar. In case of C.I. Disperse Yellow 42, at high surfactant concentrations, Triton™ X-305 exhibited the least solubilization, Tween® 40 the most, and solubilization in other surfactants was similar to each other.

Dye Pickup in the Padding Operation

The effect of surfactant type and concentration on dye pickup by fabric during the padding operation was evaluated from dye content values of the control (unfixed) samples and is shown graphically in Figures 15-19. In these plots, each data point is the mean of three observations.

The data was analyzed at a 0.05 level of significance using a split-plot experimental design with surfactant type as the whole plot factor and surfactant concentration as the split plot factor. The effects of surfactant type and concentration on dye pickup were evaluated separately for each dye. Differences in dye pickup between dye types were not analyzed. The statistical analyses are available in Appendix A.

Surfactant type or its concentration in pad liquor did not exert a significant effect on dye pickup from pad-bath for the dyes used in this investigation. The presence of surfactant in pad liquor was found to exert no influence on dye pick-up in case of the blue and brown dyes. In case of C.I. Disperse Yellow 42, it was observed that the smallest amount of surfactant in the pad liquor resulted in significantly higher dye pickup values but subsequent increases in surfactant concentration produced no further changes in dye pickup.

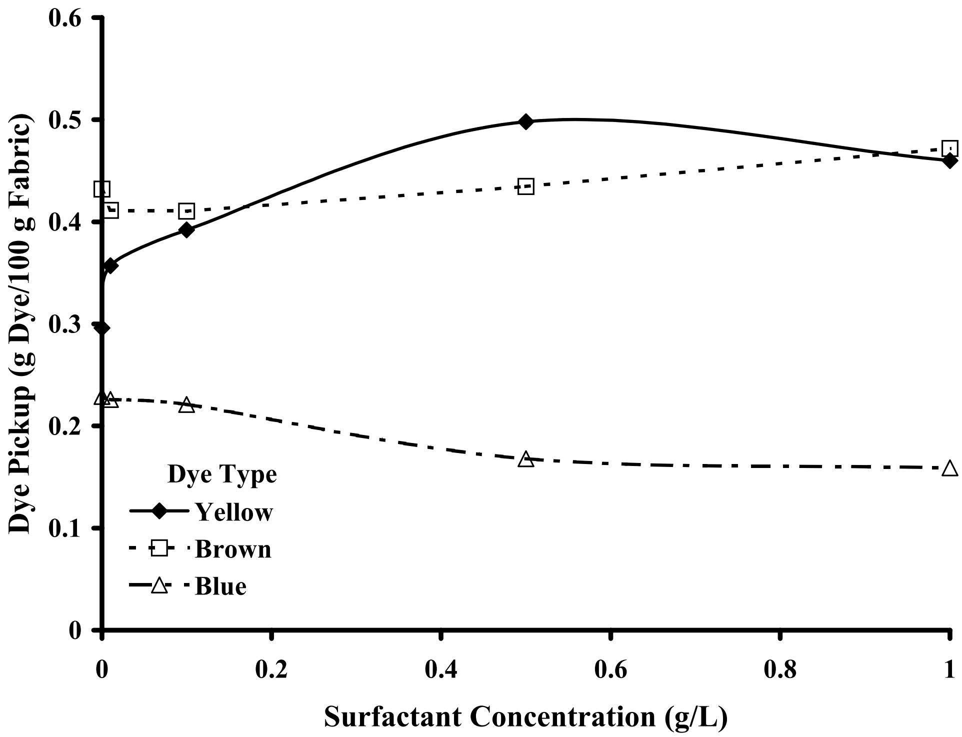


Figure 15. Effect of Tween® 20 Concentration in Pad-bath on Dye Pickup in the Padding Operation.

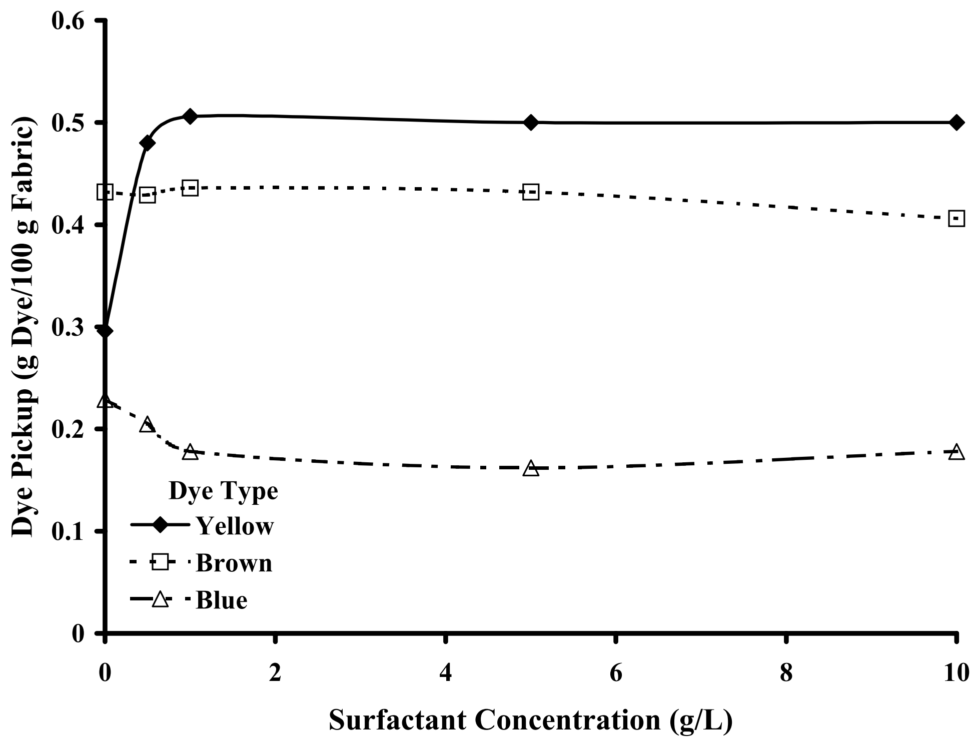


Figure 16. Effect of Tween® 40 Concentration in Pad-bath on Dye Pickup in the Padding Operation.

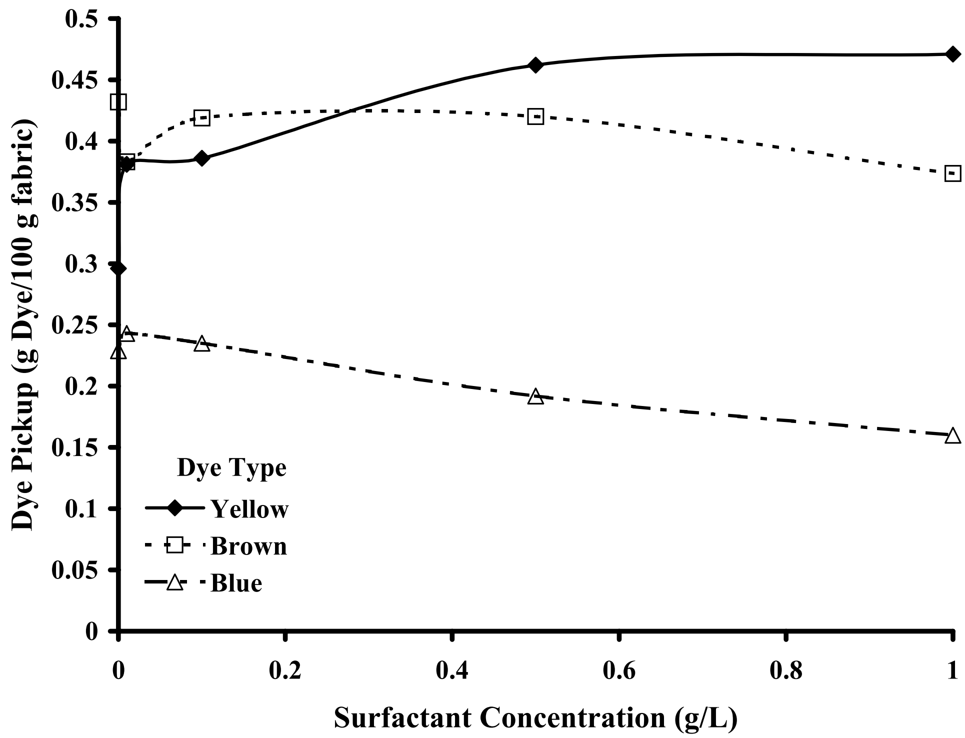


Figure 17. Effect of Triton™ X-100 Concentration in Pad-bath on Dye Pickup in the Padding Operation.

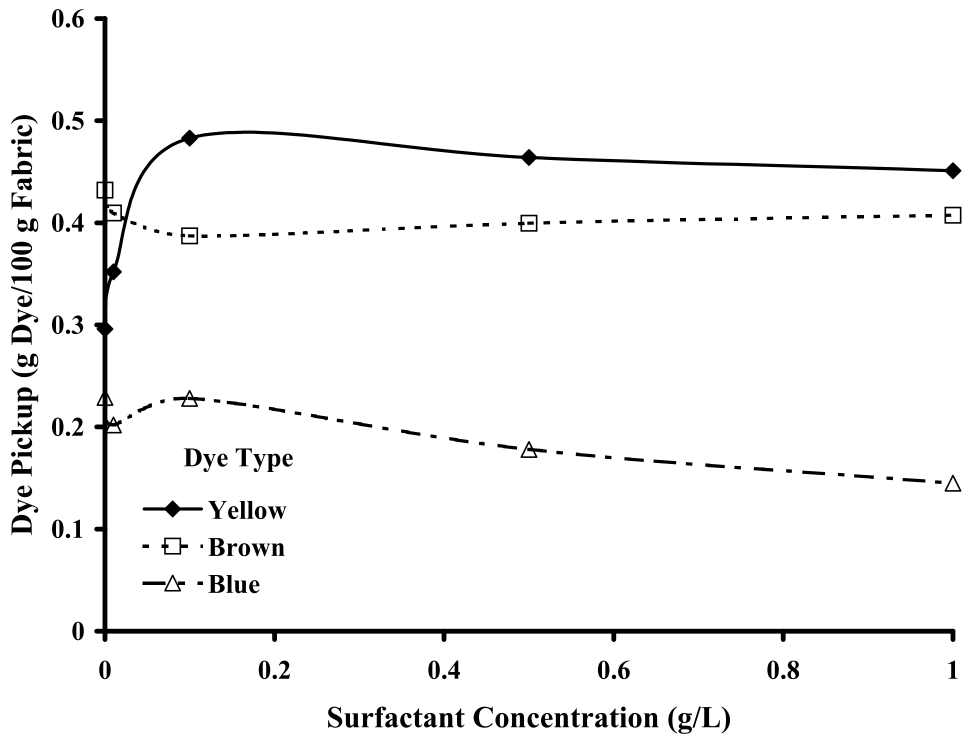


Figure 18. Effect of Triton™ X-102 Concentration in Pad-bath on Dye Pickup in the Padding Operation.

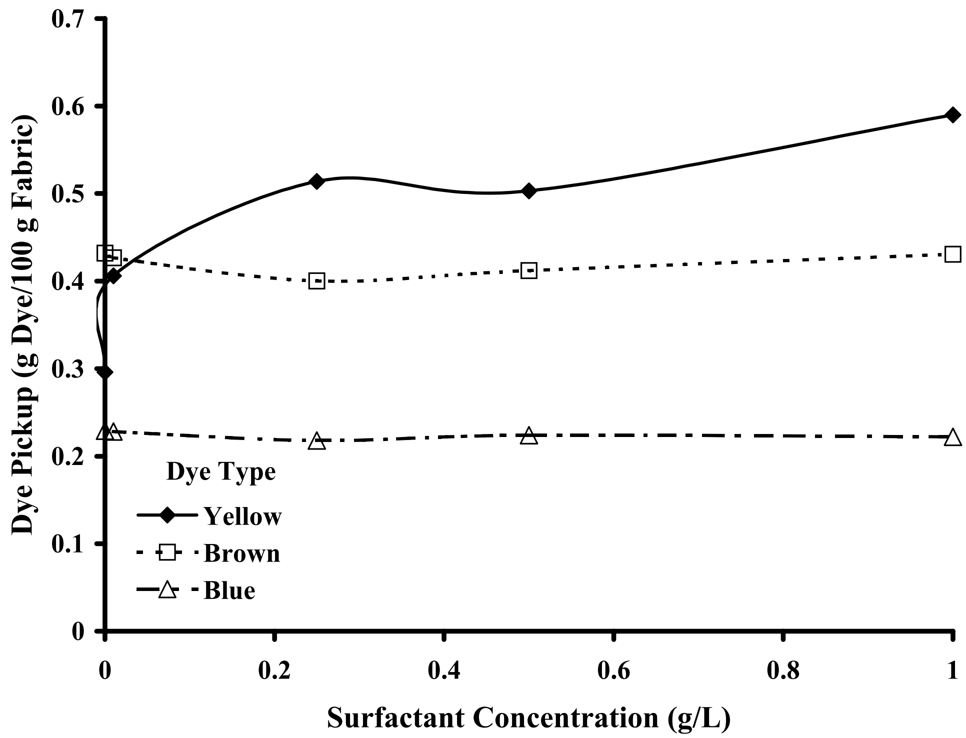


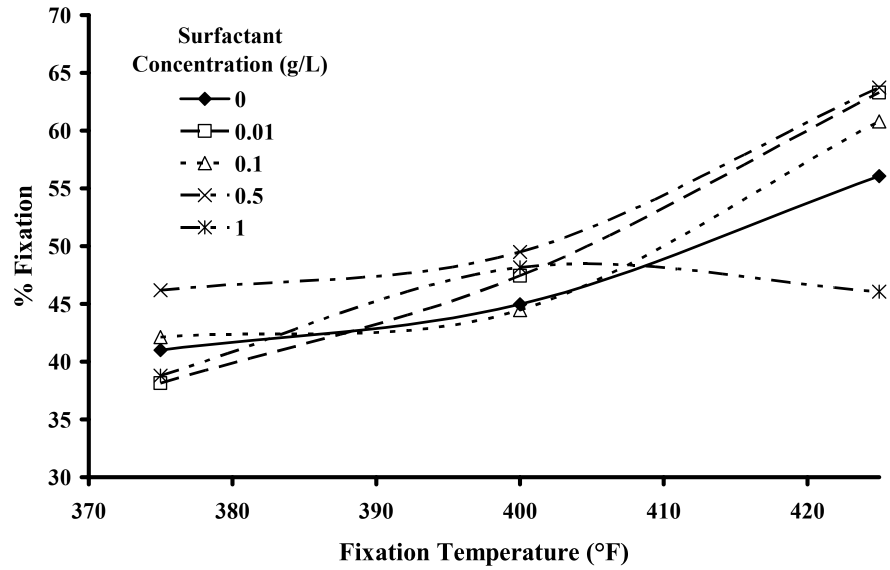
Figure 19. Effect of Triton™ X-305 Concentration in Pad-bath on Dye Pickup in the Padding Operation.

Dye pickup in the padding operation is more a function of wetting than dye solubilization. At their individual CMC, the apparent surface tension of aqueous solutions of all surfactants used in this investigation lie between 33-39 dynes/cm, suggesting that the surfactants behave equally well as wetting agents, and hence differences in dye pickup were not observed. Fox et al. [16] state that well-prepared fabrics do not show increased dye pickup upon addition of wetting agents to the pad-bath. They attribute increases in dye pickup, upon addition of a wetting agent, to deficiencies in preparatory processing.

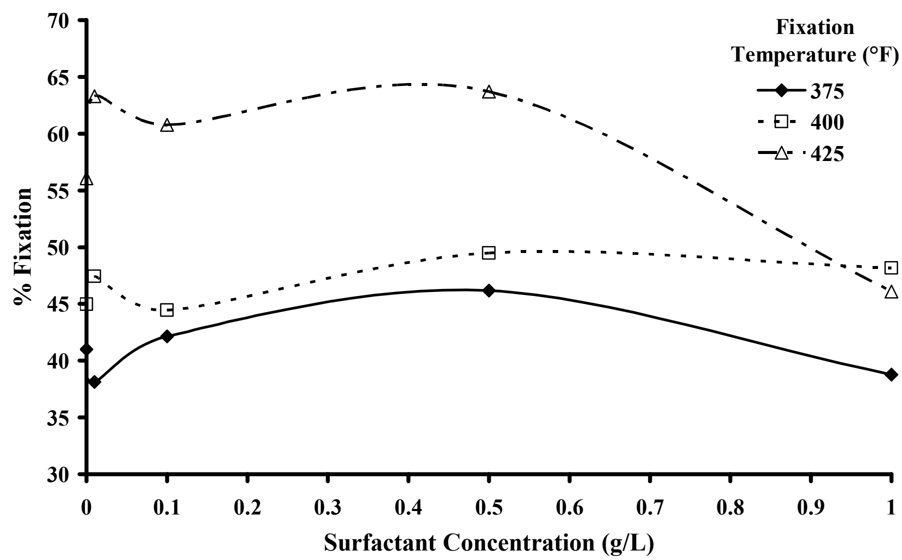
Dye Fixation

The effect of surfactant type, concentration and fixation temperature on degree of dye fixation for the dyes used in this investigation are shown graphically in Figures 20-34. In these plots, each data point is the mean of three observations.

The data was analyzed at a 0.05 level of significance using a split-plot experimental design with the whole plots in randomized complete blocks. The blocking factor was surfactant type, the whole plot factor was fixation temperature and the split plot factor was surfactant concentration. The effects of surfactant type, concentration and fixation temperature on dye fixation were

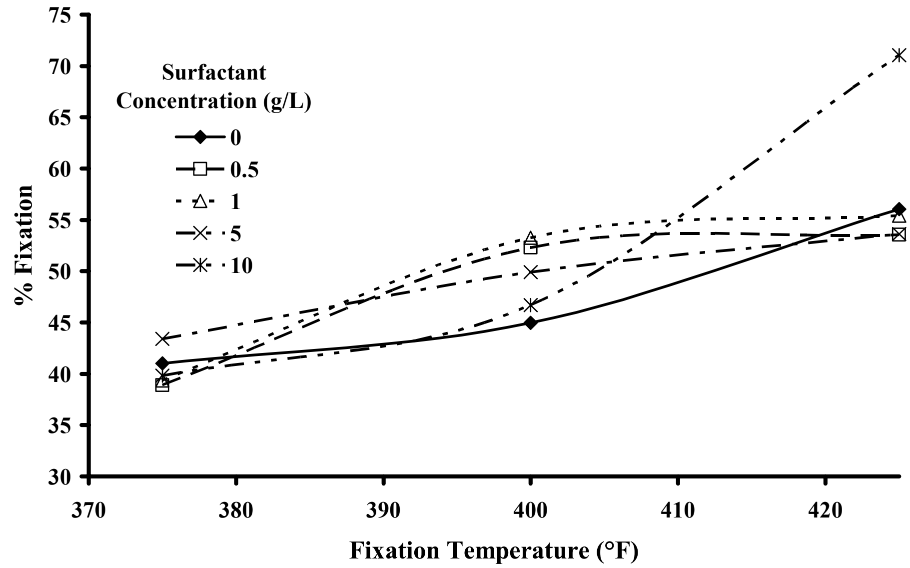


(a) Effect of Fixation Temperature on Dye Fixation

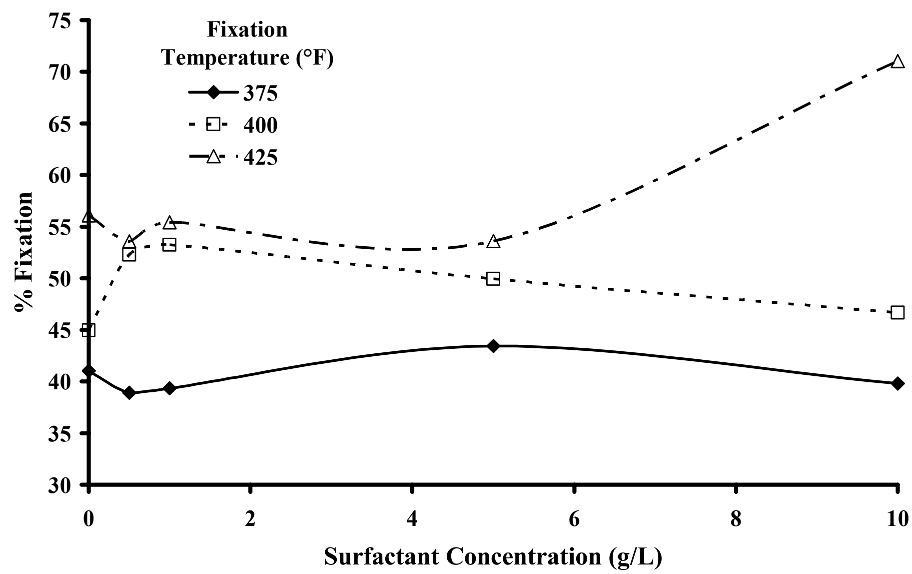


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 20. Effect of Fixation Temperature and Tween® 20 Concentration on Fixation of C.I. Disperse Blue 27.

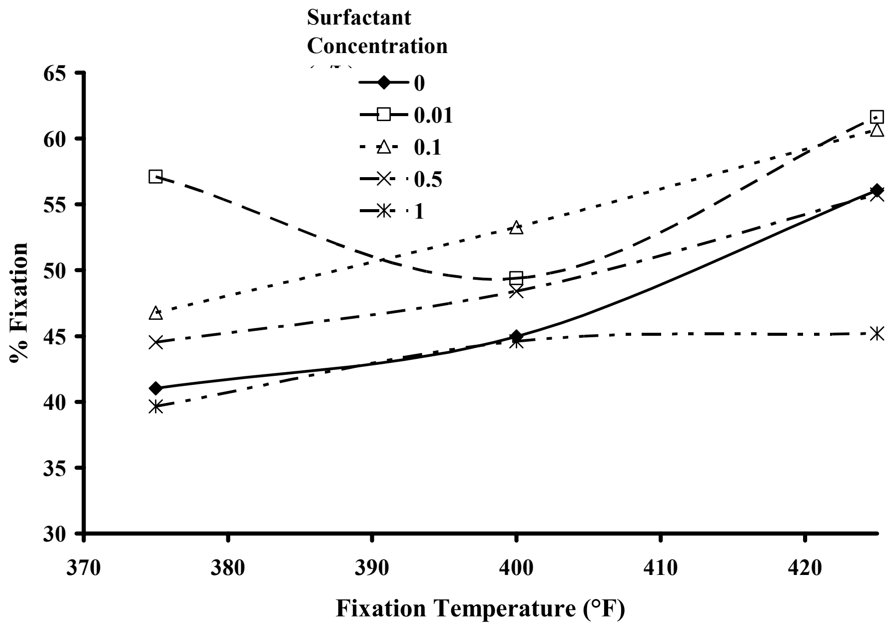


(a) Effect of Fixation Temperature on Dye Fixation

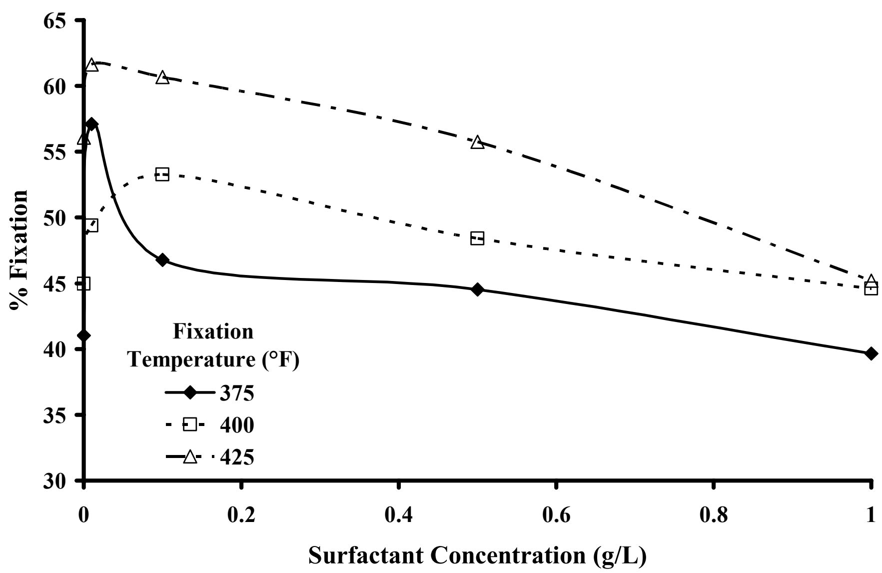


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 21. Effect of Fixation Temperature and Tween® 40 Concentration on Fixation of C.I. Disperse Blue 27.

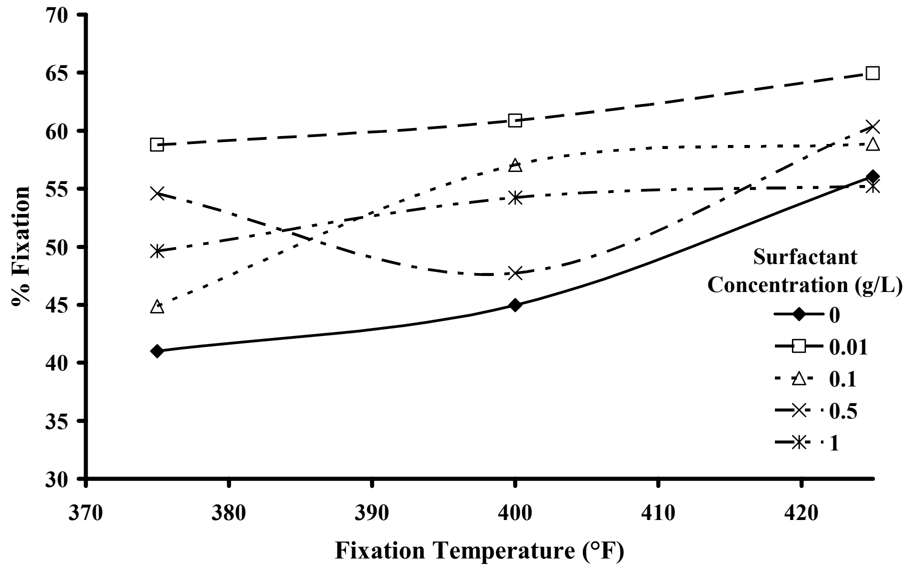


(a) Effect of Fixation Temperature on Dye Fixation

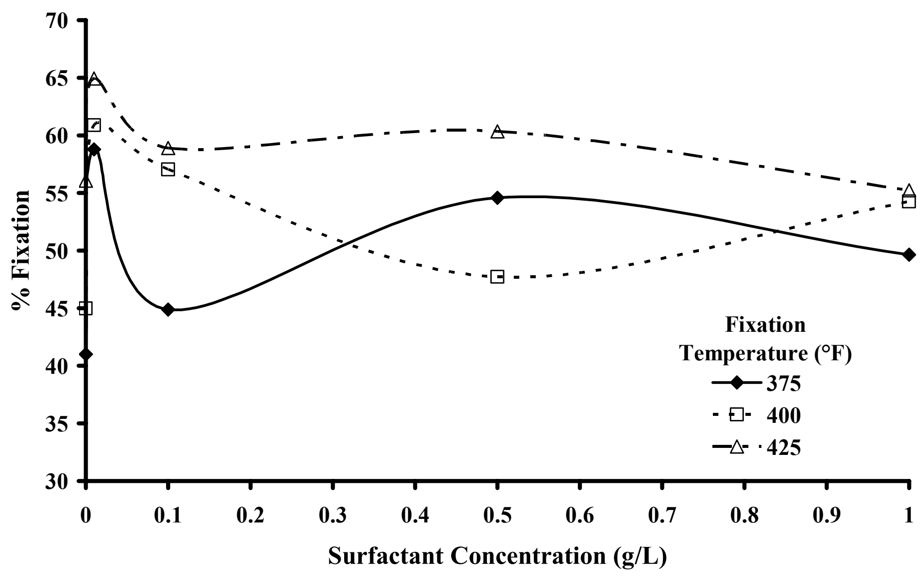


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 22. Effect of Fixation Temperature and Triton™ X-100 Concentration on Fixation of C.I. Disperse Blue 27.

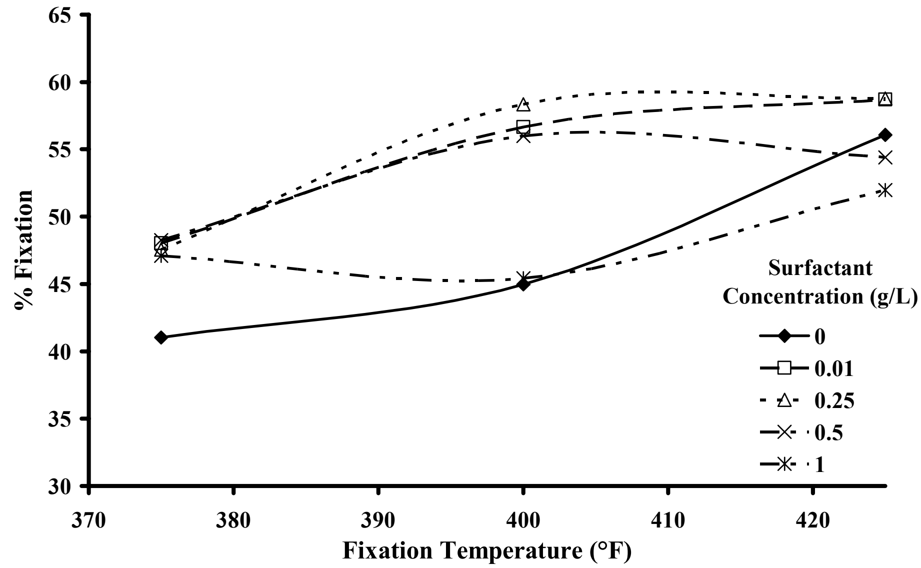


(a) Effect of Fixation Temperature on Dye Fixation

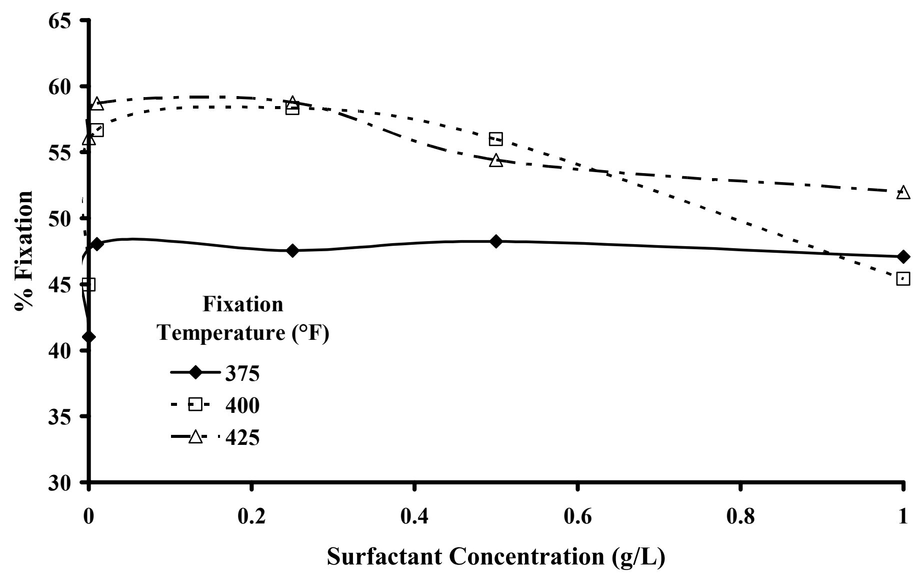


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 23. Effect of Fixation Temperature and Triton™ X-102 Concentration on Fixation of C.I. Disperse Blue 27.

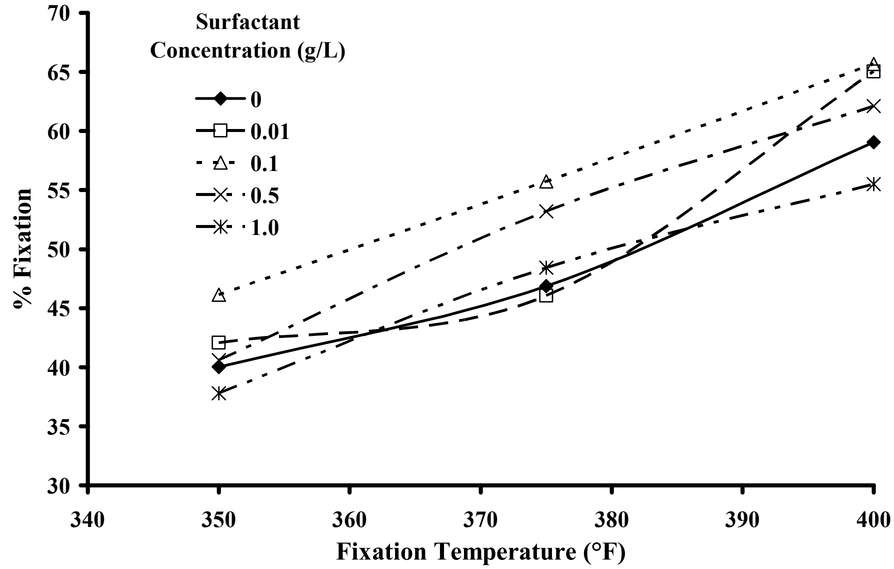


(a) Effect of Fixation Temperature on Dye Fixation

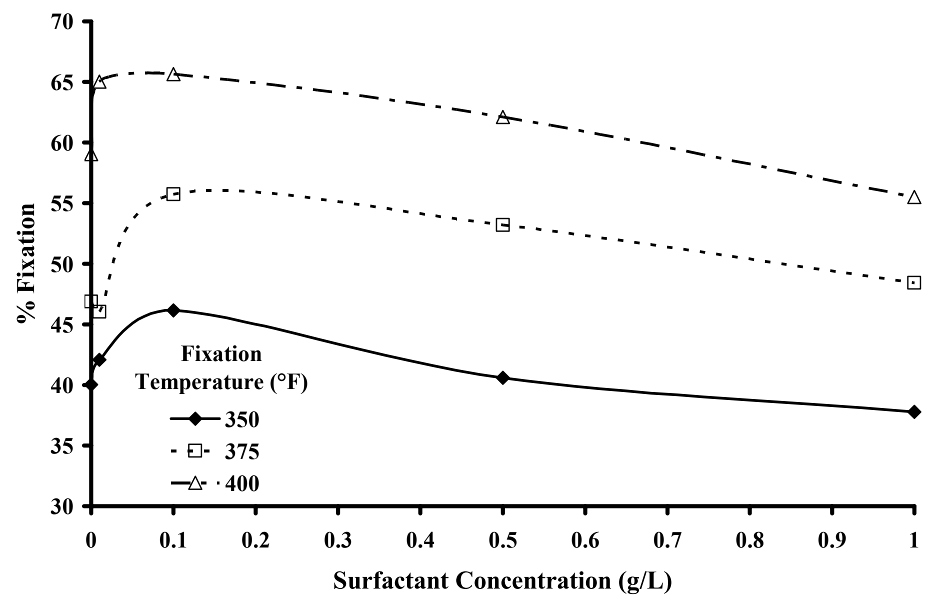


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 24. Effect of Fixation Temperature and Triton™ X-305 Concentration on Fixation of C.I. Disperse Blue 27.

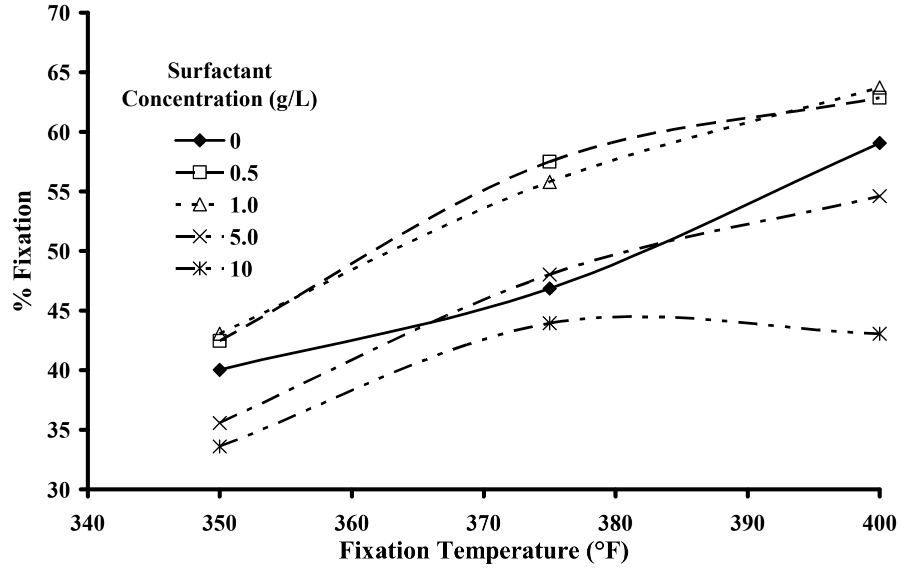


(a) Effect of Fixation Temperature on Dye Fixation

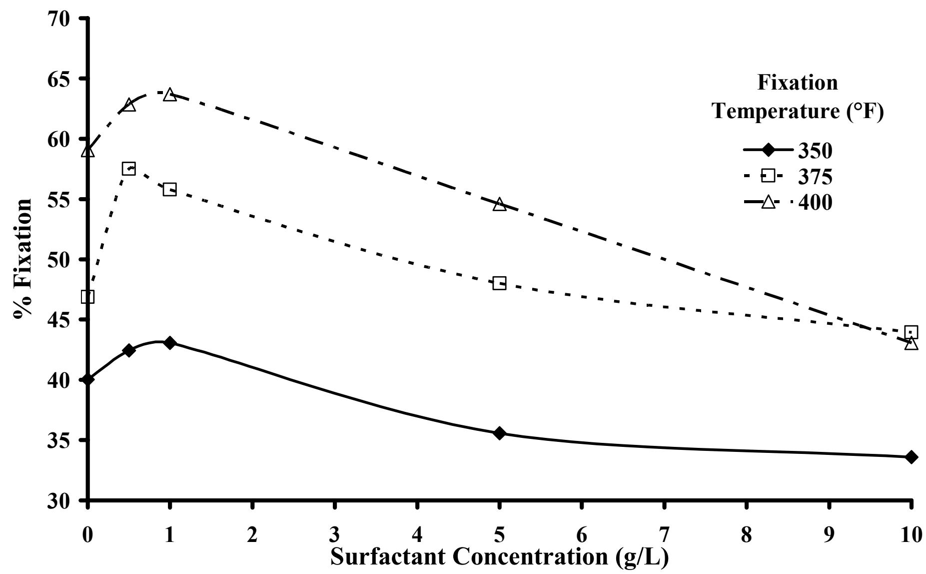


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 25. Effect of Fixation Temperature and Tween® 20 Concentration on Fixation of C.I. Disperse Brown 1.

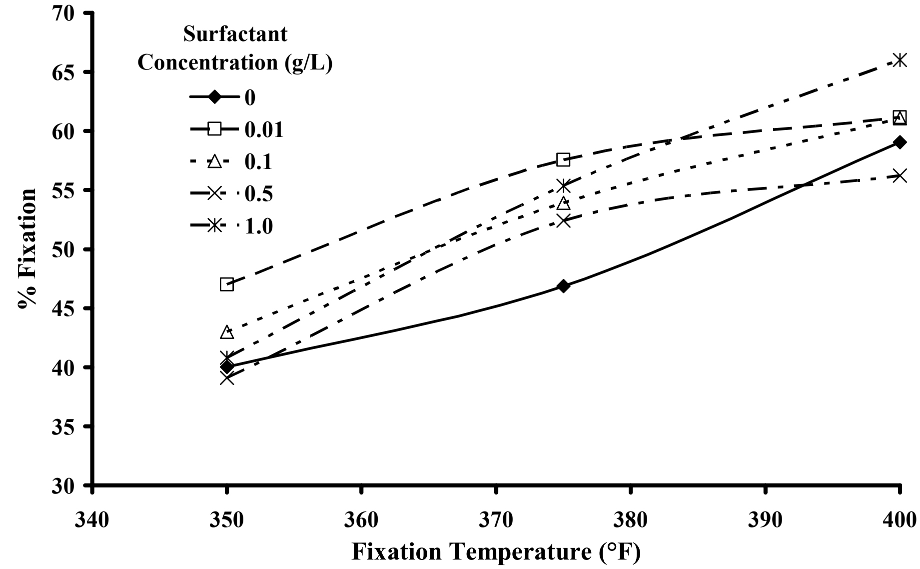


(a) Effect of Fixation Temperature on Dye Fixation

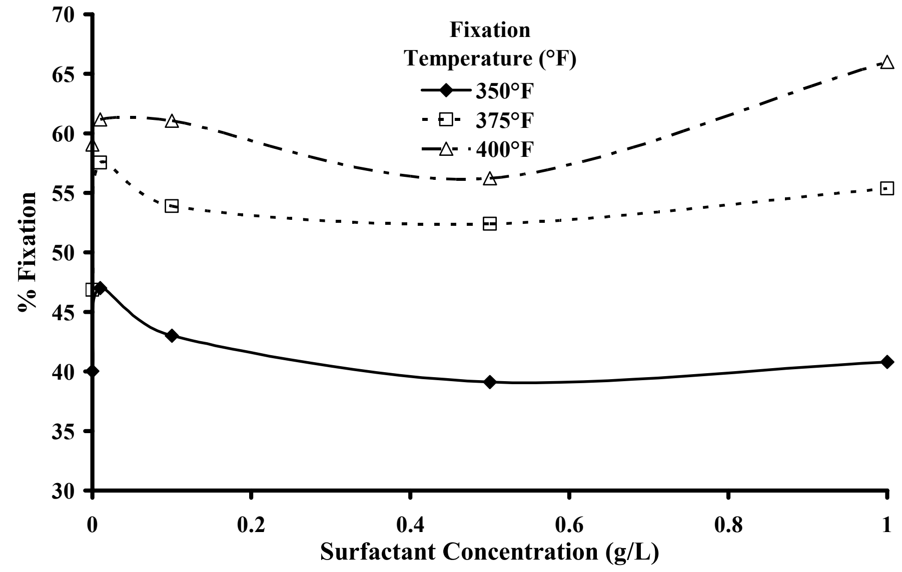


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 26. Effect of Fixation Temperature and Tween® 40 Concentration on Fixation of C.I. Disperse Brown 1.

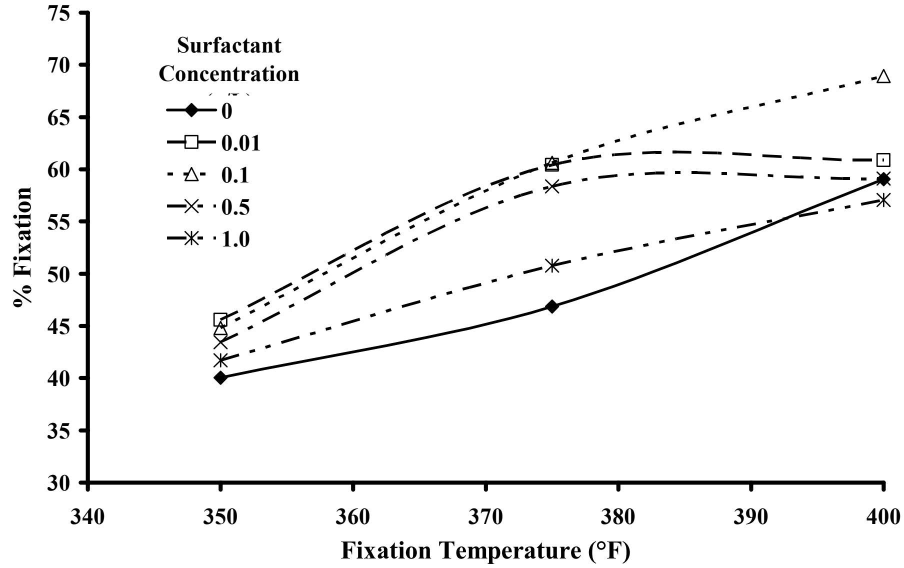


(a) Effect of Fixation Temperature on Dye Fixation

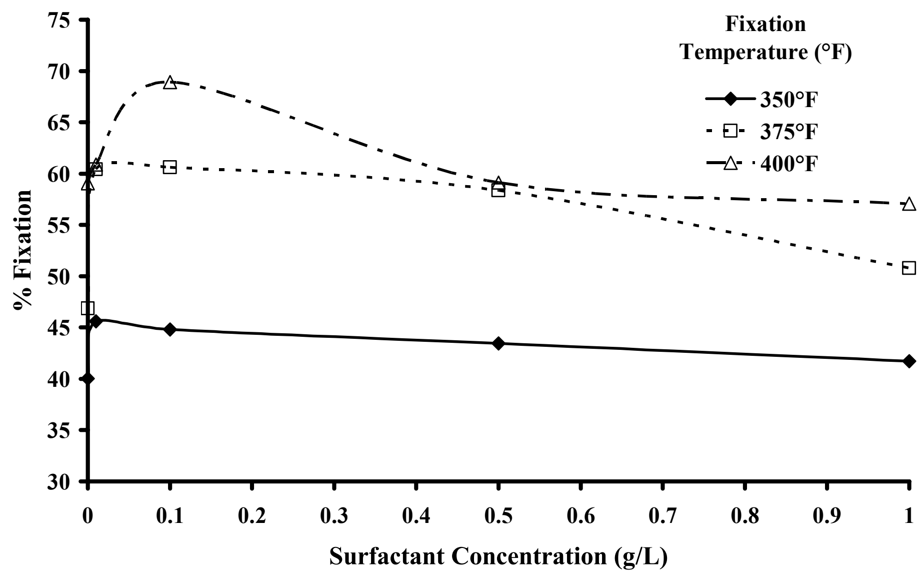


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 27. Effect of Fixation Temperature and Triton™ X-100 Concentration on Fixation of C.I. Disperse Brown 1.

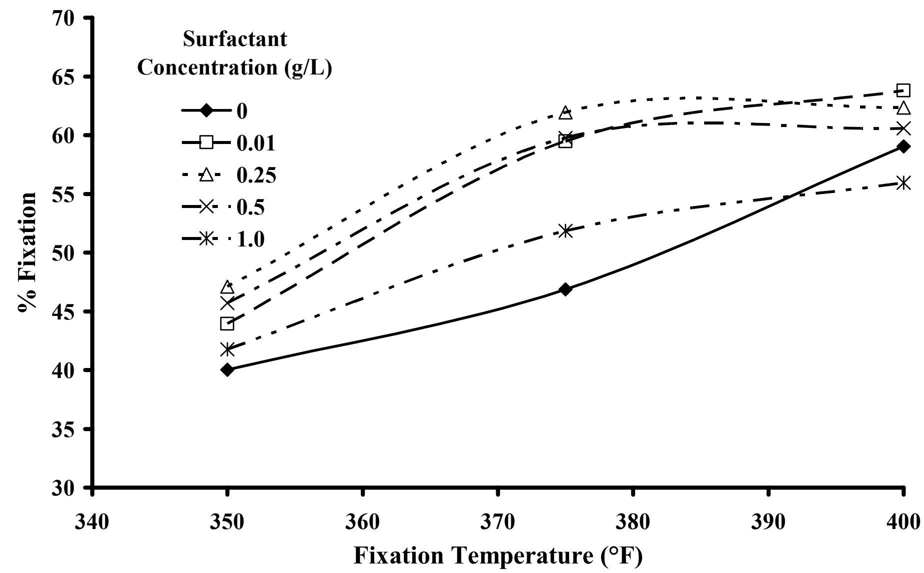


(a) Effect of Fixation Temperature on Dye Fixation

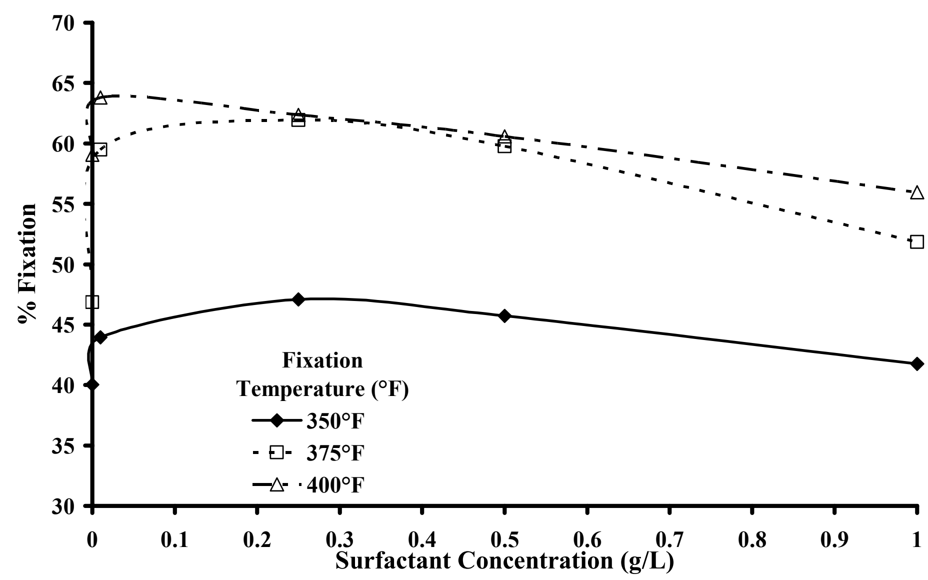


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 28. Effect of Fixation Temperature and Triton™ X-102 Concentration on Fixation of C.I. Disperse Brown 1.

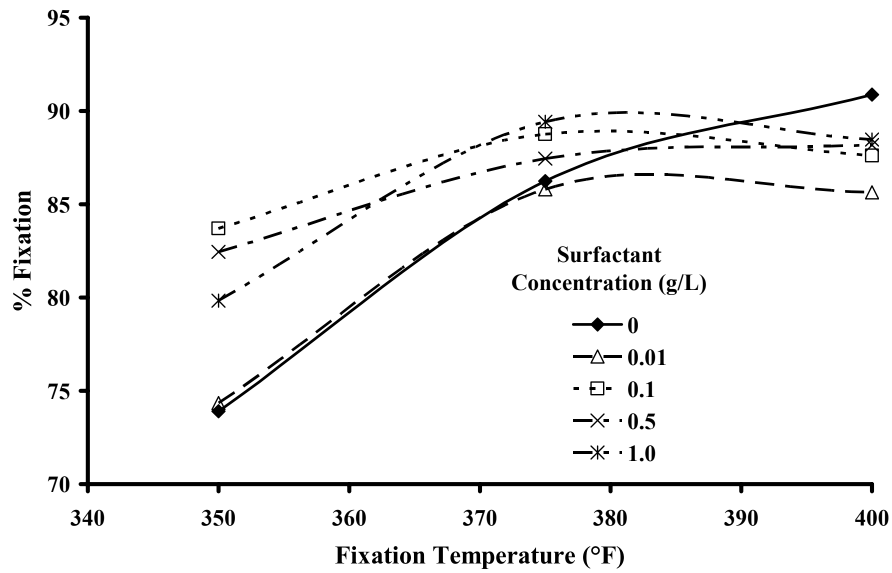


(a) Effect of Fixation Temperature on Dye Fixation

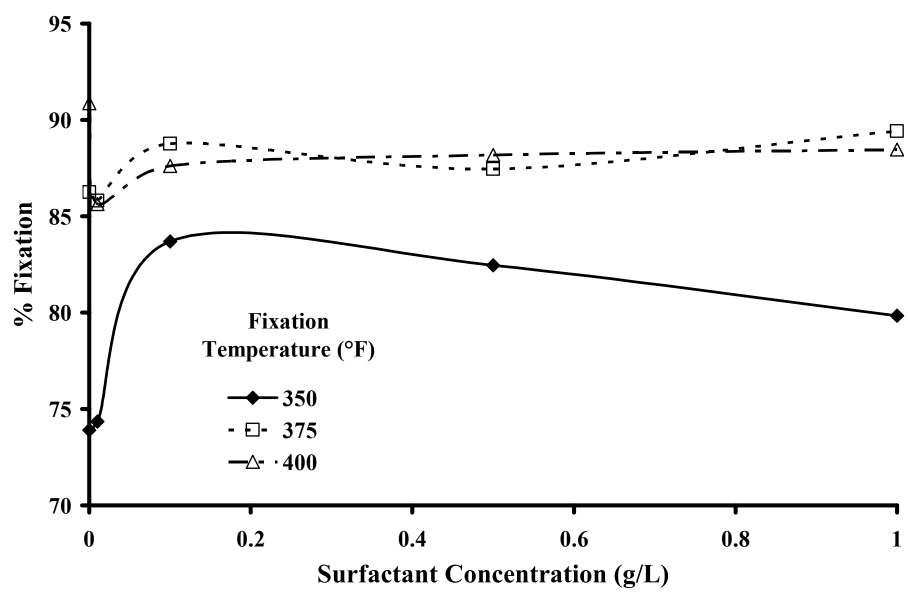


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 29. Effect of Fixation Temperature and Triton™ X-305 Concentration on Fixation of C.I. Disperse Brown 1.

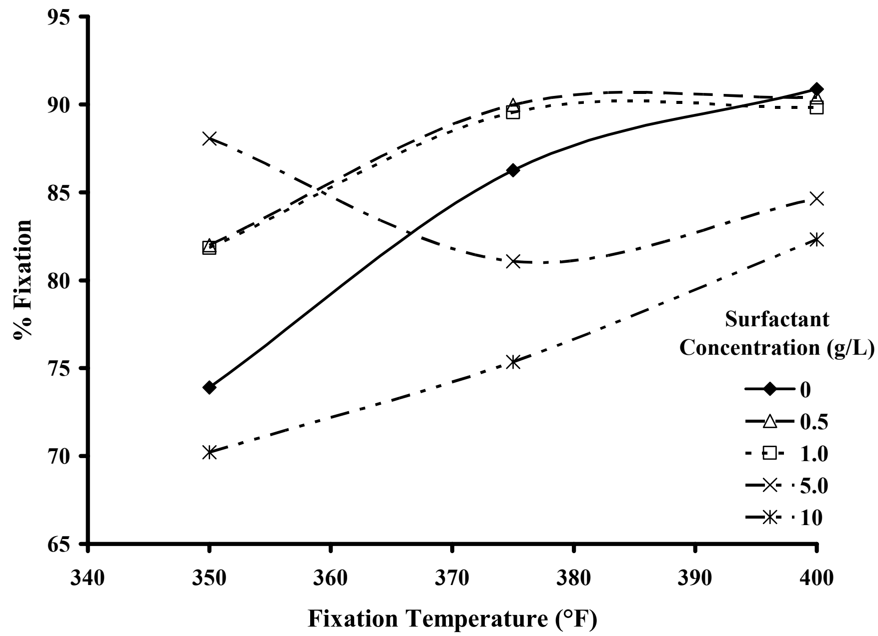


(a) Effect of Fixation Temperature on Dye Fixation

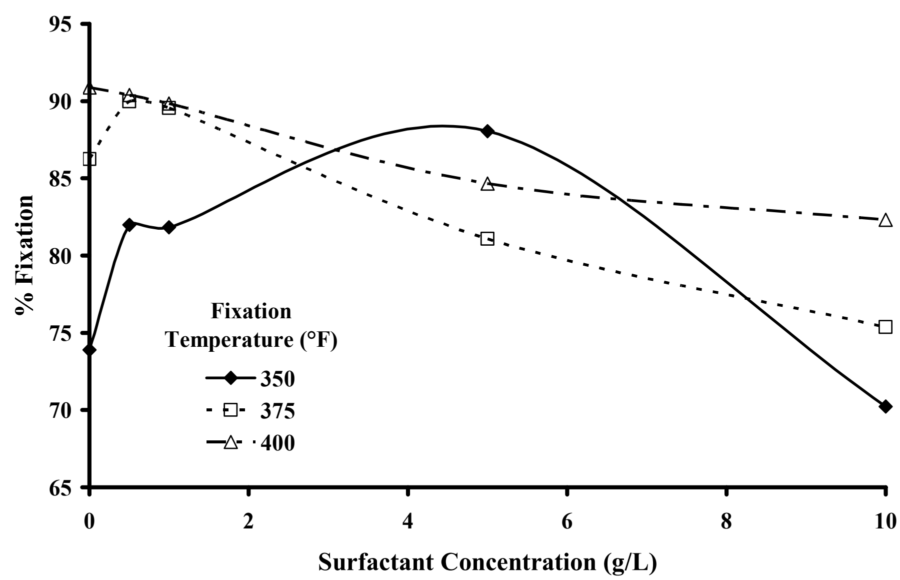


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 30. Effect of Fixation Temperature and Tween® 20 Concentration on Fixation of C.I. Disperse Yellow 42.

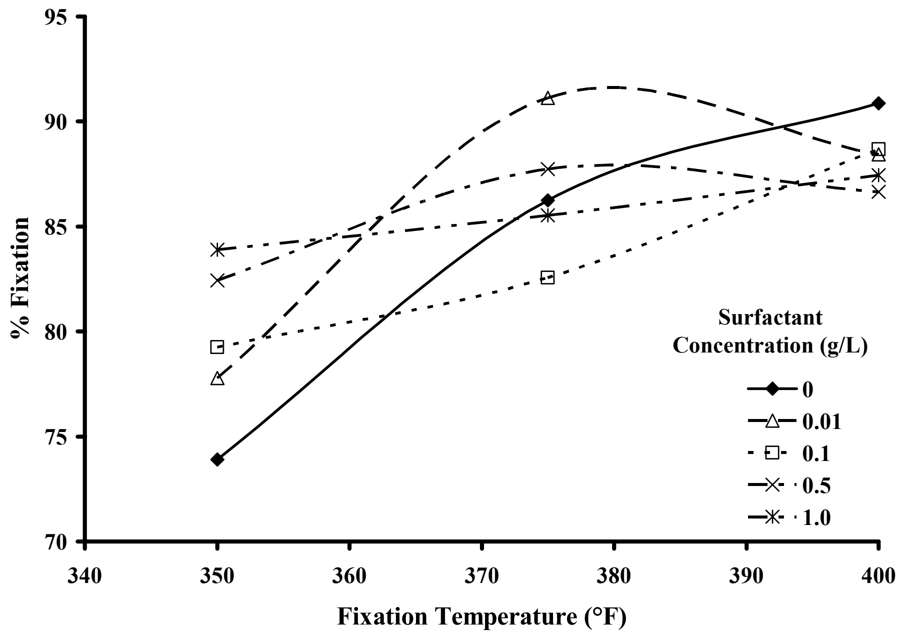


(a) Effect of Fixation Temperature on Dye Fixation

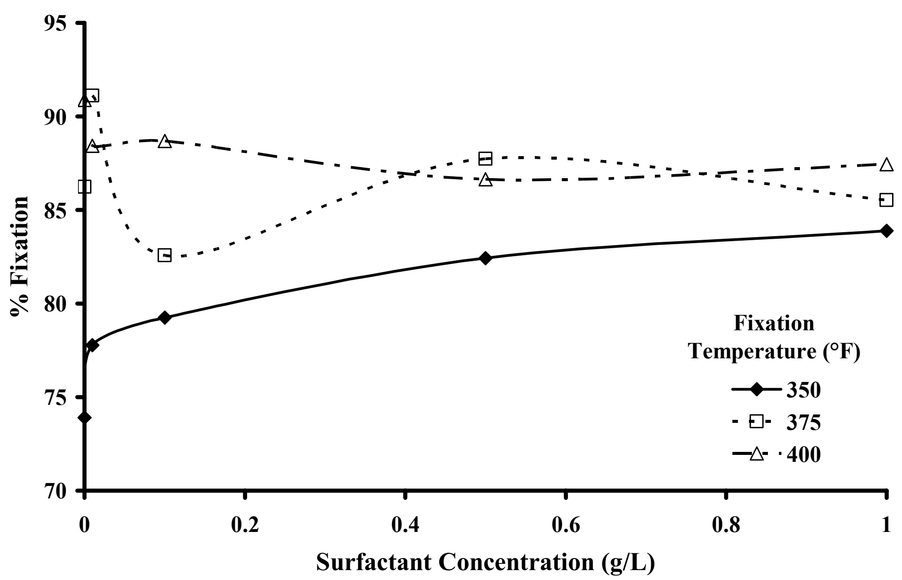


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 31. Effect of Fixation Temperature and Tween® 40 Concentration on Fixation of C.I. Disperse Yellow 42.

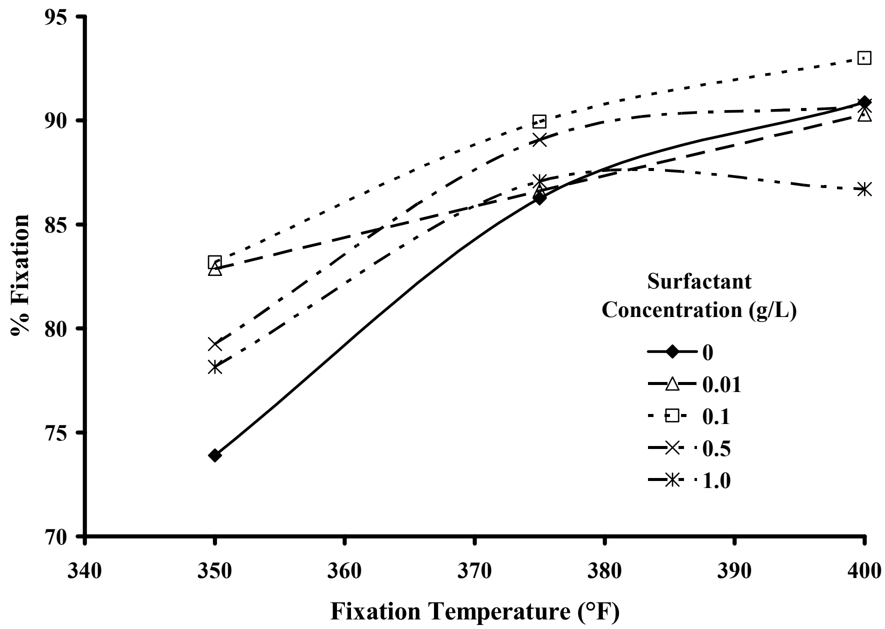


(a) Effect of Fixation Temperature on Dye Fixation

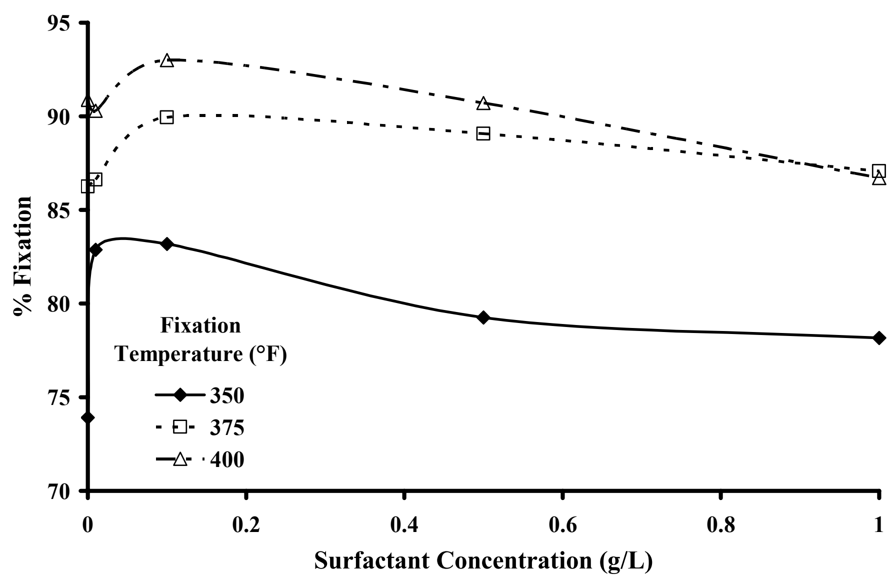


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 32. Effect of Fixation Temperature and Triton™ X-100 Concentration on Fixation of C.I. Disperse Yellow 42.

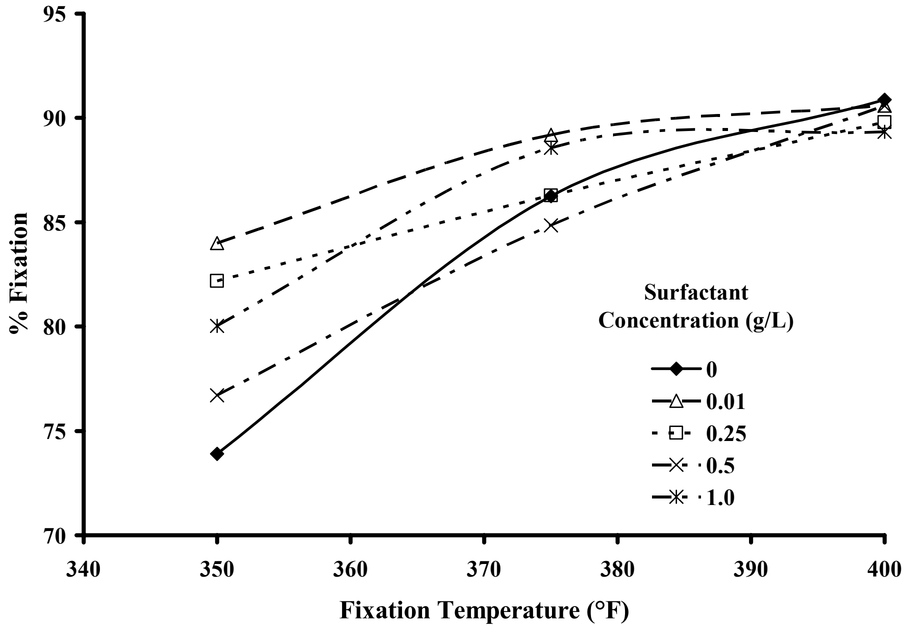


(a) Effect of Fixation Temperature on Dye Fixation

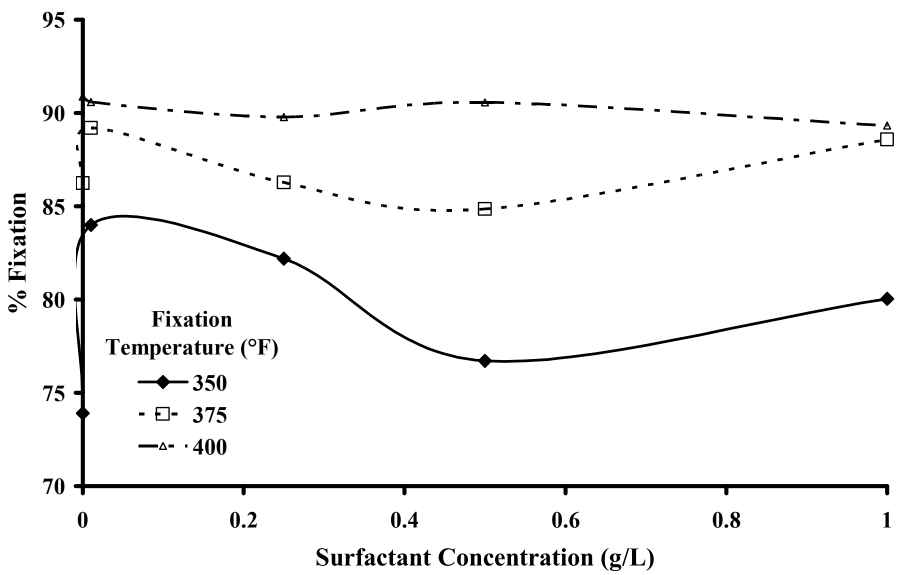


(b) Effect of Surfactant Concentration on Dye Fixation

Figure 33. Effect of Fixation Temperature and Triton™ X-102 Concentration on Fixation of C.I. Disperse Yellow 42.



(a) Effect of Fixation Temperature on Dye Fixation



(b) Effect of Surfactant Concentration on Dye Fixation

Figure 34. Effect of Fixation Temperature and Triton™ X-305 Concentration on Fixation of C.I. Disperse Yellow 42.

evaluated separately for each dye. Differences in dye fixation between dye types were not analyzed. The statistical analyses are available in Appendix B.

C.I. Disperse Blue 27

Surfactant concentration and fixation temperature were found to exert a significant effect on dye fixation. Interaction between surfactant concentration and fixation temperature was not found to be significant.

In general, dye fixation increased with fixation temperature at all levels of surfactant type and concentration. All surfactant-treated samples exhibited greater dye fixation than control samples. There was a significant effect of surfactant CMC on dye fixation in that the samples treated with surfactant at concentrations below surfactant CMC exhibited greater dye fixation than samples treated with surfactant at concentrations above surfactant CMC. Dye fixation increased with increase in surfactant concentration up to a certain level, and further increases in surfactant concentration resulted in a decrease in dye fixation.

In the statistical analysis, the effect of surfactant type on dye fixation was found to be significant but a closer examination of the data revealed otherwise. In a graphical comparison of dye fixation values between surfactant types, at the same levels of concentration, no differences in dye fixation were observed.

C.I. Disperse Brown 1

Surfactant type was not found to exert a significant effect on dye fixation. Surfactant concentration and fixation temperature exerted a significant effect on dye fixation and the interaction parameter between the two factors was found to be significant. Hence the effect of one factor was analyzed within each level of the other.

In general, dye fixation increased with increasing fixation temperature in all samples. For samples treated with 0.25, 5 and 10 g/L of surfactant, dye fixation increased with temperature up to 375°F and further increase in fixation temperature caused no significant change in dye fixation.

The effect of surfactant concentration on dye fixation varied with fixation temperature. At a fixation temperature of 350°F, dye fixation in samples treated with up to 0.25 g/L surfactant was greater than that in control samples. Dye fixation in samples treated with 0.5 and 1.0 g/L surfactant was similar to that of control samples and samples treated with higher surfactant concentrations exhibited lower dye fixation. At a fixation temperature of 375°F, dye fixation in all surfactant treated samples was higher than in control samples with the exception of samples treated with 5.0 and 10.0 g/L surfactant where dye fixation was lower. At a fixation temperature of 400°F, samples treated with surfactant at concentrations up to 0.1 g/L exhibited higher dye fixation values as compared to control samples. Treating samples with surfactants in the concentration range of 0.25 to 1.0 g/L resulted in dye fixation values similar to that of control samples, and further increase in surfactant concentration, up to 10 g/L, resulted in lower dye fixation. Samples treated with 5.0 and 10.0 g/L surfactant exhibited significantly lower dye fixation as compared to control samples in the range of fixation temperatures used for the brown dye.

At fixation temperatures of 350 and 400°F, samples treated with surfactant at concentrations below surfactant CMC exhibited greater dye fixation than samples treated with surfactant at concentrations above surfactant CMC, while at 375°F, no significant difference in dye fixation was observed.

C.I. Disperse Yellow 42

Surfactant type was not found to exert a significant effect on dye fixation. Surfactant concentration and fixation temperature exerted a significant effect on dye fixation and the interaction parameter between the two factors was found to be significant. Hence the effect of one factor was analyzed within each level of the other.

Dye fixation increased with increasing fixation temperature in control samples. In general, dye fixation in surfactant treated samples increased with temperature up to 375°F and a further increase in fixation temperature did not result in a significant change in dye fixation. In case of samples treated with 0.25, 5 and 10 g/L of surfactant there was no significant change in dye fixation with change in fixation temperature.

The effect of surfactant concentration on dye fixation varied with fixation temperature. At 350°F, dye fixation in all surfactant treated samples was greater than that in control samples, except in case of samples treated with 10 g/L surfactant, where no difference in dye fixation was observed between surfactant treated and control samples. At 375 and 400°F, in general, there was no difference in dye fixation between control and surfactant treated samples. The exceptions were samples treated with 5.0 and 10.0 g/L surfactant. Dye fixation in samples treated with 5.0 g/L surfactant was lower than that in control samples at 400°F and samples treated with 10.0 g/L exhibited lower dye fixation as compared to control samples at 375 and 400°F.

The concentration of surfactant used did not influence dye fixation values significantly. Dye fixation in samples treated with surfactant at concentrations below its CMC was similar to dye fixation in samples treated with surfactant at concentrations above its CMC.

Dye Vaporization

The experiment to determine the effect of surfactant type, its concentration and fixation temperature on the tendency of dyes to vaporize was qualitative and hence a statistical analysis of the results was not conducted. Photographs of the dyed polyester part from the sandwiches, after thermal fixation, experiments are given in Figures 35-52.

C.I. Disperse Blue 27

Dye vaporization increased with increase in fixation temperature. In case of samples treated with 5.0 and 10.0 g/L of surfactant, negligible dye vaporization was observed at 375 and 400°F but evidence of dye vaporization could be observed in samples at 425°F.

Dye vaporization was observed to decrease with increasing surfactant concentration. Within any level of fixation temperature, there was no difference in dye vaporization between control samples and samples treated with the smallest amount of surfactant but dye vaporization

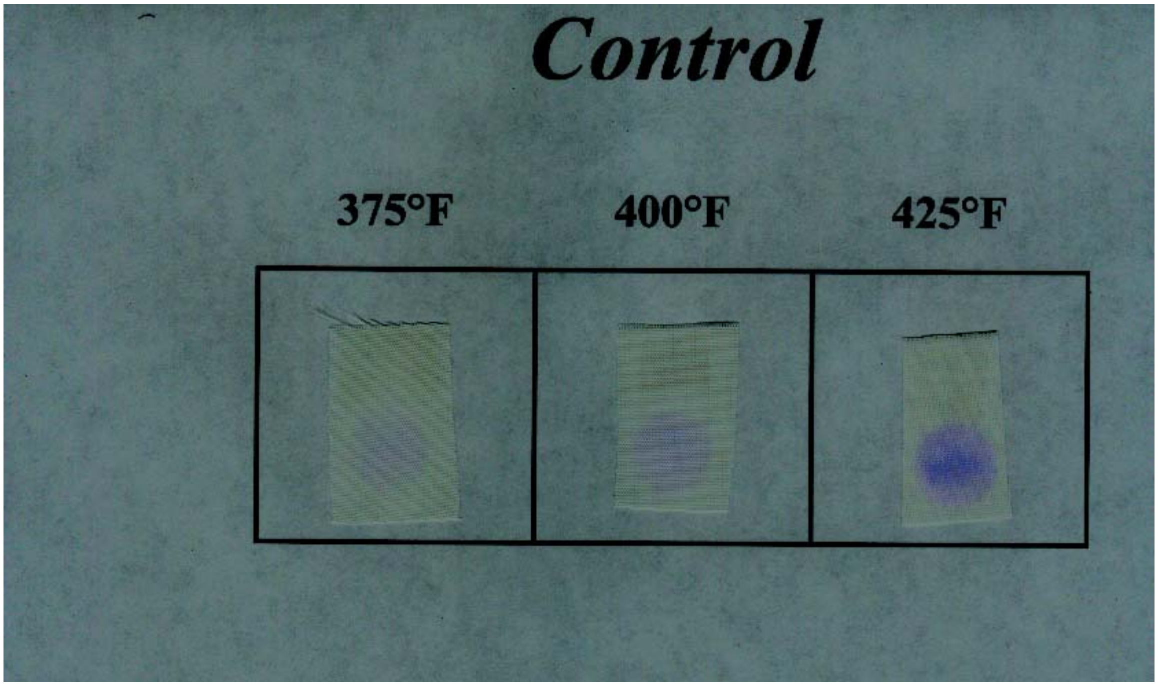


Figure 35. C.I. Disperse Blue 27 Vaporization in Control Samples.

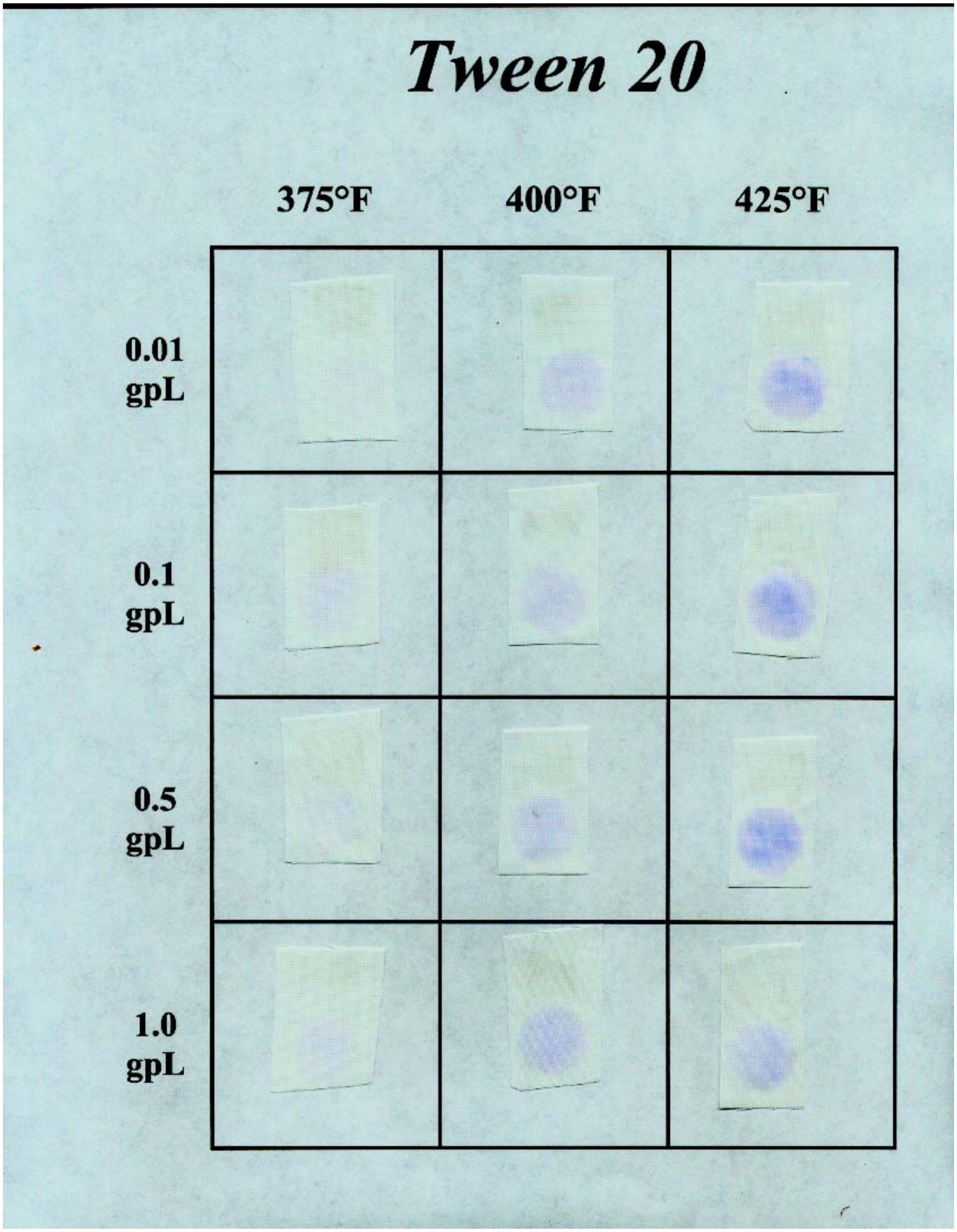


Figure 36. C.I. Disperse Blue 27 Vaporization in Presence of Tween® 20.

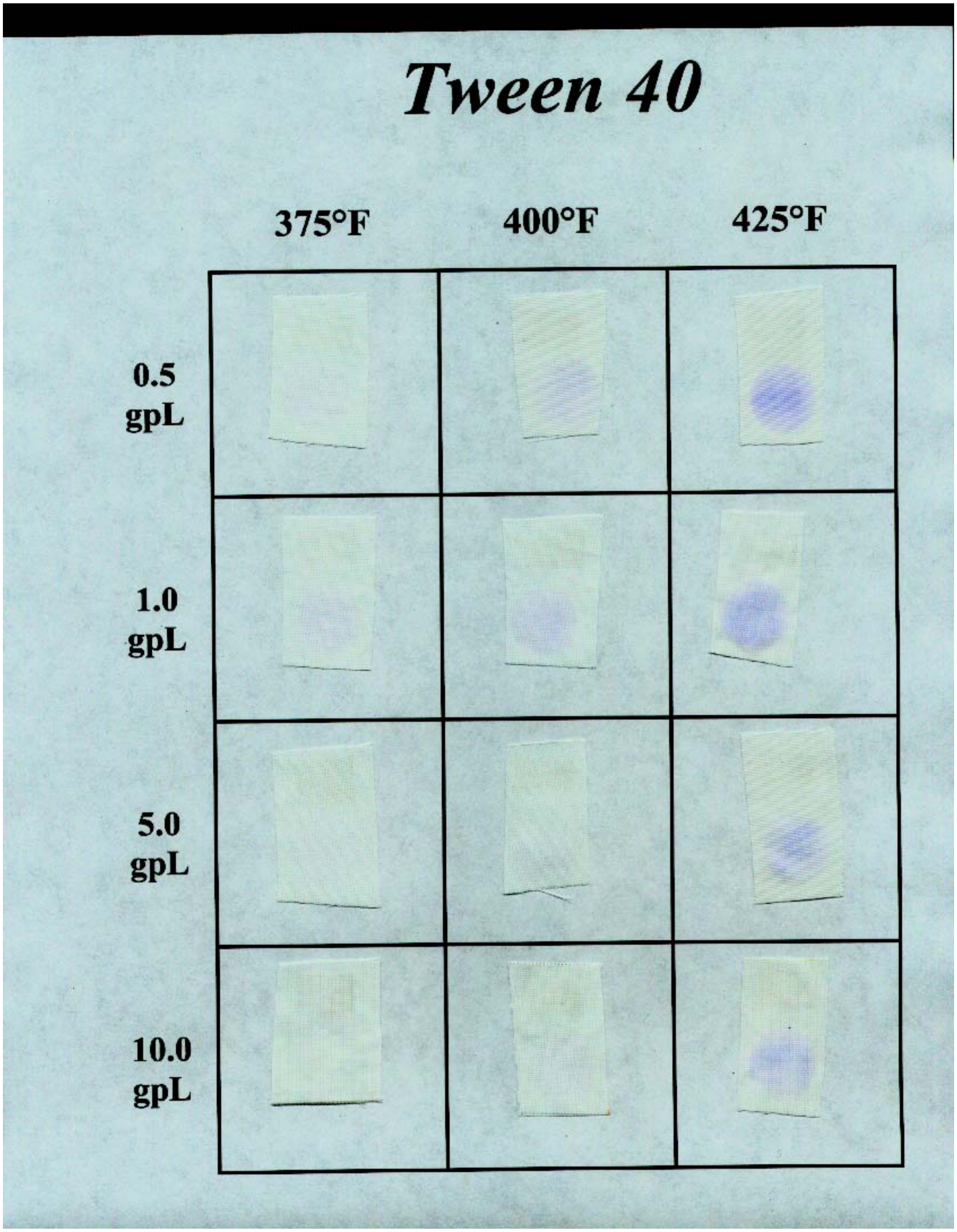


Figure 37. C.I. Disperse Blue 27 Vaporization in Presence of Tween® 40.

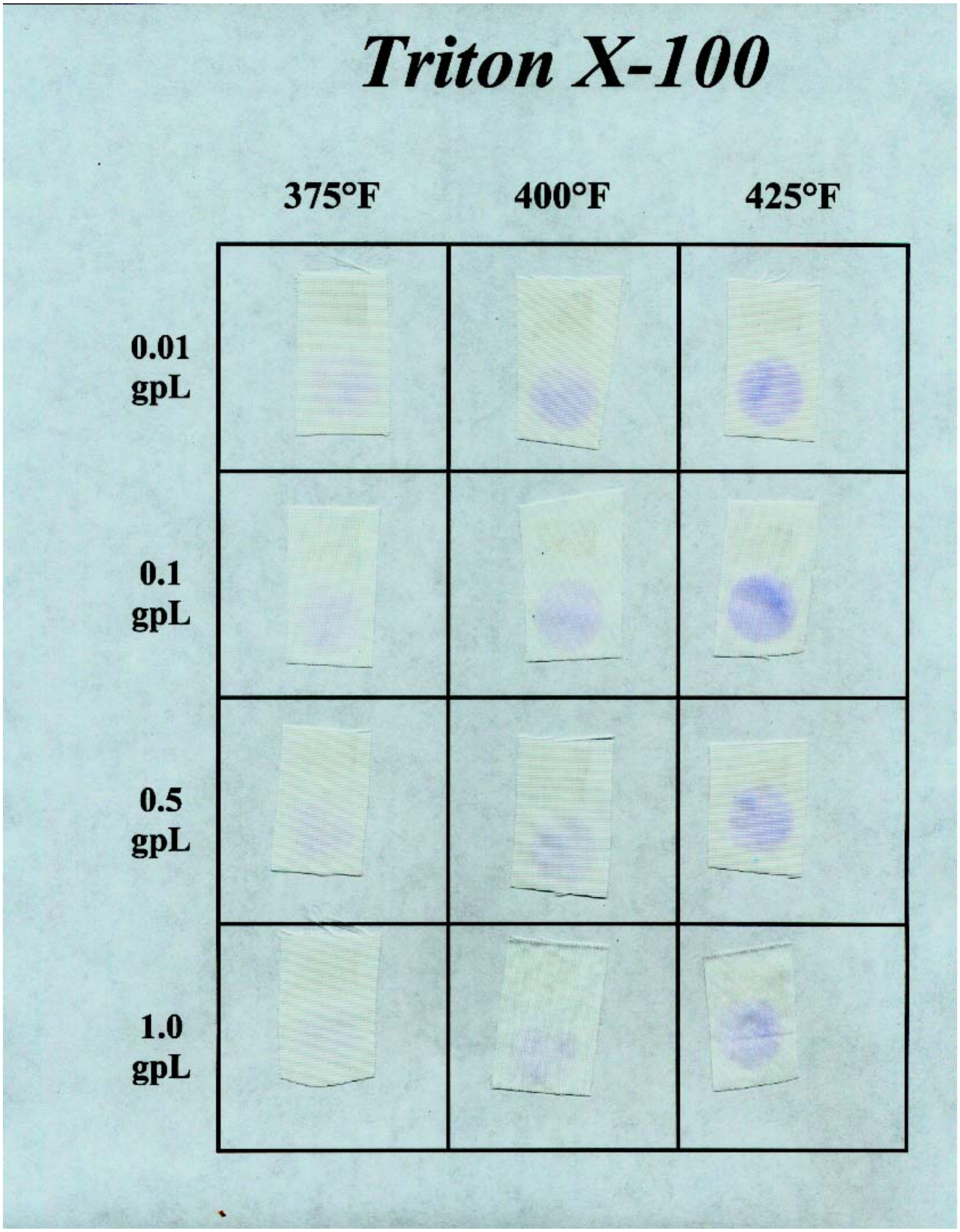


Figure 38. C.I. Disperse Blue 27 Vaporization in Presence of Triton™ X-100.

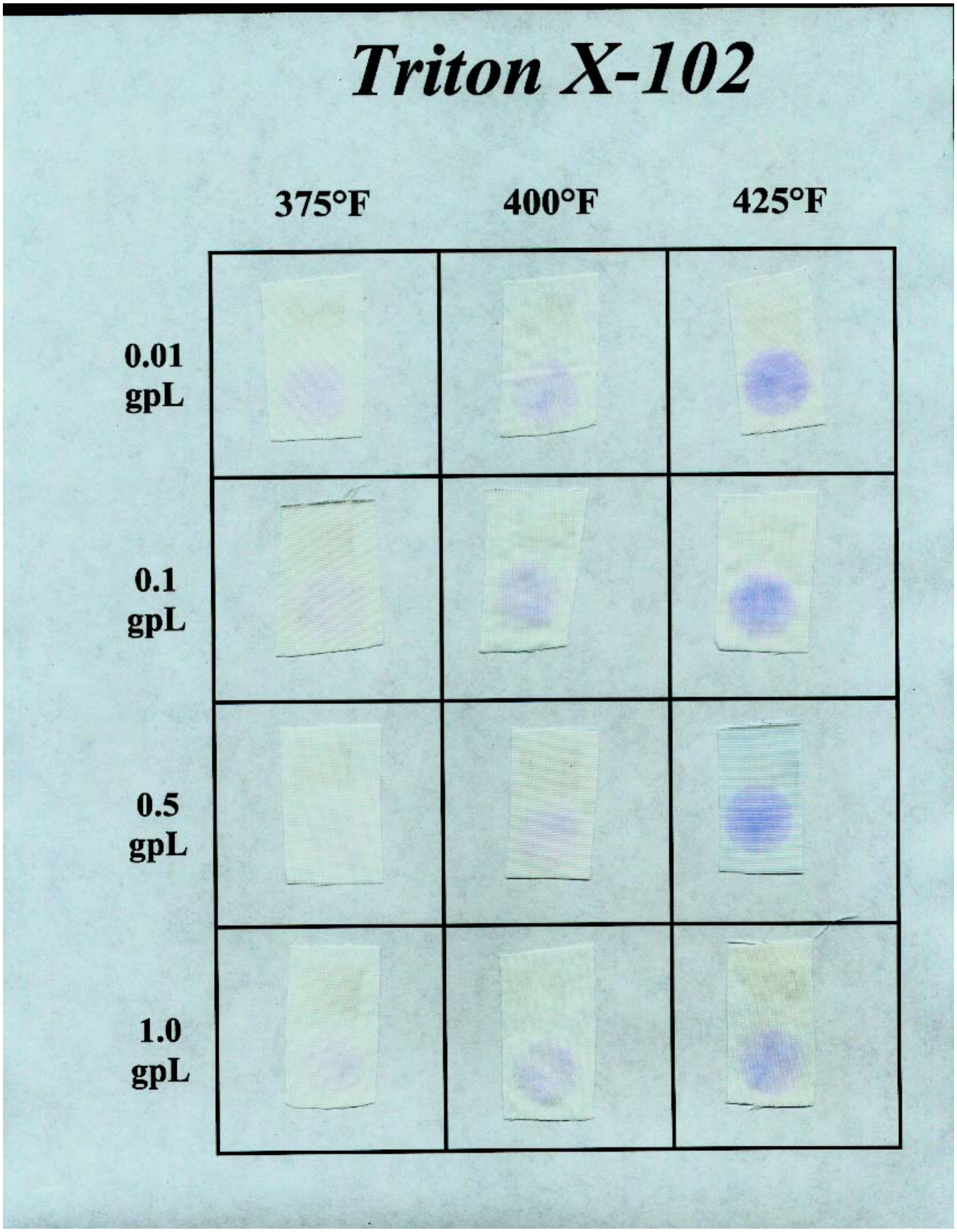


Figure 39. C.I. Disperse Blue 27 Vaporization in Presence of Triton™ X-102.

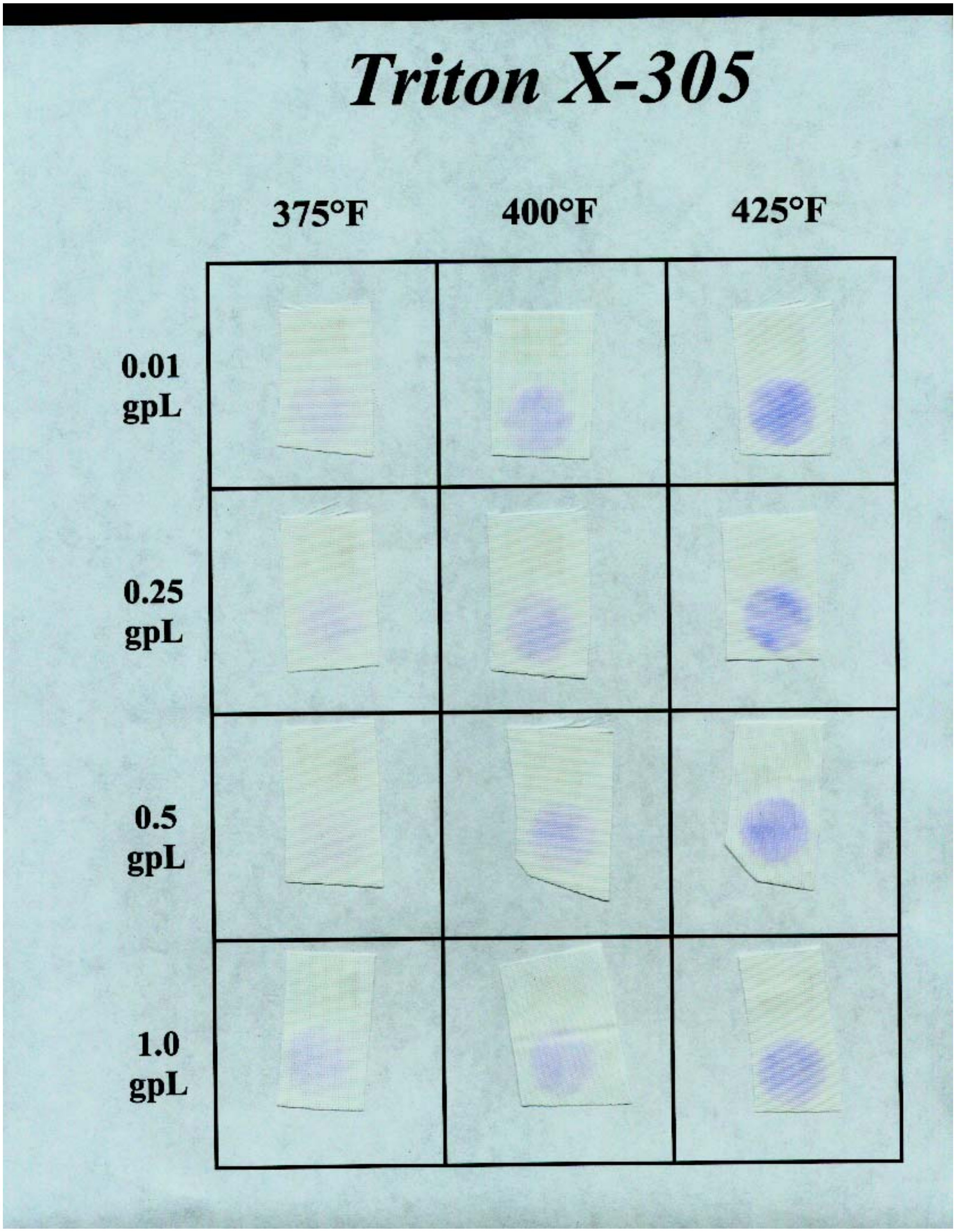


Figure 40. C.I. Disperse Blue 27 Vaporization in Presence of Triton™ X-305.

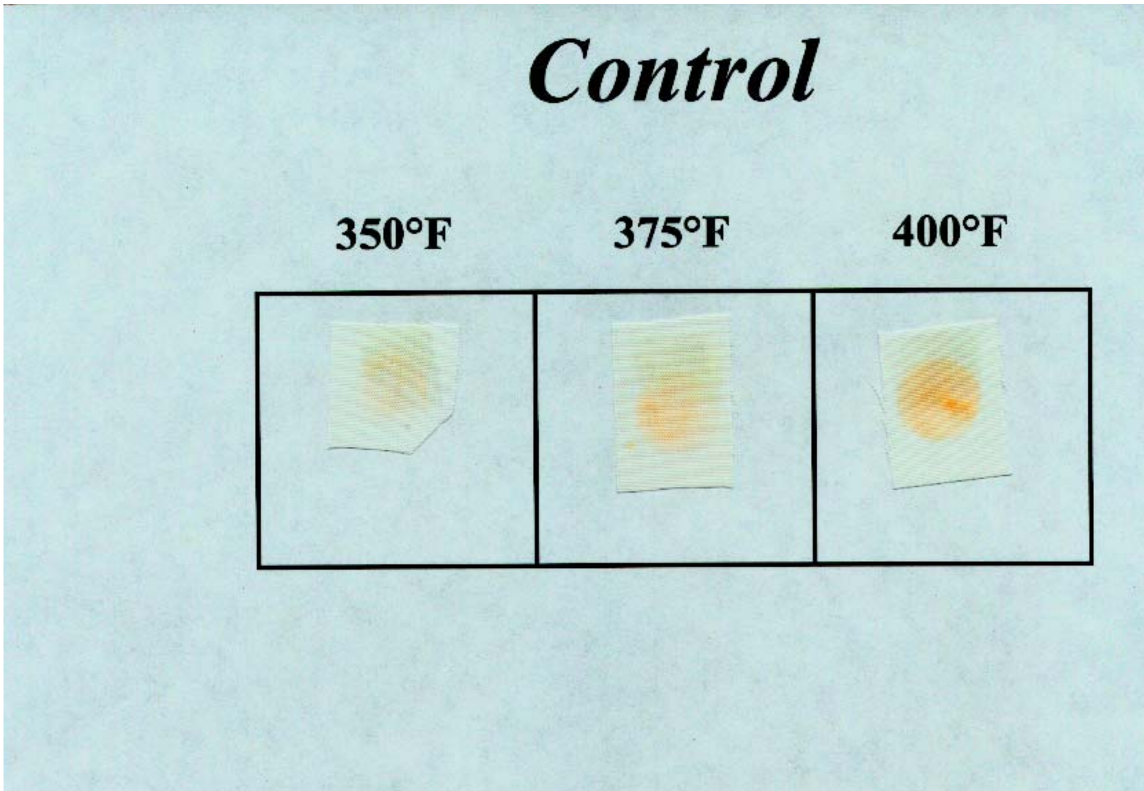


Figure 41. C.I. Disperse Brown 1 Vaporization in Control Samples.

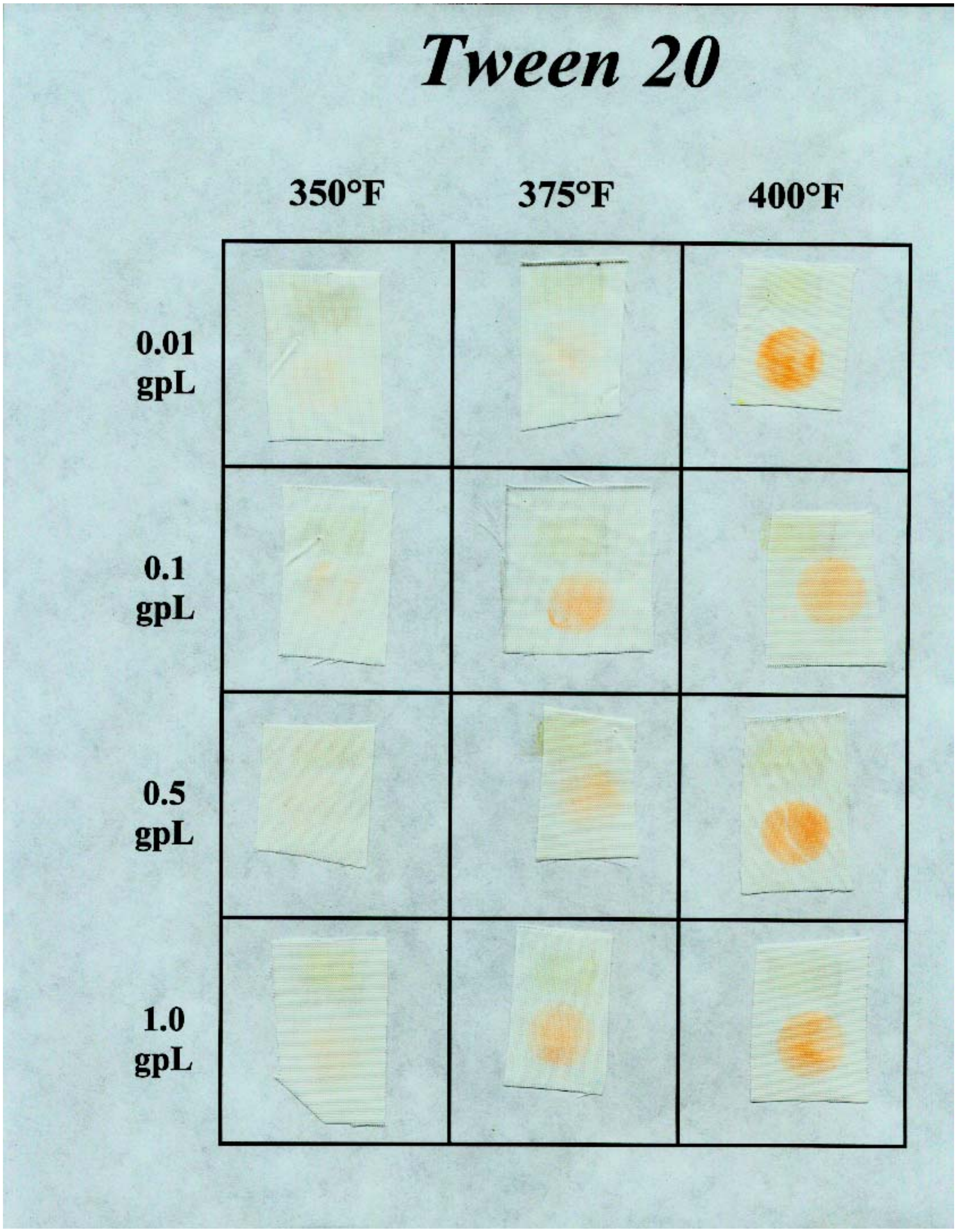


Figure 42. C.I. Disperse Brown 1 Vaporization in Presence of Tween® 20.

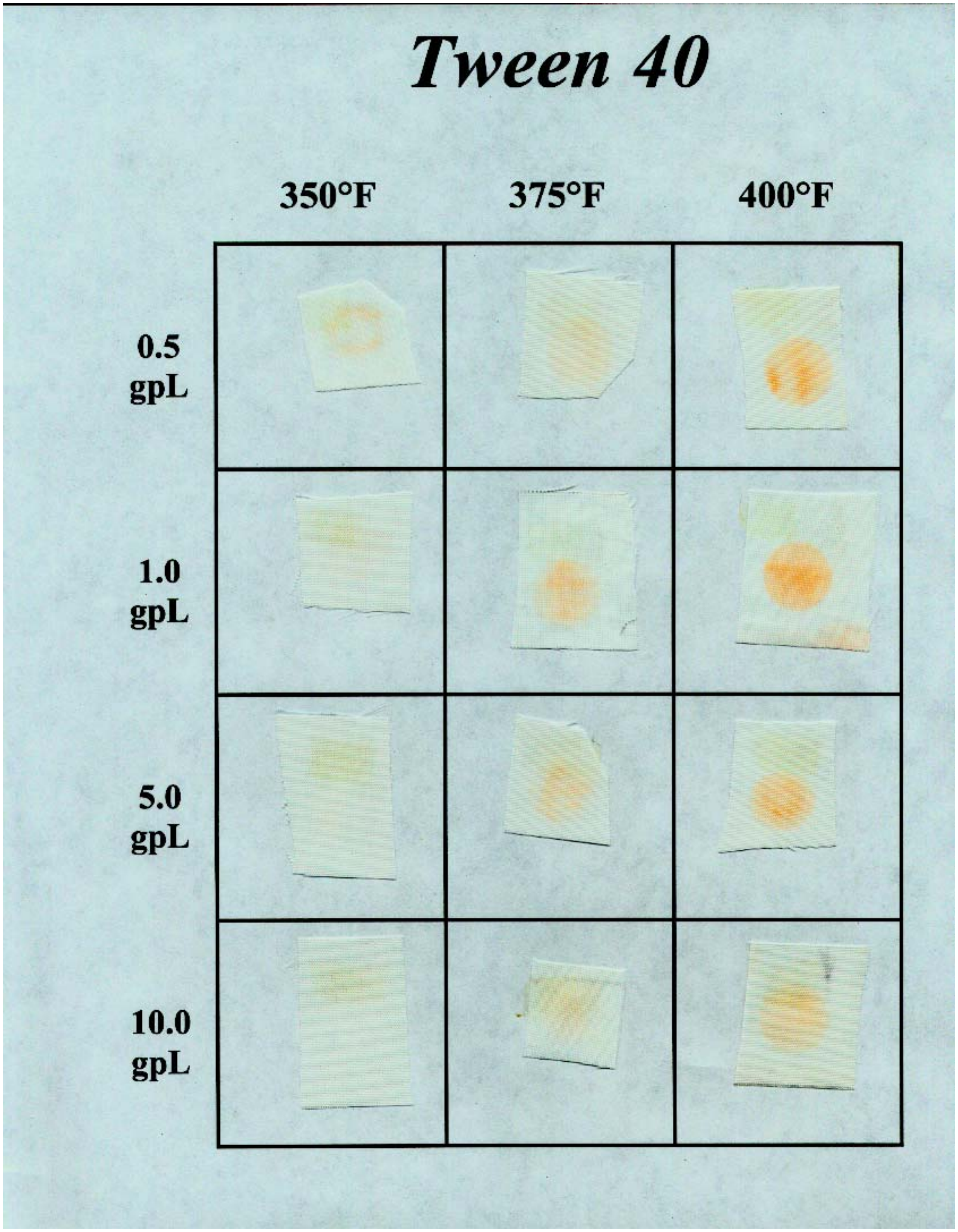


Figure 43. C.I. Disperse Brown 1 Vaporization in Presence of Tween® 40.

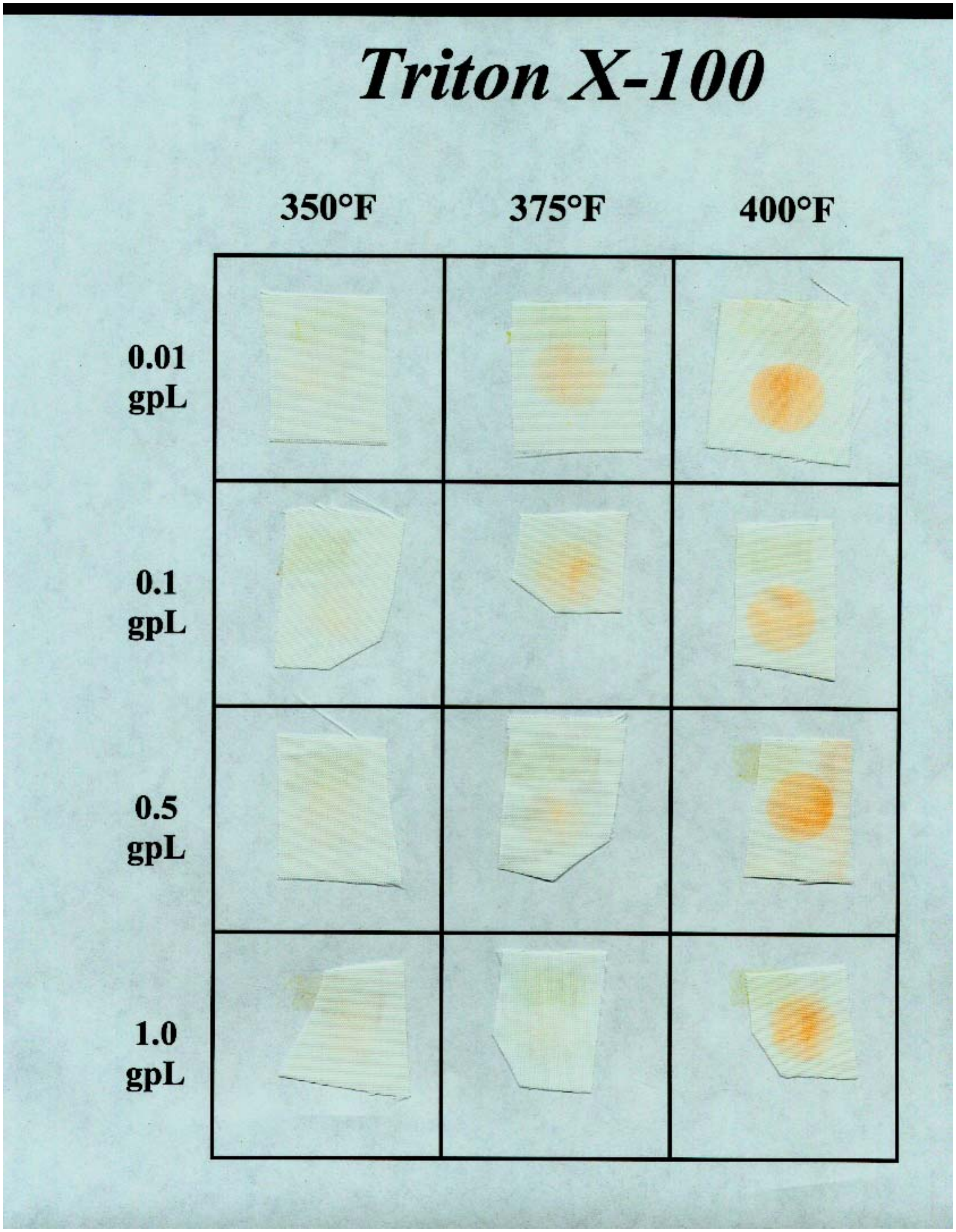


Figure 44. C.I. Disperse Brown 1 Vaporization in Presence of Triton™ X-100.

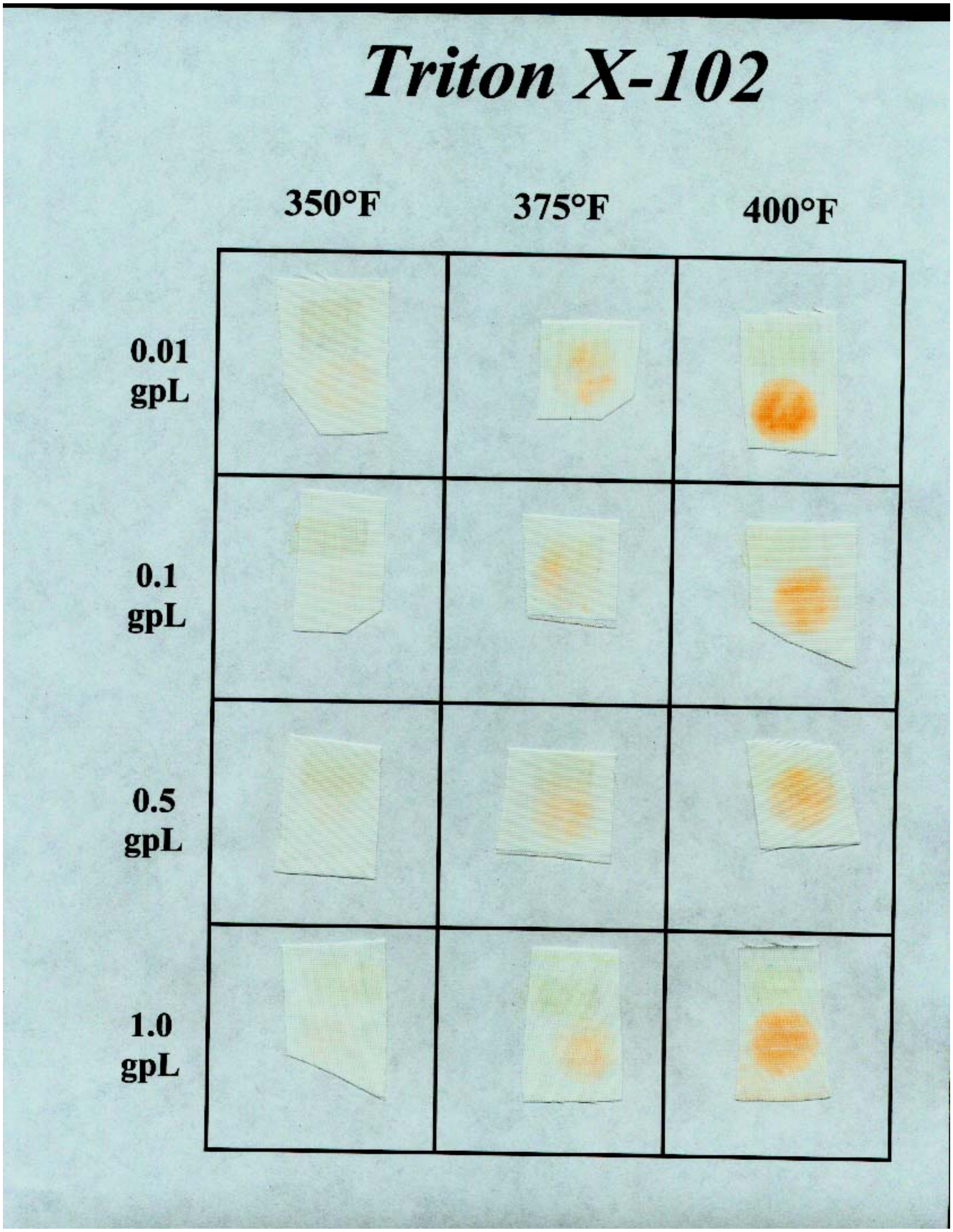


Figure 45. C.I. Disperse Brown 1 Vaporization in Presence of Triton™ X-102.

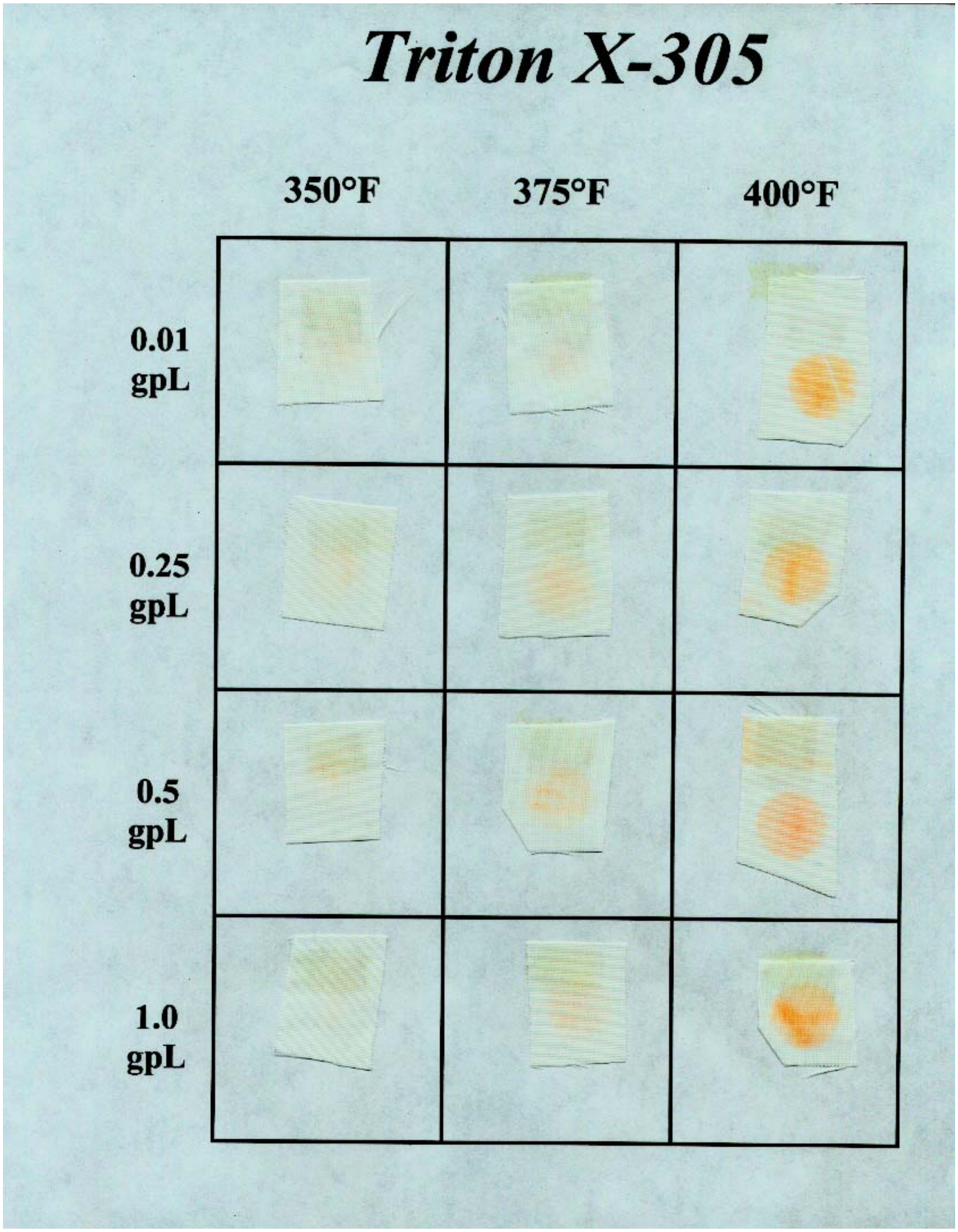


Figure 46. C.I. Disperse Brown 1 Vaporization in Presence of Triton™ X-305.

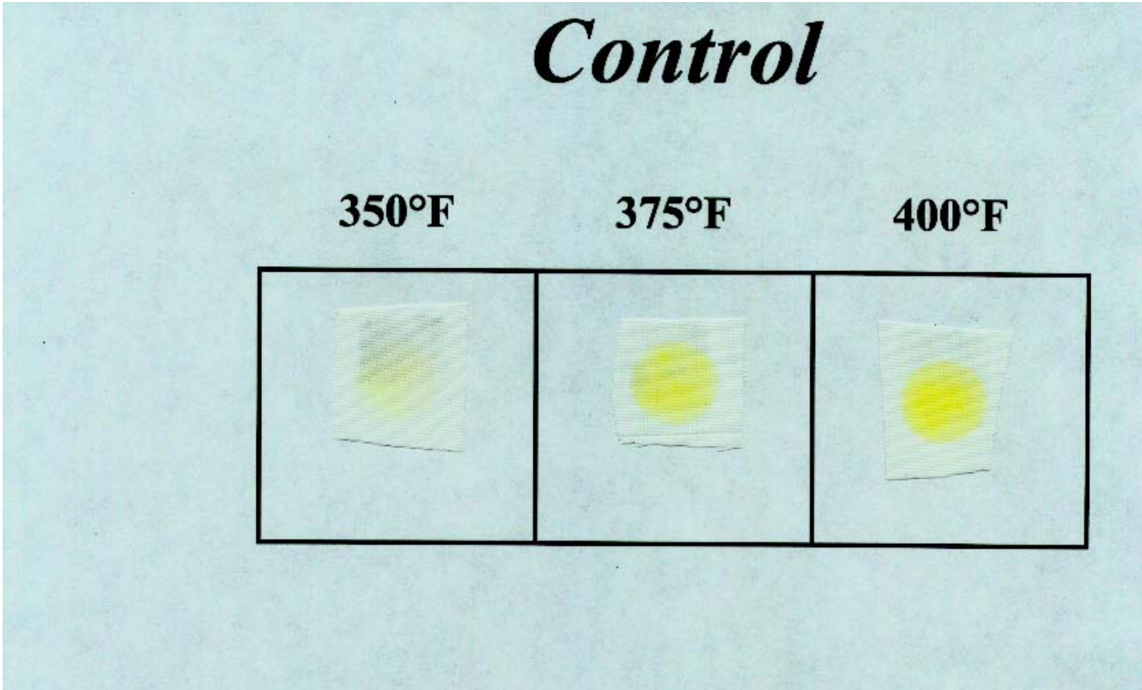


Figure 47. C.I. Disperse Yellow 42 Vaporization in Control Samples.

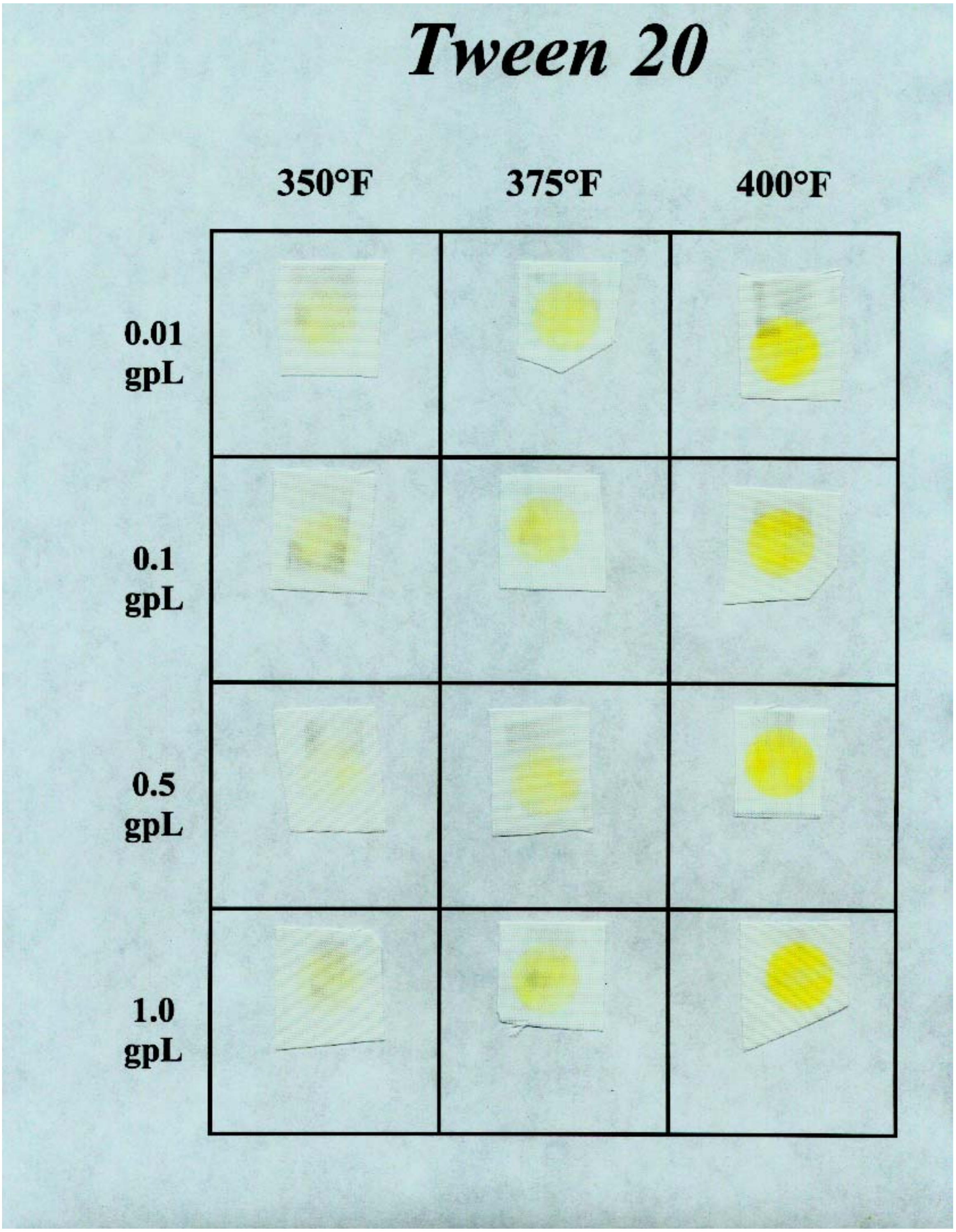


Figure 48. C.I. Disperse Yellow 42 Vaporization in Presence of Tween® 20.

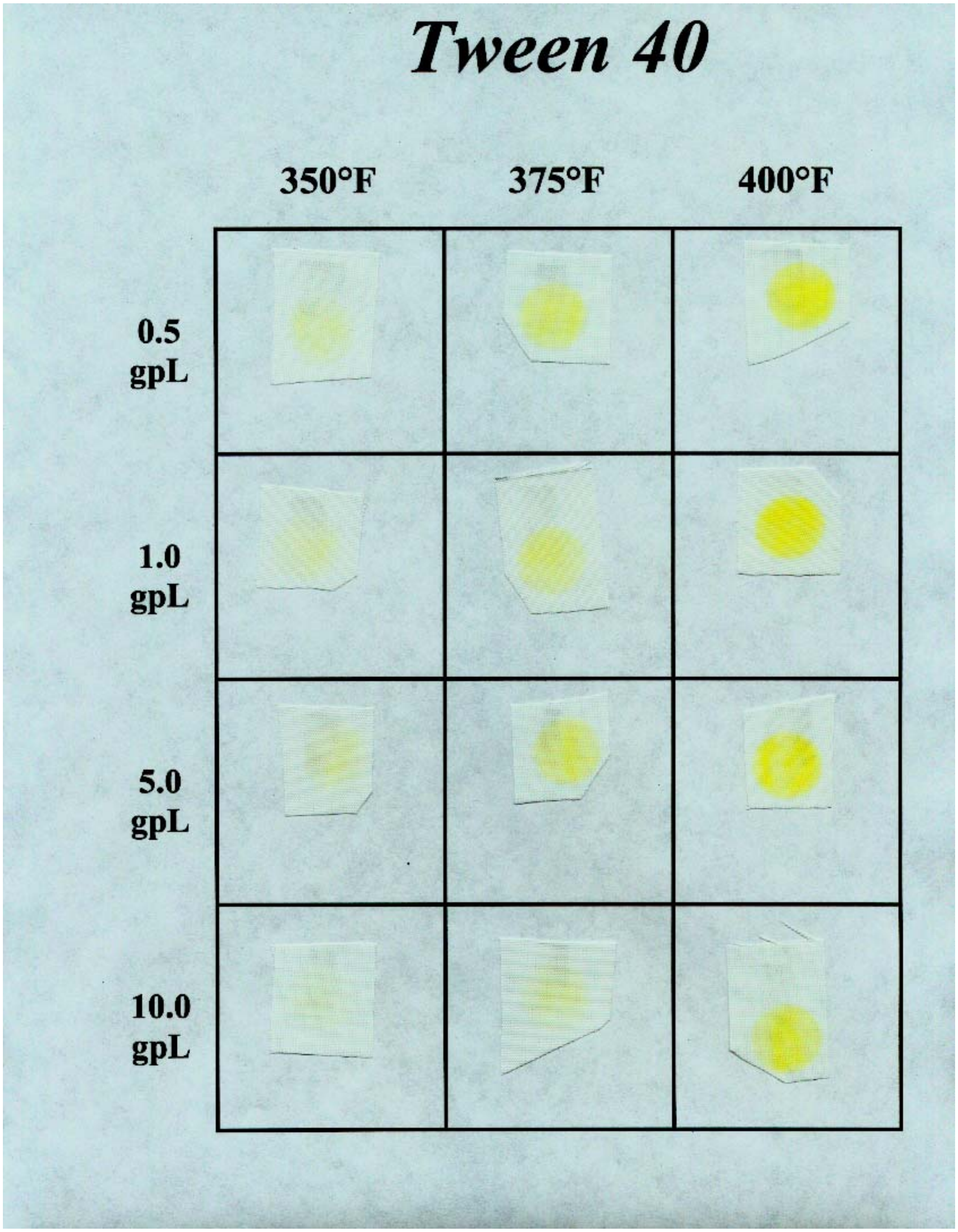


Figure 49. C.I. Disperse Yellow 42 Vaporization in Presence of Tween® 40.

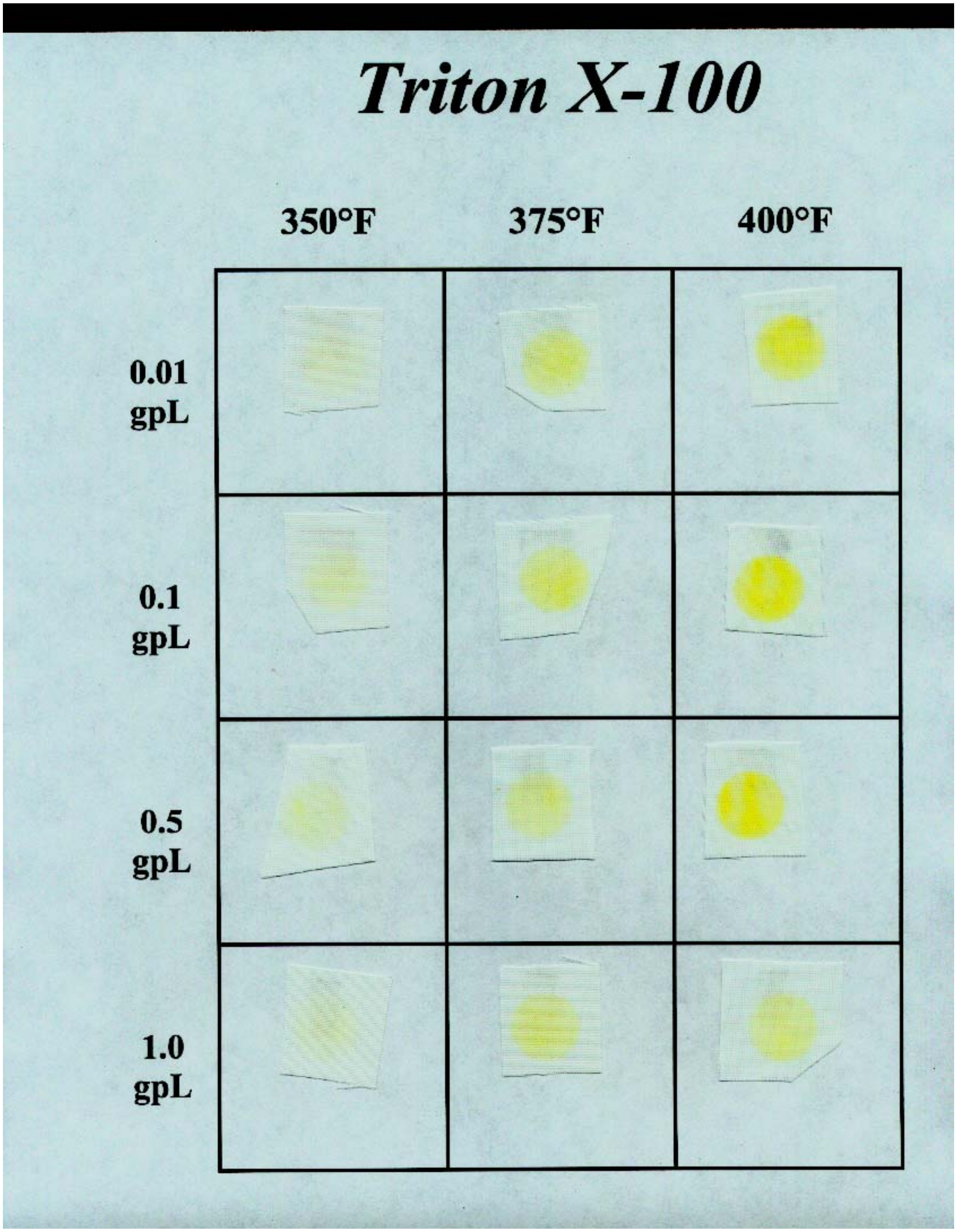


Figure 50. C.I. Disperse Yellow 42 Vaporization in Presence of Triton™ X-100.

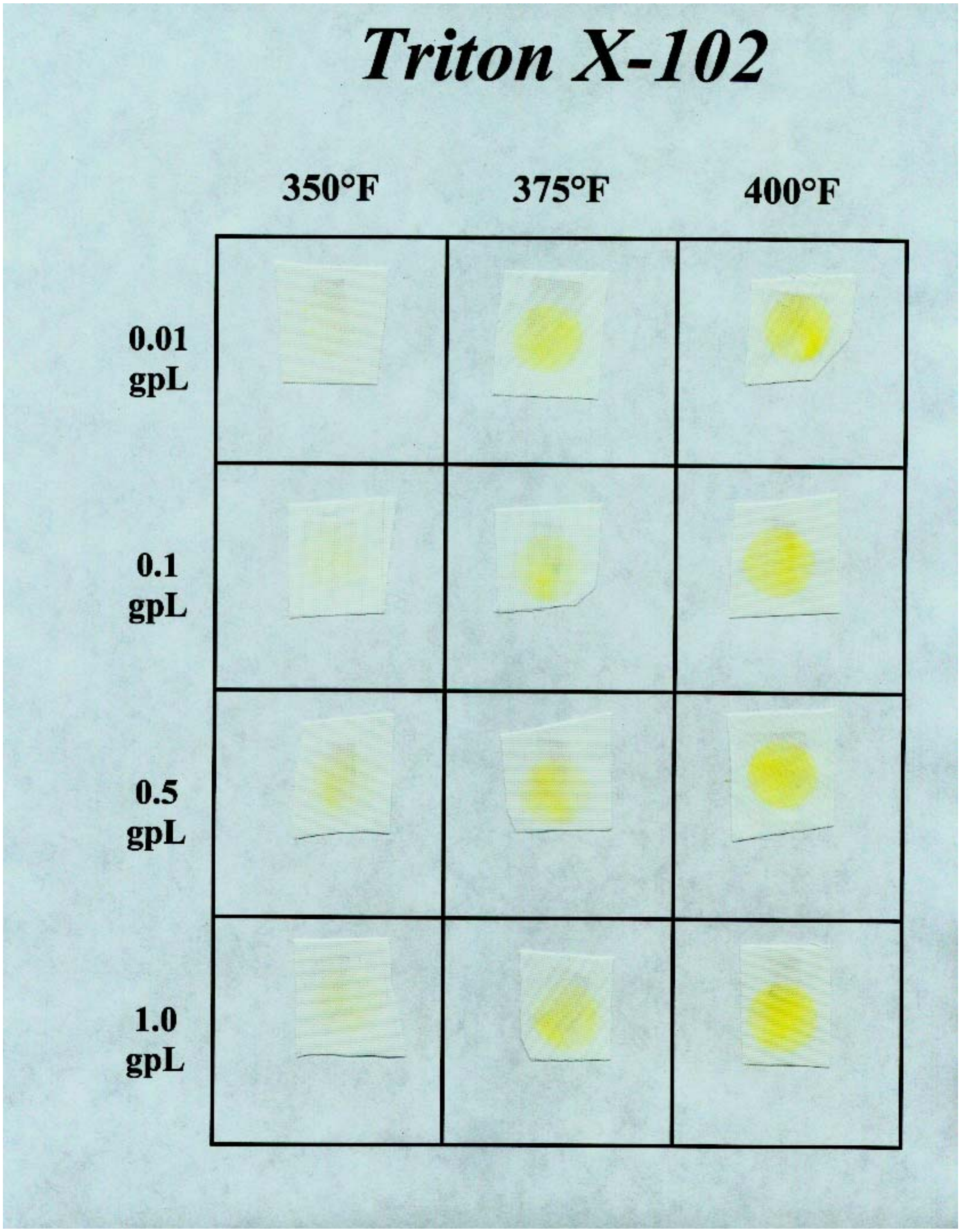


Figure 51. C.I. Disperse Yellow 42 Vaporization in Presence of Triton™ X-102.

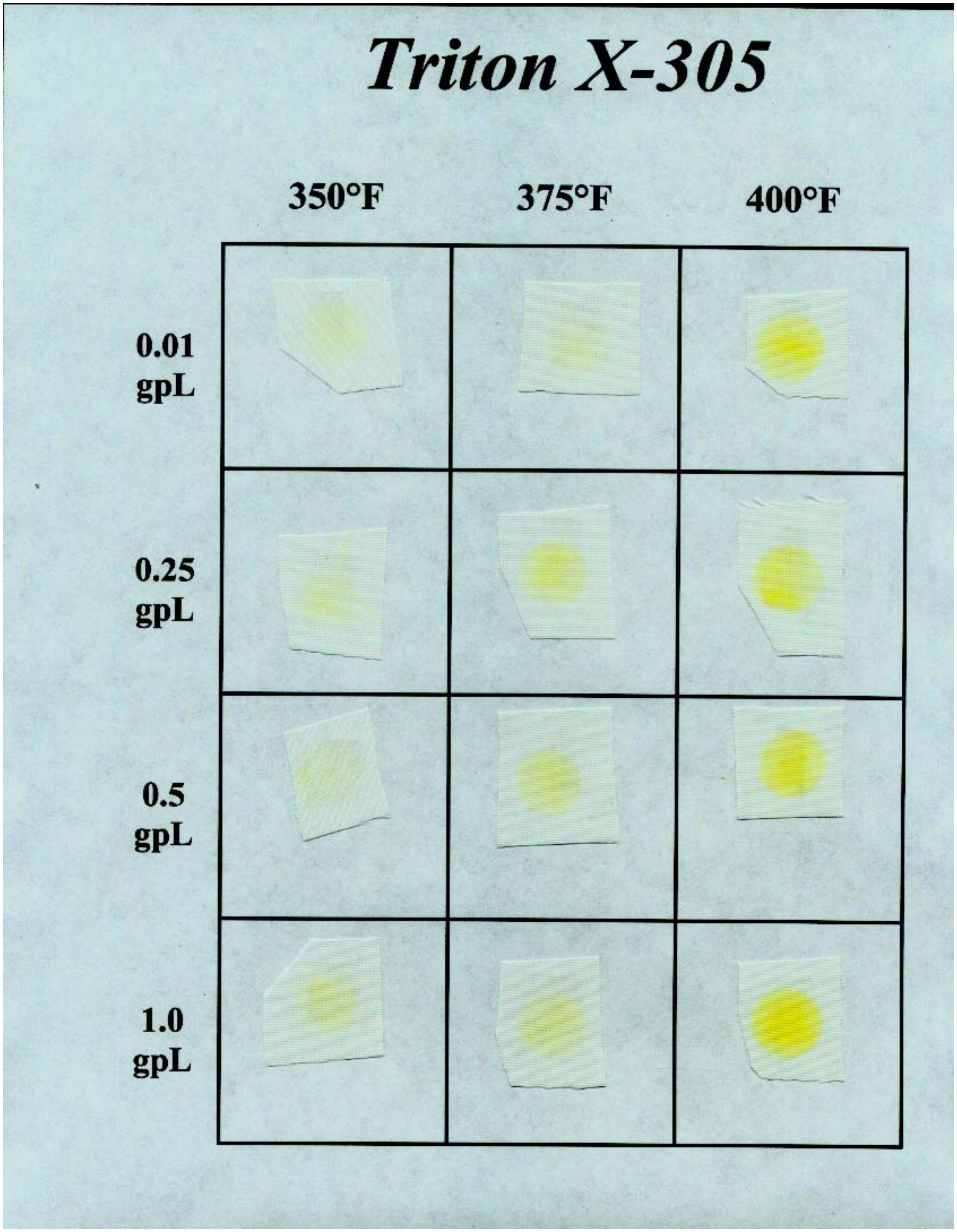


Figure 52. C.I. Disperse Yellow 42 Vaporization in Presence of Triton™ X-305.

decreased progressively with further increases in surfactant concentration.

Surfactant type influenced dye vaporization at the fixation temperature of 400°F but not at 375 and 425°F. In other words, in a comparison of samples treated with the same levels of surfactant concentration but with different surfactant types, no difference in dye vaporization between samples was observed at 375 and 425°F but differences were observed at the fixation temperature of 400°F. At 400°F, samples treated with Tween® 20 exhibited most dye vaporization among all surfactant types. Dye vaporization in samples treated with Triton™ X-100 and Triton™ X-305 was greater than that in samples treated with Tween® 40 and Triton™ X-102 but lesser than that in samples treated with Tween® 20. The difference in dye vaporization between samples treated with Triton™ X-100 and Triton™ X-305 did not appear significant.

C.I. Disperse Brown 1

Dye vaporization increased with increase in fixation temperature at all levels of surfactant type and surfactant concentration. Surfactant type did not influence dye vaporization.

The effect of surfactant concentration on dye vaporization varied with fixation temperature. At the fixation temperature of 400°F, surfactant concentration appeared to have no influence on dye vaporization. At the fixation temperatures of 350 and 375°F, dye vaporization decreased with increasing surfactant concentration.

C.I. Disperse Yellow 42

Dye vaporization increased with increase in fixation temperature at all levels of surfactant type and surfactant concentration. Surfactant type exerted no influence on dye vaporization.

The effect of surfactant concentration on dye vaporization varied with fixation temperature. At the fixation temperatures of 350 and 375° there was no difference in dye vaporization between control and surfactant treated samples. At 400°F, surfactant treated samples exhibit greater dye vaporization than control samples. No difference in dye vaporization is evident between samples treated with different surfactant concentrations.

Dye Decomposition

The absorbance intensities of control and heated dye solutions in surfactant, as evaluated from the areas under their absorbance curves over a specific range of wavelengths is given in Table 5. Dye decomposition as

Table 5. Absorbance Intensities of Control and Heated Dye Solutions in Surfactant.

Dye	**Surfactant**	**Wavelength Range (nm)**	**Absorbance Intensity**	
			Control	**Heated**
C.I. Disperse Blue 27	Tween® 20	400-700	448.3748	400.3629
	Tween® 40	400-700	314.9546	273.3374
	Triton™ X-100	400-700	324.1289	285.6893
	Triton™ X-102	505-700	105.2700	105.6126
	Triton™ X-305	400-700	441.6001	415.6992
C.I. Disperse Brown 1	Tween® 20	400-700	133.7822	51.9509
	Tween® 40	400-700	257.0487	71.9766
	Triton™ X-100	400-700	272.6944	207.1854
	Triton™ X-102	400-587	203.2304	95.2699
	Triton™ X-305	400-646	327.7986	254.0011
C.I. Disperse Yellow 42	Tween® 20	400-700	39.5427	12.1773
	Tween® 40	400-520	24.9463	6.3478
	Triton™ X-100	400-526	17.7083	11.3324
	Triton™ X-102	400-473	41.3622	20.0981
	Triton™ X-305	400-518	24.9462	6.3457

calculated from equation 3 is plotted as a function of surfactant type in Figure 53.

Among the three dyes used in this investigation, C.I. Disperse Blue 27, exhibits the least degree of decomposition in all surfactants. C.I. Disperse Yellow 42 exhibits the highest degree of decomposition in all surfactants except in Triton™ X-102, and the degree C.I. Disperse Brown 1 decomposition falls between the blue and yellow dyes. In general, the dyes appear to exhibit a greater degree of decomposition in the Tween® series of surfactants, as compared to the Triton™ series, with the exception of C.I. Disperse Yellow 42 decomposition in Triton™ X-102.

The observations from the experiments on dye decomposition do not yield any direct information about dye decomposition on the fabric surface at the fixation temperatures used in this investigation. It was considered unsafe to test dye decomposition in surfactants at the fixation temperatures used in this investigation since the flash points of these surfactants, as reported in product literature, lie in the range of 300-500°F. The observations from this experiment indicate that dye decomposition in surfactant is likely to occur at thermo-

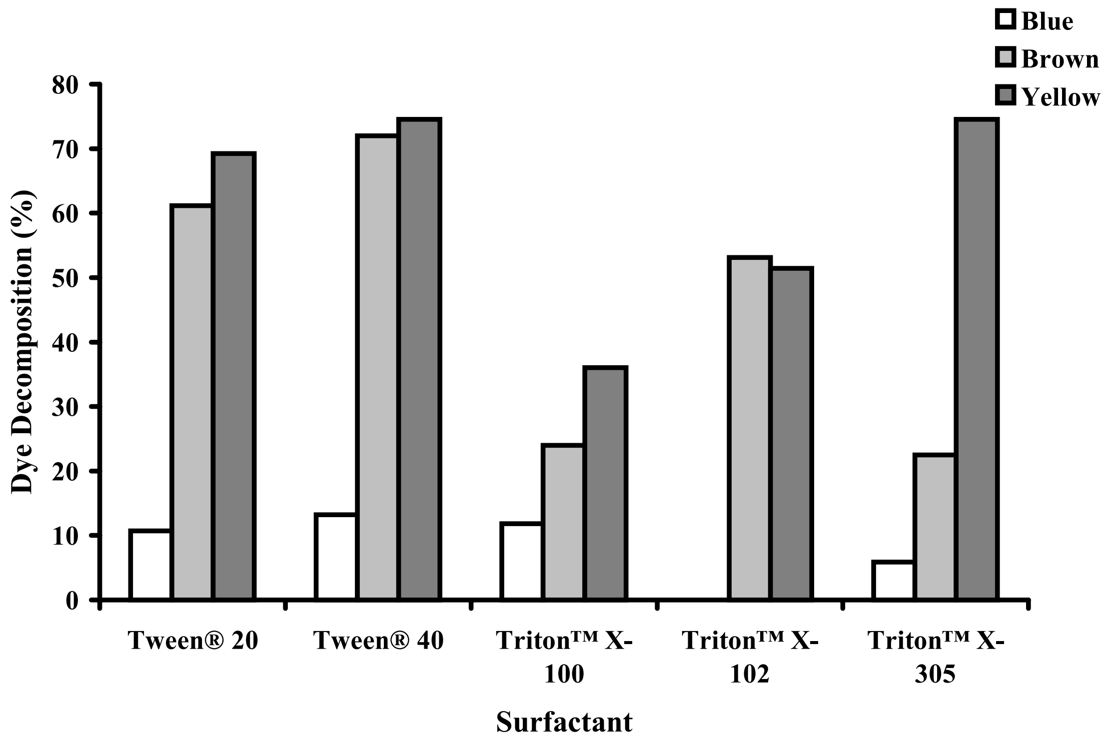


Figure 53. Dye Decomposition in Surfactants.

fixation temperatures and may exert a significant influence on dye fixation, though no information can be deduced about the extent of dye decomposition that occurs during thermo-fixation.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

From the results of the experiments conducted in this investigation, it is evident that non-ionic surfactants exerted a significant influence on dye fixation, the nature of which depended on surfactant concentration in pad liquor and thermo-fixation temperature. It is also clear that the influence was not identical for all combinations of dyes and surfactants, indicating that a measure of specificity governed dye-surfactant interactions.

Dye fixation values for the blue and brown dyes were evaluated by the direct method, and those for the yellow dye were evaluated by the indirect method. In the experiment on dye decomposition, it was observed that the yellow dye exhibits a significant degree of decomposition in surfactants. Hence, it is difficult to draw any conclusions from the dye fixation values of the yellow dye. Dye fixation values for the blue and brown dyes are thus more useful for drawing conclusions about the influence of non-ionic surfactants on dye fixation in the thermosol process.

For the brown and blue dyes, in general, dye fixation increased with increase in fixation temperature. The influence of surfactant concentration on dye fixation was not the same for both dyes. In case of the blue dye, all surfactant-treated samples exhibited greater dye fixation than control samples. In case of the brown dye, samples treated with small amounts of surfactants exhibited greater dye fixation than control samples while samples treated with large amounts of surfactant exhibited lower dye fixation than control samples. In case of both dyes, dye fixation was observed to first increase and then decrease with increasing surfactant concentration.

The CMC values of the surfactants used in this investigation lie in the range of 0.25-1.0 g/L. In analyzing the effect of surfactant CMC on dye pick up, dye fixation values of samples treated with 1.0 g/L were compared with those of samples treated with 0, 0.01 and 0.10 g/L surfactant so that observations from all surfactants could be analyzed simultaneously.

For both the blue and brown dyes, samples treated with surfactants at concentrations below surfactant CMC exhibited greater dye fixation than those treated with surfactant at concentrations above surfactant CMC. From the plots of dye fixation against surfactant concentration for the two dyes, shown in Figures 20-29, it can be seen that the surfactant concentration at which dye fixation begins to decrease is not always the surfactant CMC, but is a concentration that lies either above or below it.

Increased dye fixation, for the blue and brown dyes, in the presence of small amounts of surfactants cannot be attributed to increased dye pickup by fabric from the pad bath due to the presence of surfactants. On analyzing dye pick up values, for the blue and brown dyes, it was found that the dye pick up values in samples padded from liquors containing no surfactant were not significantly different from those in samples padded from liquors containing surfactant. This result does not support the hypothesis of Fox et al. [16], who attribute any increase in dye fixation, upon addition of wetting agents, to an increase in dye pick up from the pad bath due to their presence.

The vaporization tendency of dyes did not appear to exert any influence on the trends observed in dye fixation. It was observed that vaporization of the blue dye decreased with increase in surfactant concentration; but dye fixation first increased and then decreased with increasing surfactant concentration. Moreover, dye fixation in all surfactant-treated samples was greater than in control samples.

In case of the brown dye, vaporization was observed to decrease with increasing surfactant concentration at the fixation temperatures of 300 and 350°F, and all samples exhibited the same degree of vaporization at 400°F. On the other hand, dye fixation values showed an increase followed by a decrease with increasing surfactant concentration at all fixation temperatures. Dye fixation in samples treated with 5.0 and 10.0 g/L surfactant was significantly lower than that in control samples at all fixation temperatures while there was no discernible difference in dye vaporization between the two samples at the fixation temperature of 400°F.

This result does not support the hypothesis of Karmarkar and Hakim [51] who proposed that dye-surfactant complexes are formed by the aggregation of dye and surfactant molecules, resulting in decreased dye surface area, leading to decreased dye vaporization and to decreased dye fixation.

The results obtained in this investigation are most satisfactorily explained in the context of "medium transfer" mechanism of dye transfer from cotton to polyester during thermo-fixation. In the medium transfer mechanism, dyestuff is believed to dissolve in the melt of auxiliaries that forms and coats fibers at thermo-fixation temperatures and dye transfer to polyester is believed to occur from the dye solution in auxiliary melt.

Surfactants, at low concentrations may act as "fixation accelerants", accelerating dye dissolution in the auxiliary melt thereby increasing the overall rate of thermosol dyeing. At high concentrations of surfactant, retardation of dye fixation may result from the increased retention of dye in surfactant with increase in surfactant amount, due to the affinity of dye for surfactant.

Similar results are reported by Hashimoto and Imai [52], who observed that non-ionic surfactants accelerated the rate of dyeing and intensified dye fixation in disperse dyeing of polyester by superheated steam or hot air. The authors found that the behavior of disperse dye in non-ionic surfactant was influenced by the amount of water in the system. As the amount of water in the system increased there was an increase in dye diffusion rate and partition coefficient of dye with a concurrent decrease of dye solubility in surfactant.

The affinity of a dye for a surfactant is dictated by factors such as dye and surfactant hydrophobicity and depends on their chemical composition and molecular structures. Hence, the influence of a particular non-ionic surfactant on dyeing behavior would be dye specific. For a given surfactant, the concentration range in which dye fixation is enhanced and the concentration at which dye fixation begins to decrease would be different for different dyes.

In conclusion, the results of this investigation show that non-ionic surfactants may influence dye fixation in the thermosol process, the degree of influence being subject to the affinity of dye for the surfactant. At low concentrations surfactants may function as fixation accelerants, accelerating the rate of dye dissolution in auxiliary melt, thereby increasing the overall rate of thermo-fixation. At high surfactant concentrations, dye retention in surfactant may result in surfactants exerting an adverse influence on dye fixation. In addition, the propensity of a dye to decompose in a given surfactant may contribute to the influence that non-ionic surfactants exert on disperse dye fixation in the thermosol process.

Recommendations

Further research is recommended in the following areas:

1. The effect of anionic surfactants, present in commercial disperse dye formulations as dispersing agents, on the results of this investigation have not been considered.

The combined effect of anionic dispersing agents and non-ionic surfactants on dye fixation should be studied, by using dyestuff formulations that are controlled with respect to anionic surfactants.

2. The results of this investigation are kinetic in nature. No attempts were made to achieve equilibrium conditions. The effect of non-ionic surfactants on equilibrium dye fixation should be studied.
3. The mechanism of dye transfer from cotton to polyester may change with fabric type, and so the effect of fabric construction on the influence of non-ionic surfactants on dye fixation should be studied.

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APPENDIX A

STATISTICAL ANALYSES OF DYE PICKUP

```
options ls=78 ps=66 formdlim='*' pageno=1;

title1 'Effect of Surfactant Type and Concentration on Dye Pickup';
title2 'Dye: C.I. Disperse Blue 27';

data tbglf;
  input surf replicat conc dc;
  cards;
 1      1       1       0.237
1       2       1       0.226
1       3       1       0.224
1       1       2       0.219
1       2       2       0.235
1       3       2       0.225
1       1       3       0.217
1       2       3       0.225
1       3       3       0.222
1       1       5       0.170
1       2       5       0.166
1       3       5
1       1       6       0.152
1       2       6       0.162
1       3       6       0.163
2       1       1       0.237
2       2       1       0.226
2       3       1       0.224
2       1       5       0.202
2       2       5       0.211
2       3       5       0.202
2       1       6       0.180
2       2       6       0.178
2       3       6       0.176
2       1       7       0.157
2       2       7       0.166
2       3       7       0.163
2       1       8       0.175
2       2       8       0.177
2       3       8       0.182
3       1       1       0.237
3       2       1       0.226
3       3       1       0.224
3       1       2       0.200
3       2       2       0.263
3       3       2       0.265
3       1       3       0.243
3       2       3       0.247
3       3       3       0.215
3       1       5       0.217
3       2       5       0.182
3       3       5       0.179
3       1       6       0.185
3       2       6       0.152
3       3       6       0.142
4       1       1       0.237
4       2       1       0.226
4       3       1       0.224
```

```
4       1       2       0.145
4       2       2       0.226
4       3       2       0.236
4       1       3       0.221
4       2       3       0.234
4       3       3       0.228
4       1       5       0.170
4       2       5       0.184
4       3       5       0.181
4       1       6       0.126
4       2       6       0.156
4       3       6       0.153
5       1       1       0.237
5       2       1       0.226
5       3       1       0.224
5       1       2       0.232
5       2       2       0.225
5       3       2       0.228
5       1       4       0.211
5       2       4       0.222
5       3       4       0.222
5       1       5       0.225
5       2       5       0.228
5       3       5       0.218
5       1       6       0.221
5       2       6       0.217
5       3       6       0.228
;

proc glm data=tbglf;
  class surf replicat conc;
  model dc=surf replicat(surf) conc conc*surf;
  test h=surf e=replicat(surf);
  means surf/bon;
  means conc/bon;
run;
```

Effect of Surfactant Type and Concentration on Dye Pickup
Dye: C.I. Disperse Blue 27

The GLM Procedure

Class Level Information

Class	Levels	Values
surf	5	1 2 3 4 5
replicat	3	1 2 3
conc	8	1 2 3 4 5 6 7 8

Number of observations 74

The GLM Procedure

Dependent Variable: dc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	34	0.31855719	0.00936933	0.98	0.5265
Error	39	0.37456466	0.00960422		
Corrected Total	73	0.69312185			

R-Square	Coeff Var	Root MSE	dc Mean
0.459598	45.22659	0.098001	0.216689

Source	DF	Type I SS	Mean Square	F Value	Pr > F
surf	4	0.04858597	0.01214649	1.26	0.3003
replicat(surf)	10	0.08537233	0.00853723	0.89	0.5516
conc	7	0.04951146	0.00707307	0.74	0.6425
surf*conc	13	0.13508743	0.01039134	1.08	0.4016

Source	DF	Type III SS	Mean Square	F Value	Pr > F
surf	4	0.02306053	0.00576513	0.60	0.6647
replicat(surf)	10	0.09889584	0.00988958	1.03	0.4374
conc	7	0.05698044	0.00814006	0.85	0.5555
surf*conc	13	0.13508743	0.01039134	1.08	0.4016

Tests of Hypotheses Using the Type III MS for replicat(surf) as an Error Term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
surf	4	0.02306053	0.00576513	0.58	0.6822

Bonferroni (Dunn) t Tests for dc

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than Tukey's for all pairwise comparisons.

Alpha	0.05
Error Degrees of Freedom	39
Error Mean Square	0.009604
Critical Value of t	2.97561

Comparisons significant at the 0.05 level are indicated by ***.

surf Comparison	Difference Between Means	Simultaneous 95% Confidence Limits	
1 - 5	0.03938	-0.06899	0.14774
1 - 3	0.05184	-0.05652	0.16021
1 - 4	0.06718	-0.04119	0.17554
1 - 2	0.07324	-0.03512	0.18161
5 - 1	-0.03938	-0.14774	0.06899
5 - 3	0.01247	-0.09402	0.11895
5 - 4	0.02780	-0.07868	0.13428
5 - 2	0.03387	-0.07262	0.14035
3 - 1	-0.05184	-0.16021	0.05652
3 - 5	-0.01247	-0.11895	0.09402
3 - 4	0.01533	-0.09115	0.12182
3 - 2	0.02140	-0.08508	0.12788
4 - 1	-0.06718	-0.17554	0.04119
4 - 5	-0.02780	-0.13428	0.07868
4 - 3	-0.01533	-0.12182	0.09115
4 - 2	0.00607	-0.10042	0.11255
2 - 1	-0.07324	-0.18161	0.03512
2 - 5	-0.03387	-0.14035	0.07262
2 - 3	-0.02140	-0.12788	0.08508
2 - 4	-0.00607	-0.11255	0.10042
5 - 1	0.02000	-0.10000	0.14000
5 - 3	0.02100	-0.11757	0.15957
5 - 2	0.02408	-0.10320	0.15136
5 - 4	0.03067	-0.17718	0.23852
5 - 8	0.07100	-0.13685	0.27885
5 - 6	0.07479	-0.04734	0.19691
5 - 7	0.08700	-0.12085	0.29485
1 - 5	-0.02000	-0.14000	0.10000
1 - 3	0.00100	-0.13757	0.13957
1 - 2	0.00408	-0.12320	0.13136
1 - 4	0.01067	-0.19718	0.21852
1 - 8	0.05100	-0.15685	0.25885
1 - 6	0.05479	-0.06734	0.17691
1 - 7	0.06700	-0.14085	0.27485
3 - 5	-0.02100	-0.15957	0.11757
3 - 1	-0.00100	-0.13957	0.13757
3 - 2	0.00308	-0.14183	0.14800
3 - 4	0.00967	-0.20943	0.22876
3 - 8	0.05000	-0.16909	0.26909

3	-	6	0.05379	-0.08662	0.19420
3	-	7	0.06600	-0.15309	0.28509
2	-	5	-0.02408	-0.15136	0.10320
2	-	1	-0.00408	-0.13136	0.12320
2	-	3	-0.00308	-0.14800	0.14183
2	-	4	0.00658	-0.20555	0.21872
2	-	8	0.04692	-0.16522	0.25905
2	-	6	0.05070	-0.07858	0.17999
2	-	7	0.06292	-0.14922	0.27505
4	-	5	-0.03067	-0.23852	0.17718
4	-	1	-0.01067	-0.21852	0.19718
4	-	3	-0.00967	-0.22876	0.20943
4	-	2	-0.00658	-0.21872	0.20555
4	-	8	0.04033	-0.22800	0.30867
4	-	6	0.04412	-0.16496	0.25320
4	-	7	0.05633	-0.21200	0.32467
8	-	5	-0.07100	-0.27885	0.13685
8	-	1	-0.05100	-0.25885	0.15685
8	-	3	-0.05000	-0.26909	0.16909
8	-	2	-0.04692	-0.25905	0.16522
8	-	4	-0.04033	-0.30867	0.22800
8	-	6	0.00379	-0.20530	0.21287
8	-	7	0.01600	-0.25233	0.28433
6	-	5	-0.07479	-0.19691	0.04734
6	-	1	-0.05479	-0.17691	0.06734
6	-	3	-0.05379	-0.19420	0.08662
6	-	2	-0.05070	-0.17999	0.07858
6	-	4	-0.04412	-0.25320	0.16496
6	-	8	-0.00379	-0.21287	0.20530
6	-	7	0.01221	-0.19687	0.22130
7	-	5	-0.08700	-0.29485	0.12085
7	-	1	-0.06700	-0.27485	0.14085
7	-	3	-0.06600	-0.28509	0.15309
7	-	2	-0.06292	-0.27505	0.14922
7	-	4	-0.05633	-0.32467	0.21200
7	-	8	-0.01600	-0.28433	0.25233
7	-	6	-0.01221	-0.22130	0.19687

```
options ls=78 ps=66 formdlim='*' pageno=1;

title1 'Effect of Surfactant Type and Concentration on Dye Pickup';
title2 'Dye: C.I. Disperse Brown 1';

data tbp3r;
  input surf replicat conc dc;
  cards;

1       1       1       0.416
1       2       1       0.434
1       3       1       0.446
1       1       2       0.418
1       2       2       0.407
1       3       2       0.408
1       1       3       0.368
1       2       3       0.441
1       3       3       0.422
1       1       5       0.429
1       2       5       0.440
1       3       5       0.435
1       1       6       0.493
1       2       6       0.456
1       3       6       0.466
2       1       1       0.416
2       2       1       0.434
2       3       1       0.446
2       1       5       0.445
2       2       5       0.457
2       3       5       0.386
2       1       6       0.449
2       2       6       0.433
2       3       6       0.428
2       1       7       0.418
2       2       7       0.436
2       3       7       0.443
2       1       8       0.410
2       2       8       0.399
2       3       8       0.410
3       1       1       0.416
3       2       1       0.434
3       3       1       0.446
3       1       2       0.380
3       2       2       0.364
3       3       2       0.406
3       1       3       0.414
3       2       3       0.412
3       3       3       0.431
3       1       5       0.420
3       2       5       0.427
3       3       5       0.412
3       1       6       0.309
3       2       6       0.407
3       3       6       0.405
4       1       1       0.416
4       2       1       0.434
4       3       1       0.446
```

```
4       1       2       0.409
4       2       2       0.413
4       3       2       0.407
4       1       3       0.362
4       2       3       0.393
4       3       3       0.407
4       1       5       0.396
4       2       5       0.391
4       3       5       0.412
4       1       6       0.422
4       2       6       0.402
4       3       6       0.399
5       1       1       0.416
5       2       1       0.434
5       3       1       0.446
5       1       2       0.417
5       2       2       0.426
5       3       2       0.438
5       1       4       0.398
5       2       4       0.434
5       3       4       0.368
5       1       5       0.400
5       2       5       0.407
5       3       5       0.430
5       1       6       0.409
5       2       6       0.449
5       3       6       0.434

;

proc glm data=tbp3r;
  class surf replicat conc;
  model dc=surf replicat(surf) conc conc*surf;
  test h=surf e=replicat(surf);
  means surf/scheffe;
  means conc/scheffe;
run;
```

Effect of Surfactant Type and Concentration on Dye Pickup
Dye: C.I. Disperse Brown 1

The GLM Procedure

Class Level Information

Class	Levels	Values
surf	5	1 2 3 4 5
replicat	3	1 2 3
conc	8	1 2 3 4 5 6 7 8

Number of observations 75

The GLM Procedure

Dependent Variable: dc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	34	0.03581181	0.00105329	2.42	0.0040
Error	40	0.01743693	0.00043592		
Corrected Total	74	0.05324875			

R-Square	Coeff Var	Root MSE	dc Mean
0.672538	4.989035	0.020879	0.418493

Source	DF	Type I SS	Mean Square	F Value	Pr > F
surf	4	0.00834621	0.00208655	4.79	0.0030
replicat(surf)	10	0.00497373	0.00049737	1.14	0.3577
conc	7	0.00760247	0.00108607	2.49	0.0319
surf*conc	13	0.01488940	0.00114534	2.63	0.0096

Source	DF	Type III SS	Mean Square	F Value	Pr > F
surf	4	0.00780441	0.00195110	4.48	0.0044
replicat(surf)	10	0.00497373	0.00049737	1.14	0.3577
conc	7	0.00760247	0.00108607	2.49	0.0319
surf*conc	13	0.01488940	0.00114534	2.63	0.0096

Tests of Hypotheses Using the Type III MS for replicat(surf) as an Error Term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
surf	4	0.00780441	0.00195110	3.92	0.0362

Scheffe's Test for dc

NOTE: This test controls the Type I experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	40
Error Mean Square	0.000436
Critical Value of F	2.60597
Minimum Significant Difference	0.0246

Means with the same letter are not significantly different.

Scheffe Grouping		Mean	N	surf
	A	0.431933	15	1
	A			
B	A	0.427333	15	2
B	A			
B	A	0.420400	15	5
B				
B		0.407267	15	4
B				
B		0.405533	15	3

The GLM Procedure

Scheffe's Test for dc

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than Tukey's for all pairwise comparisons.

Alpha	0.05
Error Degrees of Freedom	40
Error Mean Square	0.000436
Critical Value of F	2.24902

Comparisons significant at the 0.05 level are indicated by ***.

conc Comparison	Difference Between Means	Simultaneous 95% Confidence Limits	
7 - 1	0.000333	-0.052061	0.052727
7 - 6	0.008267	-0.044127	0.060661
7 - 5	0.013200	-0.039194	0.065594
7 - 2	0.024583	-0.028891	0.078058
7 - 8	0.026000	-0.041640	0.093640
7 - 3	0.026778	-0.028450	0.082006
7 - 4	0.032333	-0.035307	0.099974
1 - 7	-0.000333	-0.052727	0.052061
1 - 6	0.007933	-0.022316	0.038183
1 - 5	0.012867	-0.017383	0.043116
1 - 2	0.024250	-0.007835	0.056335

1	- 8	0.025667	-0.026727	0.078061
1	- 3	0.026444	-0.008485	0.061374
1	- 4	0.032000	-0.020394	0.084394
6	- 7	-0.008267	-0.060661	0.044127
6	- 1	-0.007933	-0.038183	0.022316
6	- 5	0.004933	-0.025316	0.035183
6	- 2	0.016317	-0.015768	0.048401
6	- 8	0.017733	-0.034661	0.070127
6	- 3	0.018511	-0.016418	0.053440
6	- 4	0.024067	-0.028327	0.076461
5	- 7	-0.013200	-0.065594	0.039194
5	- 1	-0.012867	-0.043116	0.017383
5	- 6	-0.004933	-0.035183	0.025316
5	- 2	0.011383	-0.020701	0.043468
5	- 8	0.012800	-0.039594	0.065194
5	- 3	0.013578	-0.021352	0.048507
5	- 4	0.019133	-0.033261	0.071527
2	- 7	-0.024583	-0.078058	0.028891
2	- 1	-0.024250	-0.056335	0.007835
2	- 6	-0.016317	-0.048401	0.015768
2	- 5	-0.011383	-0.043468	0.020701
2	- 8	0.001417	-0.052058	0.054891
2	- 3	0.002194	-0.034335	0.038724
2	- 4	0.007750	-0.045724	0.061224
8	- 7	-0.026000	-0.093640	0.041640
8	- 1	-0.025667	-0.078061	0.026727
8	- 6	-0.017733	-0.070127	0.034661
8	- 5	-0.012800	-0.065194	0.039594
8	- 2	-0.001417	-0.054891	0.052058
8	- 3	0.000778	-0.054450	0.056006
8	- 4	0.006333	-0.061307	0.073974
3	- 7	-0.026778	-0.082006	0.028450
3	- 1	-0.026444	-0.061374	0.008485
3	- 6	-0.018511	-0.053440	0.016418
3	- 5	-0.013578	-0.048507	0.021352
3	- 2	-0.002194	-0.038724	0.034335
3	- 8	-0.000778	-0.056006	0.054450
3	- 4	0.005556	-0.049673	0.060784
4	- 7	-0.032333	-0.099974	0.035307
4	- 1	-0.032000	-0.084394	0.020394
4	- 6	-0.024067	-0.076461	0.028327
4	- 5	-0.019133	-0.071527	0.033261
4	- 2	-0.007750	-0.061224	0.045724
4	- 8	-0.006333	-0.073974	0.061307
4	- 3	-0.005556	-0.060784	0.049673

```
options ls=78 ps=66 formdlim='*' pageno=1;

title1 'Effect of Surfactant Type and Concentration on Dye Pickup';
title2 'Dye: C.I. Disperse Yellow 42';

data tygwl;
  input surf replicat conc dc;
  cards;

1       1       0       0.232
1       1       0.01    0.369
1       1       0.1     0.252
1       1       0.5     0.275
1       1       1       0.354
1       2       0       0.327
1       2       0.01    0.425
1       2       0.1     0.473
1       2       0.5     0.594
1       2       1       0.467
1       3       0       0.331
1       3       0.01    0.276
1       3       0.1     0.450
1       3       0.5     0.625
1       3       1       0.559
2       1       0       0.232
2       1       0.5     0.406
2       1       1       0.523
2       1       5       0.487
2       1       10      0.432
2       2       0       0.327
2       2       0.5     0.498
2       2       1       0.462
2       2       5       0.572
2       2       10      0.578
2       3       0       0.331
2       3       0.5     0.536
2       3       1       0.532
2       3       5       0.439
2       3       10      0.490
3       1       0       0.232
3       1       0.01    0.374
3       1       0.1     0.408
3       1       0.5     0.523
3       1       1       0.452
3       2       0       0.327
3       2       0.01    0.391
3       2       0.1     0.394
3       2       0.5     0.448
3       2       1       0.533
3       3       0       0.331
3       3       0.01    0.377
3       3       0.1     0.357
3       3       0.5     0.415
3       3       1       0.428
4       1       0       0.232
4       1       0.01    0.386
4       1       0.1     0.590
```

```
4       1       0.5     0.452
4       1       1       0.429
4       2       0       0.327
4       2       0.01    0.321
4       2       0.1     0.542
4       2       0.5     0.449
4       2       1       0.475
4       3       0       0.331
4       3       0.01    0.348
4       3       0.1     0.318
4       3       0.5     0.492
4       3       1       0.450
5       1       0       0.232
5       1       0.01    0.338
5       1       0.25    0.376
5       1       0.5     0.528
5       1       1       0.578
5       2       0       0.327
5       2       0.01    0.370
5       2       0.25    0.448
5       2       0.5     0.550
5       2       1       0.583
5       3       0       0.331
5       3       0.01    0.510
5       3       0.25    0.717
5       3       0.5     0.432
5       3       1       0.609
;

proc glm data=tygwl;
  class surf replicat conc;
  model dc=surf replicat(surf) conc conc*surf;
  test h=surf e=replicat(surf);
  means surf/bon;
  means conc/lsd;
run;
```

Effect of Surfactant Type and Concentration on Dye Pickup
Dye: C.I. Disperse Yellow 42

The GLM Procedure

Class Level Information

Class	Levels	Values
surf	5	1 2 3 4 5
replicat	3	1 2 3
conc	8	0 0.01 0.1 0.25 0.5 1 5 10

Number of observations 75

The GLM Procedure

Dependent Variable: dc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	34	0.65699227	0.01932330	3.55	<.0001
Error	40	0.21787240	0.00544681		
Corrected Total	74	0.87486467			

R-Square	Coeff Var	Root MSE	dc Mean
0.750964	17.34353	0.073803	0.425533

Source	DF	Type I SS	Mean Square	F Value	Pr > F
surf	4	0.05759773	0.01439943	2.64	0.0475
replicat(surf)	10	0.13226893	0.01322689	2.43	0.0229
conc	7	0.42455136	0.06065019	11.13	<.0001
surf*conc	13	0.04257424	0.00327494	0.60	0.8384

Source	DF	Type III SS	Mean Square	F Value	Pr > F
surf	4	0.02368090	0.00592022	1.09	0.3760
replicat(surf)	10	0.13226893	0.01322689	2.43	0.0229
conc	7	0.42455136	0.06065019	11.13	<.0001
surf*conc	13	0.04257424	0.00327494	0.60	0.8384

Tests of Hypotheses Using the Type III MS for replicat(surf) as an Error Term

Source	DF	Type III SS	Mean Square	F Value	Pr > F
surf	4	0.02368090	0.00592022	0.45	0.7721

Bonferroni (Dunn) t Tests for dc

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	40
Error Mean Square	0.005447
Critical Value of t	2.97117
Minimum Significant Difference	0.0801

Means with the same letter are not significantly different.

Bon Grouping	Mean	N	surf
A	0.46193	15	5
A			
A	0.45633	15	2
A			
A	0.40947	15	4
A			
A	0.40060	15	1
A			
A	0.39933	15	3

The GLM Procedure

t Tests (LSD) for dc

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	40
Error Mean Square	0.005447
Critical Value of t	2.02108

Comparisons significant at the 0.05 level are indicated by ***.

conc Comparison	Difference Between Means	95% Confidence Limits		
0.25 - 10	0.01367	-0.10812	0.13546	
0.25 - 5	0.01433	-0.10746	0.13612	
0.25 - 1	0.01807	-0.07627	0.11240	
0.25 - 0.5	0.03213	-0.06220	0.12647	
0.25 - 0.1	0.09322	-0.00622	0.19266	
0.25 - 0.01	0.13992	0.04363	0.23620	***
0.25 - 0	0.21700	0.12266	0.31134	***
10 - 0.25	-0.01367	-0.13546	0.10812	
10 - 5	0.00067	-0.12112	0.12246	
10 - 1	0.00440	-0.08994	0.09874	
10 - 0.5	0.01847	-0.07587	0.11280	
10 - 0.1	0.07956	-0.01988	0.17900	
10 - 0.01	0.12625	0.02997	0.22253	***

10	- 0	0.20333	0.10900	0.29767	***
5	- 0.25	-0.01433	-0.13612	0.10746	
5	- 10	-0.00067	-0.12246	0.12112	
5	- 1	0.00373	-0.09060	0.09807	
5	- 0.5	0.01780	-0.07654	0.11214	
5	- 0.1	0.07889	-0.02055	0.17833	
5	- 0.01	0.12558	0.02930	0.22187	***
5	- 0	0.20267	0.10833	0.29700	***
1	- 0.25	-0.01807	-0.11240	0.07627	
1	- 10	-0.00440	-0.09874	0.08994	
1	- 5	-0.00373	-0.09807	0.09060	
1	- 0.5	0.01407	-0.04040	0.06853	
1	- 0.1	0.07516	0.01226	0.13805	***
1	- 0.01	0.12185	0.06408	0.17962	***
1	- 0	0.19893	0.14447	0.25340	***
0.5	- 0.25	-0.03213	-0.12647	0.06220	
0.5	- 10	-0.01847	-0.11280	0.07587	
0.5	- 5	-0.01780	-0.11214	0.07654	
0.5	- 1	-0.01407	-0.06853	0.04040	
0.5	- 0.1	0.06109	-0.00180	0.12398	
0.5	- 0.01	0.10778	0.05001	0.16555	***
0.5	- 0	0.18487	0.13040	0.23933	***
0.1	- 0.25	-0.09322	-0.19266	0.00622	
0.1	- 10	-0.07956	-0.17900	0.01988	
0.1	- 5	-0.07889	-0.17833	0.02055	
0.1	- 1	-0.07516	-0.13805	-0.01226	***
0.1	- 0.5	-0.06109	-0.12398	0.00180	
0.1	- 0.01	0.04669	-0.01908	0.11247	
0.1	- 0	0.12378	0.06089	0.18667	***
0.01	- 0.25	-0.13992	-0.23620	-0.04363	***
0.01	- 10	-0.12625	-0.22253	-0.02997	***
0.01	- 5	-0.12558	-0.22187	-0.02930	***
0.01	- 1	-0.12185	-0.17962	-0.06408	***
0.01	- 0.5	-0.10778	-0.16555	-0.05001	***
0.01	- 0.1	-0.04669	-0.11247	0.01908	
0.01	- 0	0.07708	0.01931	0.13485	***
0	- 0.25	-0.21700	-0.31134	-0.12266	***
0	- 10	-0.20333	-0.29767	-0.10900	***
0	- 5	-0.20267	-0.29700	-0.10833	***
0	- 1	-0.19893	-0.25340	-0.14447	***
0	- 0.5	-0.18487	-0.23933	-0.13040	***
0	- 0.1	-0.12378	-0.18667	-0.06089	***
0	- 0.01	-0.07708	-0.13485	-0.01931	***

APPENDIX B

STATISTICAL ANALYSES OF DYE FIXATION

```
options ls=78 ps=66 formdlim='*' pageno=1;

title1 'Effect of Surfactant Type, Concentration and Fixation Temperature on Dye
Fixation';
title2 'Dye: C.I. Disperse Blue 27';

data tbglf;
  input surf temp conc pfix;
  cards;
1       1       1       39.58
1       1       1       40.64
1       1       1       42.83
1       1       2       39.50
1       1       2       36.87
1       1       2       38.00
1       1       3       40.11
1       1       3       45.06
1       1       3       41.23
1       1       5       42.79
1       1       5       49.55
1       1       5
1       1       6       43.78
1       1       6       36.61
1       1       6       35.97
1       2       1       43.74
1       2       1       48.26
1       2       1       42.91
1       2       2       45.15
1       2       2       47.89
1       2       2       49.28
1       2       3       45.67
1       2       3       45.83
1       2       3       41.90
1       2       5       49.95
1       2       5       49.04
1       2       5
1       2       6       45.93
1       2       6       47.38
1       2       6       51.20
1       3       1       58.00
1       3       1       52.39
1       3       1       57.81
1       3       2       64.53
1       3       2       60.83
1       3       2       64.51
1       3       3       60.28
1       3       3       61.34
1       3       3       60.76
1       3       5       61.89
1       3       5       65.56
1       3       5
1       3       6       48.34
1       3       6       40.85
1       3       6       49.04
2       1       1       39.58
2       1       1       40.64
2       1       1       42.83
```

2	1	5	36.87
2	1	5	40.40
2	1	5	39.43
2	1	6	37.51
2	1	6	37.57
2	1	6	42.97
2	1	7	40.66
2	1	7	38.59
2	1	7	51.01
2	1	8	38.77
2	1	8	40.04
2	1	8	40.63
2	2	1	43.74
2	2	1	48.26
2	2	1	42.91
2	2	5	52.82
2	2	5	53.61
2	2	5	50.46
2	2	6	53.80
2	2	6	52.41
2	2	6	53.54
2	2	7	50.36
2	2	7	48.79
2	2	7	50.62
2	2	8	48.43
2	2	8	48.43
2	2	8	43.19
2	3	1	58.00
2	3	1	52.39
2	3	1	57.81
2	3	5	55.47
2	3	5	56.28
2	3	5	48.95
2	3	6	54.85
2	3	6	58.57
2	3	6	52.88
2	3	7	52.45
2	3	7	52.85
2	3	7	55.55
2	3	8	59.97
2	3	8	85.09
2	3	8	68.08
3	1	1	39.58
3	1	1	40.64
3	1	1	42.83
3	1	2	69.92
3	1	2	49.58
3	1	2	51.82
3	1	3	48.12
3	1	3	44.27
3	1	3	47.94
3	1	5	39.89
3	1	5	50.27
3	1	5	43.44
3	1	6	32.29
3	1	6	44.78
3	1	6	41.91

3	2	1	43.74
3	2	1	48.26
3	2	1	42.91
3	2	2	58.25
3	2	2	42.16
3	2	2	47.75
3	2	3	50.66
3	2	3	55.20
3	2	3	53.93
3	2	5	44.14
3	2	5	45.46
3	2	5	55.64
3	2	6	31.76
3	2	6	39.42
3	2	6	62.60
3	3	1	58.00
3	3	1	52.39
3	3	1	57.81
3	3	2	75.45
3	3	2	47.05
3	3	2	62.44
3	3	3	63.41
3	3	3	53.94
3	3	3	64.70
3	3	5	48.63
3	3	5	56.47
3	3	5	62.15
3	3	6	37.42
3	3	6	51.82
3	3	6	46.39
4	1	1	39.58
4	1	1	40.64
4	1	1	42.83
4	1	2	77.75
4	1	2	52.82
4	1	2	45.78
4	1	3	45.92
4	1	3	43.46
4	1	3	45.26
4	1	5	49.11
4	1	5	57.32
4	1	5	57.36
4	1	6	63.94
4	1	6	42.81
4	1	6	42.16
4	2	1	43.74
4	2	1	48.26
4	2	1	42.91
4	2	2	71.20
4	2	2	55.42
4	2	2	56.00
4	2	3	65.54
4	2	3	54.94
4	2	3	50.69
4	2	5	47.83
4	2	5	42.81
4	2	5	52.56

4	2	6	55.83
4	2	6	44.40
4	2	6	62.53
4	3	1	58.00
4	3	1	52.39
4	3	1	57.81
4	3	2	87.67
4	3	2	50.26
4	3	2	56.90
4	3	3	58.18
4	3	3	56.70
4	3	3	61.79
4	3	5	61.75
4	3	5	54.15
4	3	5	65.15
4	3	6	62.75
4	3	6	48.81
4	3	6	54.18
5	1	1	39.58
5	1	1	40.64
5	1	1	42.83
5	1	2	51.63
5	1	2	46.11
5	1	2	46.36
5	1	4	46.81
5	1	4	48.80
5	1	4	47.08
5	1	5	42.06
5	1	5	50.87
5	1	5	51.83
5	1	6	47.08
5	1	6	48.28
5	1	6	45.93
5	2	1	43.74
5	2	1	48.26
5	2	1	42.91
5	2	2	50.35
5	2	2	59.93
5	2	2	59.69
5	2	4	54.65
5	2	4	58.59
5	2	4	61.80
5	2	5	53.47
5	2	5	55.65
5	2	5	58.89
5	2	6	43.44
5	2	6	49.55
5	2	6	43.25
5	3	1	58.00
5	3	1	52.39
5	3	1	57.81
5	3	2	59.49
5	3	2	57.71
5	3	2	58.90
5	3	4	56.31
5	3	4	60.53
5	3	4	59.51

```
5      3      5      58.86
5      3      5      52.80
5      3      5      51.57
5      3      6      50.89
5      3      6      51.71
5      3      6      53.36

;

proc mixed data=tbglf method=reml noitprint;
  class surf temp conc;
  model pfix=surf temp conc temp*conc/ddfm=satterth;
  random surf*temp;
  estimate 'Temp (400-375)' temp -1 1 0;
  estimate 'Temp (425-400)' temp 0 -1 1;
  estimate 'Surf vs. Control' conc 7 -1 -1 -1 -1 -1 -1 -1;
  estimate 'Above CMC-Below CMC' conc -1 -1 -1 0 0 3 0 0;
  run;
```

Effect of Surfactant Type, Concentration and Fixation Temperature on Dye Fix
Dye: C.I. Disperse Blue 27

The Mixed Procedure

Model Information

Data Set	WORK.TBGLF
Dependent Variable	pfix
Covariance Structure	Variance Components
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
surf	5	1 2 3 4 5
temp	3	1 2 3
conc	8	1 2 3 4 5 6 7 8

Dimensions

Covariance Parameters	2
Columns in X	41
Columns in Z	15
Subjects	1
Max Obs Per Subject	222
Observations Used	222
Observations Not Used	0
Total Observations	222

Covariance Parameter Estimates

Cov Parm	Estimate
surf*temp	0
Residual	70.9989

Fit Statistics

-2 Res Log Likelihood	1438.4
AIC (smaller is better)	1440.4
AICC (smaller is better)	1440.4
BIC (smaller is better)	1441.1

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
surf	4	194	6.43	<.0001
temp	2	194	32.26	<.0001
conc	7	194	4.35	0.0002
temp*conc	14	194	1.23	0.2534

Estimates

Label	Estimate	Standard Error	DF	t Value	Pr > |t|
Temp (400-375)	6.0980	1.7619	194	3.46	0.0007
Temp (425-400)	8.0121	1.7619	194	4.55	<.0001
Surf vs. Control	-26.2120	10.6299	194	-2.47	0.0145
Above CMC-Below CMC	-13.6022	4.7280	194	-2.88	0.0045

```
options ls=78 ps=66 formdlim='*' pageno=1;

title1 'Effect of Surfactant Type, Concentration and Fixation Temperature on Dye
Fixation';
title2 'Dye: C.I. Disperse Brown 1';

data tbp3r;
  input surf temp conc pfix;
  cards;
1       1       1       39.39
1       1       1       41.65
1       1       1       39.06
1       1       2       40.15
1       1       2       42.22
1       1       2       43.85
1       1       3       48.20
1       1       3       43.87
1       1       3       46.38
1       1       5       40.77
1       1       5       40.26
1       1       5       40.77
1       1       6       35.01
1       1       6       38.71
1       1       6       39.64
1       2       1       48.18
1       2       1       46.98
1       2       1       45.46
1       2       2       44.11
1       2       2       48.51
1       2       2       45.51
1       2       3       57.81
1       2       3       56.32
1       2       3       53.02
1       2       5       54.32
1       2       5       53.14
1       2       5       52.12
1       2       6       40.53
1       2       6       51.74
1       2       6       52.99
1       3       1       55.92
1       3       1       60.05
1       3       1       61.17
1       3       2       62.39
1       3       2       71.17
1       3       2       61.53
1       3       3       68.59
1       3       3       68.37
1       3       3       60.03
1       3       5       58.16
1       3       5       61.46
1       3       5       66.71
1       3       6       46.90
1       3       6       59.33
1       3       6       60.28
2       1       1       39.39
2       1       1       41.65
2       1       1       39.06
```

2	1	5	39.94
2	1	5	43.22
2	1	5	44.18
2	1	6	45.26
2	1	6	42.94
2	1	6	40.95
2	1	7	35.49
2	1	7	36.07
2	1	7	35.17
2	1	8	34.57
2	1	8	31.28
2	1	8	34.92
2	2	1	48.18
2	2	1	46.98
2	2	1	45.46
2	2	5	54.14
2	2	5	56.36
2	2	5	62.01
2	2	6	55.62
2	2	6	54.72
2	2	6	57.05
2	2	7	47.98
2	2	7	48.38
2	2	7	47.69
2	2	8	38.46
2	2	8	46.18
2	2	8	47.14
2	3	1	55.92
2	3	1	60.05
2	3	1	61.17
2	3	5	58.13
2	3	5	63.84
2	3	5	66.58
2	3	6	64.92
2	3	6	64.57
2	3	6	61.64
2	3	7	56.72
2	3	7	50.85
2	3	7	56.22
2	3	8	39.86
2	3	8	47.38
2	3	8	41.99
3	1	1	39.39
3	1	1	41.65
3	1	1	39.06
3	1	2	43.50
3	1	2	50.23
3	1	2	47.26
3	1	3	43.19
3	1	3	44.51
3	1	3	41.30
3	1	5	34.26
3	1	5	38.96
3	1	5	44.11
3	1	6	43.50
3	1	6	37.46
3	1	6	41.43

3	2	1	48.18
3	2	1	46.98
3	2	1	45.46
3	2	2	57.67
3	2	2	61.21
3	2	2	53.77
3	2	3	48.26
3	2	3	56.16
3	2	3	57.29
3	2	5	53.16
3	2	5	49.84
3	2	5	54.22
3	2	6	61.68
3	2	6	48.01
3	2	6	56.40
3	3	1	55.92
3	3	1	60.05
3	3	1	61.17
3	3	2	58.22
3	3	2	65.77
3	3	2	59.52
3	3	3	59.11
3	3	3	61.90
3	3	3	62.19
3	3	5	61.33
3	3	5	51.42
3	3	5	55.95
3	3	6	80.69
3	3	6	55.41
3	3	6	61.92
4	1	1	39.39
4	1	1	41.65
4	1	1	39.06
4	1	2	46.28
4	1	2	45.91
4	1	2	44.62
4	1	3	45.51
4	1	3	46.46
4	1	3	42.50
4	1	5	44.19
4	1	5	42.97
4	1	5	43.20
4	1	6	41.59
4	1	6	42.12
4	1	6	41.40
4	2	1	48.18
4	2	1	46.98
4	2	1	45.46
4	2	2	59.37
4	2	2	63.78
4	2	2	58.10
4	2	3	63.89
4	2	3	59.87
4	2	3	58.07
4	2	5	59.05
4	2	5	59.36
4	2	5	56.67

4	2	6	41.32
4	2	6	56.87
4	2	6	54.15
4	3	1	55.92
4	3	1	60.05
4	3	1	61.17
4	3	2	65.82
4	3	2	60.93
4	3	2	55.88
4	3	3	73.78
4	3	3	66.09
4	3	3	66.93
4	3	5	51.43
4	3	5	66.90
4	3	5	59.04
4	3	6	59.54
4	3	6	60.18
4	3	6	51.50
5	1	1	39.39
5	1	1	41.65
5	1	1	39.06
5	1	2	47.48
5	1	2	41.72
5	1	2	42.66
5	1	4	44.65
5	1	4	45.23
5	1	4	51.40
5	1	5	46.91
5	1	5	44.34
5	1	5	45.90
5	1	6	42.84
5	1	6	40.00
5	1	6	42.45
5	2	1	48.18
5	2	1	46.98
5	2	1	45.46
5	2	2	61.54
5	2	2	59.71
5	2	2	57.22
5	2	4	60.59
5	2	4	59.03
5	2	4	66.18
5	2	5	59.45
5	2	5	62.62
5	2	5	57.20
5	2	6	50.11
5	2	6	50.76
5	2	6	54.71
5	3	1	55.92
5	3	1	60.05
5	3	1	61.17
5	3	2	57.91
5	3	2	66.96
5	3	2	66.50
5	3	4	60.80
5	3	4	58.24
5	3	4	68.02

```
5       3       5       65.77
5       3       5       57.93
5       3       5       58.07
5       3       6       49.11
5       3       6       55.32
5       3       6       63.43

;

proc mixed data=tbp3r method=reml noitprint;
  class surf temp conc;
  model pfix=surf temp conc temp*conc/ddfm=satterth;
  random surf*temp;
  estimate 'Temp (375-350)' temp -1 1 0;
  estimate 'Temp (400-375)' temp 0 -1 1;
  estimate '350 (control vs. surf.)' conc -7 1 1 1 1 1 1 1
           temp*conc -7 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '375 (control vs. surf.)' conc -7 1 1 1 1 1 1 1
           temp*conc 0 0 0 0 0 0 0 0 -7 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0;
  estimate '400 (control vs. surf.)' conc -7 1 1 1 1 1 1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -7 1 1 1 1 1 1 1;
  estimate '350 (Above-Below CMC)' conc -1 -1 -1 0 0 3 0 0
           temp*conc -1 -1 -1 0 0 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '375 (Above-Below CMC)' conc -1 -1 -1 0 0 3 0 0
           temp*conc 0 0 0 0 0 0 0 0 -1 -1 -1 0 0 3 0 0 0 0 0 0 0 0 0 0;
  estimate '400 (Above-Below CMC)' conc -1 -1 -1 0 0 3 0 0
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 -1 -1 0 0 3 0 0;
  estimate '0 gpL (375-350)' temp -1 1 0
           temp*conc -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.01 gpL (375-350)' temp -1 1 0
           temp*conc 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.1 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.25 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.5 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0;
  estimate '1.0 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0;
  estimate '5.0 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0;
  estimate '10.0 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0;
  estimate '0 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0;
  estimate '0.01 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0;
  estimate '0.1 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0;
  estimate '0.25 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0;
  estimate '0.5 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0;
  estimate '1.0 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0;
  estimate '5.0 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0;
```

```
  estimate '10.0 gpL (400-375)' temp 0 -1 1
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1;
  estimate '400 (0 vs. 0.01)' conc -1 1 0 0 0 0 0 0
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 1 0 0 0 0 0 0;
 estimate '400 (0 vs. 0.1)' conc -1 0 1 0 0 0 0 0
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 1 0 0 0 0 0;
 estimate '400 (0 vs. 0.25)' conc -1 0 0 1 0 0 0 0
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 1 0 0 0 0;
 estimate '400 (0 vs. 0.5)' conc -1 0 0 0 1 0 0 0
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 1 0 0 0;
 estimate '400 (0 vs. 1.0)' conc -1 0 0 0 0 1 0 0
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 1 0 0;
 estimate '400 (0 vs. 5)' conc -1 0 0 0 0 0 1 0
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 1 0;
 estimate '400 (0 vs. 10)' conc -1 0 0 0 0 0 0 1
          temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 1;
 estimate '375 (0 vs. 0.01)' conc -1 1 0 0 0 0 0 0
          temp*conc  0 0 0 0 0 0 0 0 -1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
 estimate '375 (0 vs. 0.1)' conc -1 0 1 0 0 0 0 0
          temp*conc  0 0 0 0 0 0 0 0 -1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0;
 estimate '375 (0 vs. 0.25)' conc -1 0 0 1 0 0 0 0
          temp*conc  0 0 0 0 0 0 0 0 -1 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0;
 estimate '375 (0 vs. 0.5)' conc -1 0 0 0 1 0 0 0
          temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0;
 estimate '375 (0 vs. 1.0)' conc -1 0 0 0 0 1 0 0
          temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0;
 estimate '375 (0 vs. 5)' conc -1 0 0 0 0 0 1 0
          temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0;
 estimate '375 (0 vs. 10)' conc -1 0 0 0 0 0 0 1
          temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0;
 estimate '350 (0 vs. 0.01)' conc -1 1 0 0 0 0 0 0
          temp*conc -1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
 estimate '350 (0 vs. 0.1)' conc -1 0 1 0 0 0 0 0
          temp*conc -1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
 estimate '350 (0 vs. 0.25)' conc -1 0 0 1 0 0 0 0
          temp*conc -1 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
 estimate '350 (0 vs. 0.5)' conc -1 0 0 0 1 0 0 0
          temp*conc -1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
 estimate '350 (0 vs. 1.0)' conc -1 0 0 0 0 1 0 0
          temp*conc -1 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
 estimate '350 (0 vs. 5)' conc -1 0 0 0 0 0 1 0
          temp*conc -1 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
 estimate '350 (0 vs. 10)' conc -1 0 0 0 0 0 0 1
          temp*conc -1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;

run;
```

Effect of Surfactant Type, Concentration and Fixation Temperature on Dye Fix

Dye: C.I. Disperse Brown 1

The Mixed Procedure

Model Information

Data Set	WORK.TBP3R
Dependent Variable	pfix
Covariance Structure	Variance Components
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
surf	5	1 2 3 4 5
temp	3	1 2 3
conc	8	1 2 3 4 5 6 7 8

Dimensions

Covariance Parameters	2
Columns in X	41
Columns in Z	15
Subjects	1
Max Obs Per Subject	225
Observations Used	225
Observations Not Used	0
Total Observations	225

Covariance Parameter Estimates

Cov Parm	Estimate
surf*temp	0.5224
Residual	16.9761

Fit Statistics

-2 Res Log Likelihood	1180.8
AIC (smaller is better)	1184.8
AICC (smaller is better)	1184.8
BIC (smaller is better)	1186.2

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
surf	4	8.75	2.46	0.1223
temp	2	13.2	159.17	<.0001
conc	7	190	20.84	<.0001
temp*conc	14	172	2.25	0.0078

Estimates

Label	Estimate	Standard Error	DF	t Value	Pr > |t|
Temp (375-350)	11.5978	0.9842	13.2	11.78	<.0001
Temp (400-375)	5.6205	0.9842	13.2	5.71	<.0001
350 (control vs. surf.)	6.3160	8.9087	194	0.71	0.4792
375 (control vs. surf.)	44.3781	8.9087	194	4.98	<.0001
400 (control vs. surf.)	-8.0446	8.9087	194	-0.90	0.3676
350 (Above-Below CMC)	-7.2756	3.8547	194	-1.89	0.0606
375 (Above-Below CMC)	-3.3164	3.8547	194	-0.86	0.3907
400 (Above-Below CMC)	-9.0848	3.8547	194	-2.36	0.0194
0 gpL (375-350)	6.8400	1.5724	77.7	4.35	<.0001
0.01 gpL (375-350)	11.2617	1.7548	86.3	6.42	<.0001
0.1 gpL (375-350)	12.2110	2.0214	98.6	6.04	<.0001
0.25 gpL (375-350)	14.6371	3.4842	129	4.20	<.0001
0.5 gpL (375-350)	13.9787	1.5724	77.7	8.89	<.0001
1.0 gpL (375-350)	11.4240	1.5724	77.7	7.27	<.0001
5.0 gpL (375-350)	12.2664	3.4901	119	3.51	0.0006
10.0 gpL (375-350)	10.1631	3.4901	119	2.91	0.0043
0 gpL (400-375)	12.1733	1.5724	77.7	7.74	<.0001
0.01 gpL (400-375)	6.8799	1.7548	86.3	3.92	0.0002
0.1 gpL (400-375)	8.3311	2.0214	98.6	4.12	<.0001
0.25 gpL (400-375)	1.0131	3.4842	129	0.29	0.7717
0.5 gpL (400-375)	3.9373	1.5724	77.7	2.50	0.0144
1.0 gpL (400-375)	7.2053	1.5724	77.7	4.58	<.0001
5.0 gpL (400-375)	6.4269	3.4901	119	1.84	0.0680
10.0 gpL (400-375)	-1.0031	3.4901	119	-0.29	0.7743
400 (0 vs. 0.01)	4.0864	1.6098	194	2.54	0.0119
400 (0 vs. 0.1)	6.8063	1.7674	197	3.85	0.0002
400 (0 vs. 0.25)	3.0768	2.7166	193	1.13	0.2588
400 (0 vs. 0.5)	1.1347	1.5045	190	0.75	0.4517
400 (0 vs. 1.0)	0.6027	1.5045	190	0.40	0.6892
400 (0 vs. 5)	-6.1158	2.7407	190	-2.23	0.0268
400 (0 vs. 10)	-17.6358	2.7407	190	-6.43	<.0001
375 (0 vs. 0.01)	9.3798	1.6098	194	5.83	<.0001
375 (0 vs. 0.1)	10.6485	1.7674	197	6.03	<.0001
375 (0 vs. 0.25)	14.2371	2.7166	193	5.24	<.0001
375 (0 vs. 0.5)	9.3707	1.5045	190	6.23	<.0001
375 (0 vs. 1.0)	5.5707	1.5045	190	3.70	0.0003
375 (0 vs. 5)	-0.3693	2.7407	190	-0.13	0.8929
375 (0 vs. 10)	-4.4593	2.7407	190	-1.63	0.1054
350 (0 vs. 0.01)	4.9581	1.6098	194	3.08	0.0024
350 (0 vs. 0.1)	5.2775	1.7674	197	2.99	0.0032
350 (0 vs. 0.25)	6.4399	2.7166	193	2.37	0.0187
350 (0 vs. 0.5)	2.2320	1.5045	190	1.48	0.1396
350 (0 vs. 1.0)	0.9867	1.5045	190	0.66	0.5127
350 (0 vs. 5)	-5.7958	2.7407	190	-2.11	0.0358
350 (0 vs. 10)	-7.7824	2.7407	190	-2.84	0.005

```
options ls=78 ps=66 formdlim='*' pageno=1;

title1 'Effect of Surfactant Type, Concentration and Fixation Temperature on Dye
Fixation';
title2 'Dye: C.I. Disperse Yellow 42';

data tygwl;
  input surf temp conc pfix;
  cards;
1       1       1       67.839
1       1       1       78.361
1       1       1       75.487
1       1       2       77.013
1       1       2       82.548
1       1       2       63.457
1       1       3       74.337
1       1       3       89.728
1       1       3       87.032
1       1       5       68.109
1       1       5       89.927
1       1       5       89.311
1       1       6       70.542
1       1       6       82.639
1       1       6       86.34
2       1       1       67.839
2       1       1       78.361
2       1       1       75.487
2       1       5       81.371
2       1       5       82.556
2       1       5       82.03
2       1       6       89.7
2       1       6       74.94
2       1       6       80.888
2       1       7       83.774
2       1       7       99.301
2       1       7       81.1
2       1       8       66.222
2       1       8       82.367
2       1       8       62.056
3       1       1       67.839
3       1       1       78.361
3       1       1       75.487
3       1       2       67.964
3       1       2       79.161
3       1       2       86.216
3       1       3       82.579
3       1       3       83.57
3       1       3       71.606
3       1       5       88.664
3       1       5       75.946
3       1       5       82.679
3       1       6       87.497
3       1       6       84.393
3       1       6       79.786
4       1       1       67.839
4       1       1       78.361
4       1       1       75.487
```

4	1	2	90.622
4	1	2	76.156
4	1	2	81.833
4	1	3	91.056
4	1	3	89.748
4	1	3	68.75
4	1	5	77.606
4	1	5	77.074
4	1	5	83.083
4	1	6	80.122
4	1	6	72.979
4	1	6	81.378
5	1	1	67.839
5	1	1	78.361
5	1	1	75.487
5	1	2	86.47
5	1	2	82.079
5	1	2	83.437
5	1	4	84.475
5	1	4	75.564
5	1	4	86.522
5	1	5	85.899
5	1	5	78.057
5	1	5	66.175
5	1	6	84.247
5	1	6	80.043
5	1	6	75.83
1	2	1	82.225
1	2	1	88.702
1	2	1	87.818
1	2	2	85.426
1	2	2	87.617
1	2	2	84.399
1	2	3	86.595
1	2	3	89.831
1	2	3	89.863
1	2	5	81.343
1	2	5	92.236
1	2	5	88.777
1	2	6	90.544
1	2	6	90.141
1	2	6	87.55
2	2	1	82.225
2	2	1	88.702
2	2	1	87.818
2	2	5	87.589
2	2	5	92.779
2	2	5	89.582
2	2	6	87.407
2	2	6	89.937
2	2	6	91.291
2	2	7	79.296
2	2	7	86.017
2	2	7	77.937
2	2	8	77.744
2	2	8	75.178
2	2	8	73.155

3	2	1	82.225
3	2	1	88.702
3	2	1	87.818
3	2	2	92.697
3	2	2	90.687
3	2	2	89.971
3	2	3	76.01
3	2	3	89.571
3	2	3	82.14
3	2	5	90.324
3	2	5	85.762
3	2	5	87.111
3	2	6	85.281
3	2	6	87.068
3	2	6	84.245
4	2	1	82.225
4	2	1	88.702
4	2	1	87.818
4	2	2	92.088
4	2	2	80.155
4	2	2	87.613
4	2	3	94.899
4	2	3	92.79
4	2	3	82.115
4	2	5	92.101
4	2	5	87.038
4	2	5	88.089
4	2	6	89.273
4	2	6	86.418
4	2	6	85.556
5	2	1	82.225
5	2	1	88.702
5	2	1	87.818
5	2	2	85.801
5	2	2	91.315
5	2	2	90.45
5	2	4	84.77
5	2	4	84.304
5	2	4	89.756
5	2	5	86.793
5	2	5	88.459
5	2	5	79.306
5	2	6	91.264
5	2	6	88.391
5	2	6	86.053
1	3	1	91.454
1	3	1	91.296
1	3	1	89.859
1	3	2	84.358
1	3	2	91.232
1	3	2	81.297
1	3	3	84.844
1	3	3	89.83
1	3	3	88.16
1	3	5	83.101
1	3	5	91.102
1	3	5	90.335

1	3	6	89.298
1	3	6	86.834
1	3	6	89.272
2	3	1	91.454
2	3	1	91.296
2	3	1	89.859
2	3	5	92.082
2	3	5	89.844
2	3	5	89.27
2	3	6	93.817
2	3	6	88.59
2	3	6	87.069
2	3	7	86.225
2	3	7	88.558
2	3	7	79.17
2	3	8	87.056
2	3	8	80.388
2	3	8	79.483
3	3	1	91.454
3	3	1	91.296
3	3	1	89.859
3	3	2	85.561
3	3	2	89.678
3	3	2	90.061
3	3	3	90.394
3	3	3	88.664
3	3	3	86.971
3	3	5	88.333
3	3	5	88.462
3	3	5	83.162
3	3	6	87.811
3	3	6	88.771
3	3	6	85.749
4	3	1	91.454
4	3	1	91.296
4	3	1	89.859
4	3	2	90.985
4	3	2	90.242
4	3	2	89.645
4	3	3	94.655
4	3	3	94.361
4	3	3	89.993
4	3	5	93.751
4	3	5	88.194
4	3	5	90.189
4	3	6	87.888
4	3	6	86.857
4	3	6	85.37
5	3	1	91.454
5	3	1	91.296
5	3	1	89.859
5	3	2	90.562
5	3	2	90.726
5	3	2	90.488
5	3	4	85.659
5	3	4	90.559
5	3	4	93.161

```
5       3       5       92.344
5       3       5       92.151
5       3       5       87.219
5       3       6       87.96
5       3       6       88.745
5       3       6       91.3

;

proc mixed data=tygwl method=reml noitprint;
  class surf temp conc;
  model pfix=surf temp conc temp*conc/ddfm=satterth;
  random surf*temp;
  estimate 'Temp (375-350)' temp -1 1 0;
  estimate 'Temp (400-375)' temp 0 -1 1;
  estimate '350 (control vs. surf.)' conc -7 1 1 1 1 1 1 1
           temp*conc -7 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '375 (control vs. surf.)' conc -7 1 1 1 1 1 1 1
           temp*conc 0 0 0 0 0 0 0 0 -7 1 1 1 1 1 1 1 0 0 0 0 0 0 0 0;
  estimate '400 (control vs. surf.)' conc -7 1 1 1 1 1 1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -7 1 1 1 1 1 1 1;
  estimate '350 (Above-Below CMC)' conc -1 -1 -1 0 0 3 0 0
           temp*conc -1 -1 -1 0 0 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '375 (Above-Below CMC)' conc -1 -1 -1 0 0 3 0 0
           temp*conc 0 0 0 0 0 0 0 0 -1 -1 -1 0 0 3 0 0 0 0 0 0 0 0 0 0;
  estimate '400 (Above-Below CMC)' conc -1 -1 -1 0 0 3 0 0
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 -1 -1 0 0 3 0 0;
  estimate '0 gpL (375-350)' temp -1 1 0
           temp*conc -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.01 gpL (375-350)' temp -1 1 0
           temp*conc 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.1 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.25 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0;
  estimate '0.5 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0;
  estimate '1.0 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0;
  estimate '5.0 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0;
  estimate '10.0 gpL (375-350)' temp -1 1 0
           temp*conc 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0;
  estimate '0 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0;
  estimate '0.01 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0 0;
  estimate '0.1 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0 0;
  estimate '0.25 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0 0;
  estimate '0.5 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0 0;
  estimate '1.0 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0 0;
  estimate '5.0 gpL (400-375)' temp 0 -1 1
           temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1 0;
```

```
estimate '10.0 gpL (400-375)' temp 0 -1 1
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 0 1;
estimate '400 (0 vs. 0.01)' conc -1 1 0 0 0 0 0 0
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 1 0 0 0 0 0 0;
estimate '400 (0 vs. 0.1)' conc -1 0 1 0 0 0 0 0
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 1 0 0 0 0 0;
estimate '400 (0 vs. 0.25)' conc -1 0 0 1 0 0 0 0
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 1 0 0 0 0;
estimate '400 (0 vs. 0.5)' conc -1 0 0 0 1 0 0 0
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 1 0 0 0;
estimate '400 (0 vs. 1.0)' conc -1 0 0 0 0 1 0 0
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 1 0 0;
estimate '400 (0 vs. 5)' conc -1 0 0 0 0 0 1 0
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 1 0;
estimate '400 (0 vs. 10)' conc -1 0 0 0 0 0 0 1
        temp*conc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 1;
estimate '375 (0 vs. 0.01)' conc -1 1 0 0 0 0 0 0
        temp*conc  0 0 0 0 0 0 0 0 -1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0;
estimate '375 (0 vs. 0.1)' conc -1 0 1 0 0 0 0 0
        temp*conc  0 0 0 0 0 0 0 0 -1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0;
estimate '375 (0 vs. 0.25)' conc -1 0 0 1 0 0 0 0
        temp*conc  0 0 0 0 0 0 0 0 -1 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0;
estimate '375 (0 vs. 0.5)' conc -1 0 0 0 1 0 0 0
        temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0;
estimate '375 (0 vs. 1.0)' conc -1 0 0 0 0 1 0 0
        temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0;
estimate '375 (0 vs. 5)' conc -1 0 0 0 0 0 1 0
        temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0;
estimate '375 (0 vs. 10)' conc -1 0 0 0 0 0 0 1
        temp*conc  0 0 0 0 0 0 0 0 -1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0;
estimate '350 (0 vs. 0.01)' conc -1 1 0 0 0 0 0 0
        temp*conc -1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
estimate '350 (0 vs. 0.1)' conc -1 0 1 0 0 0 0 0
        temp*conc -1 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
estimate '350 (0 vs. 0.25)' conc -1 0 0 1 0 0 0 0
        temp*conc -1 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
estimate '350 (0 vs. 0.5)' conc -1 0 0 0 1 0 0 0
        temp*conc -1 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
estimate '350 (0 vs. 1.0)' conc -1 0 0 0 0 1 0 0
        temp*conc -1 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
estimate '350 (0 vs. 5)' conc -1 0 0 0 0 0 1 0
        temp*conc -1 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 ;
estimate '350 (0 vs. 10)' conc -1 0 0 0 0 0 0 1
        temp*conc -1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;

run;
```

Effect of Surfactant Type, Concentration and Fixation Temperature on Dye Fix
Dye: C.I. Disperse Yellow 42

The Mixed Procedure

Model Information

Data Set	WORK.TYGWL
Dependent Variable	pfix
Covariance Structure	Variance Components
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Satterthwaite

Class Level Information

Class	Levels	Values
surf	5	1 2 3 4 5
temp	3	1 2 3
conc	8	1 2 3 4 5 6 7 8

Dimensions

Covariance Parameters	2
Columns in X	41
Columns in Z	15
Subjects	1
Max Obs Per Subject	225
Observations Used	225
Observations Not Used	0
Total Observations	225

Covariance Parameter
Estimates

Cov Parm	Estimate
surf*temp	0
Residual	22.6068

Fit Statistics

-2 Res Log Likelihood	1234.5
AIC (smaller is better)	1236.5
AICC (smaller is better)	1236.6
BIC (smaller is better)	1237.3

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
surf	4	197	0.77	0.5427
temp	2	197	35.82	<.0001
conc	7	197	5.65	<.0001
temp*conc	14	197	2.97	0.0004

Estimates

Label	Estimate	Standard Error	DF	t Value	Pr > |t|
Temp (375-350)	5.3277	0.9925	197	5.37	<.0001
Temp (400-375)	2.9613	0.9925	197	2.98	0.0032
350 (control vs. surf.)	44.8341	10.2529	197	4.37	<.0001
375 (control vs. surf.)	-11.3655	10.2529	197	-1.11	0.2690
400 (control vs. surf.)	-24.6456	10.2529	197	-2.40	0.0172
350 (Above-Below CMC)	5.9649	4.4370	197	1.34	0.1804
375 (Above-Below CMC)	1.9473	4.4370	197	0.44	0.6612
400 (Above-Below CMC)	-4.9160	4.4370	197	-1.11	0.2692
0 gpL (375-350)	12.3527	1.7362	197	7.11	<.0001
0.01 gpL (375-350)	8.4386	1.9411	197	4.35	<.0001
0.1 gpL (375-350)	5.0453	2.2414	197	2.25	0.0255
0.25 gpL (375-350)	4.0897	3.8822	197	1.05	0.2934
0.5 gpL (375-350)	7.2535	1.7362	197	4.18	<.0001
1.0 gpL (375-350)	7.2730	1.7362	197	4.19	<.0001
5.0 gpL (375-350)	-6.9750	3.8822	197	-1.80	0.0739
10.0 gpL (375-350)	5.1440	3.8822	197	1.33	0.1867
0 gpL (400-375)	4.6213	1.7362	197	2.66	0.0084
0.01 gpL (400-375)	0.5513	1.9411	197	0.28	0.7767
0.1 gpL (400-375)	2.6731	2.2414	197	1.19	0.2345
0.25 gpL (400-375)	3.5163	3.8822	197	0.91	0.3662
0.5 gpL (400-375)	1.4833	1.7362	197	0.85	0.3939
1.0 gpL (400-375)	0.3275	1.7362	197	0.19	0.8506
5.0 gpL (400-375)	3.5677	3.8822	197	0.92	0.3592
10.0 gpL (400-375)	6.9500	3.8822	197	1.79	0.0750
400 (0 vs. 0.01)	-1.8902	1.8528	197	-1.02	0.3089
400 (0 vs. 0.1)	-0.7365	2.0281	197	-0.36	0.7169
400 (0 vs. 0.25)	-1.2126	3.0912	197	-0.39	0.6953
400 (0 vs. 0.5)	-1.5671	1.7362	197	-0.90	0.3678
400 (0 vs. 1.0)	-2.5143	1.7362	197	-1.45	0.1492
400 (0 vs. 5)	-7.1914	3.1165	197	-2.31	0.0221
400 (0 vs. 10)	-9.5334	3.1165	197	-3.06	0.0025
375 (0 vs. 0.01)	2.1798	1.8528	197	1.18	0.2408
375 (0 vs. 0.1)	1.2117	2.0281	197	0.60	0.5509
375 (0 vs. 0.25)	-0.1076	3.0912	197	-0.03	0.9723
375 (0 vs. 0.5)	1.5709	1.7362	197	0.90	0.3667
375 (0 vs. 1.0)	1.7796	1.7362	197	1.03	0.3066
375 (0 vs. 5)	-6.1377	3.1165	197	-1.97	0.0503
375 (0 vs. 10)	-11.8621	3.1165	197	-3.81	0.0002
350 (0 vs. 0.01)	6.0939	1.8528	197	3.29	0.0012
350 (0 vs. 0.1)	8.5190	2.0281	197	4.20	<.0001
350 (0 vs. 0.25)	8.1554	3.0912	197	2.64	0.0090
350 (0 vs. 0.5)	6.6701	1.7362	197	3.84	0.0002
350 (0 vs. 1.0)	6.8593	1.7362	197	3.95	0.0001
350 (0 vs. 5)	13.1899	3.1165	197	4.23	<.0001
350 (0 vs. 10)	-4.6534	3.1165	197	-1.49	0.1370