INFLUENCE OF SURFACE TENSION AND CONCENTRATION OF A NON-IONIC SURFACTANT ON THE BARRIER EFFECTIVENESS OF A MICROPOROUS POLYPROPYLENE FABRIC FOR PESTICIDE PROTECTIVE CLOTHING

by

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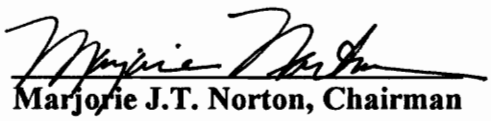

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(ABSTRACT)

This research evaluated the influence of concentration and surface tension (γ) of aqueous solutions of a non-ionic surfactant on the barrier effectiveness of a fabric containing microporous polypropylene (PP) film that may be used in pesticide protective clothing (PPC). Aqueous solutions of Triton® X-100, a non-ionic surfactant, at various concentrations were prepared, and the γ of each solution was determined. The immediate advancing contact angles (θ), made by a 5-μL drop of each test liquid on the test fabric, were measured.

Barrier effectiveness was evaluated from the capillary penetration, wicking, and wetting characteristics of the fabric using the surfactant solutions at various concentrations. Wetting characteristics were evaluated from the drop absorbency test, a modified Draves test, the spreading coefficient (S_c) values and, by inference, from a Zisman plot.

As surfactant concentration increased, γ decreased, and then remained relatively steady past the 0.0134 percent concentration level, the critical micelle concentration

(CMC) of Triton® X-100. As Triton® X-100 concentration increased, θ decreased, even past the CMC. Results of the study indicate that, as surfactant concentration increases, the amount of capillary penetration and the wicking distance increase even past the CMC. The time for drop absorbency and the Draves wetting tests were very high (> 600 seconds) for all liquids below CMC. Beyond the CMC, drop absorbency times were significantly lower for solutions of 2.0 and 5.0 percent concentration, and the Draves wetting times were also significantly lower.

The values of the cos θ and the γ were used to calculate the S_c for each liquid. The calculated spreading coefficients indicate that the liquids at all concentrations did not spread (wet) on the micro-porous PP test fabric for the advancing θ measured within 10 seconds of placing the drop.

Results of the statistical analysis showed that surfactant concentration was a significant factor in determining the barrier effectiveness of the fabric tested. Even though γ remained relatively unchanged beyond the CMC of the surfactant, the inability of the test fabric to serve as an effective barrier against liquid penetration by capillary action, wicking, and wetting increased significantly. Surface energy terms, that are normally used to explain liquid transport and wetting phenomena, may not in themselves be sufficient to determine the effectiveness of a fabric for PPC, especially since concentration of the surfactant, a pesticide adjuvant, is a significant factor in determining the barrier effectiveness of PPC. Consideration must be made for the fact that very high concentrations of surfactants are routinely used in pesticide application.

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Chapter I

INTRODUCTION

Pesticides are chemicals that combat insects, rodents, weeds, and other pests. In agriculture, herbicides are used to control weeds, insects, and other undesirable agents. Certain additives called 'adjuvants' are blended with a herbicide, at the formulation and/or the spraying stage, so as to enhance the herbicidal efficacy and efficiency and for other purposes. Adjuvants are used more with herbicides than with any other type of pesticide. Adjuvants are credited with the delivery, optimization, and persistence of herbicide phytotoxicity (Chow, 1984; Foy, 1989, 1991). Thus, adjuvants play a significant role in helping to realize the potential of a herbicide in combating undesirable elements.

Among all adjuvants used, surfactants have the largest and most wide use. Surfactants reduce the surface free energy, or the surface tension (γ), of the herbicide spray 'solution', and thereby enhance the wetting of the sprayed area and optimize the efficacy and efficiency of the herbicide (Foy & Smith, 1965, 1969; Seaman, 1990). Other positive effects have been attributed to surfactants' use as adjuvants in herbicide formulations. In this study, a pesticide or herbicide mixture containing the active ingredient, water, and the surfactant, along with the other ingredients, is referred to as an 'emulsion' rather than as a 'solution'.

Of the several hundred surfactants used as adjuvants in agrochemicals, non-ionic surfactants (NIS) are used the most. Unlike other ionogenic types, NIS do not pose the

potential of reacting nor of being incompatible with other ingredients of a pesticide/herbicide formulation (Chow, 1984; Foy, 1979-80, 1991).

Surfactant adsorption on solid surfaces is influenced by the polarity of solid surfaces (Porter, 1991). This could explain why non-polar or non-ionic surfactants are used more extensively than polar anionic and cationic surfactants as herbicidal adjuvants. Leaf surfaces of crops/plants have a layer of non-polar wax on their outer, cuticular region. A non-polar surfactant (a NIS) would facilitate the adsorption and, consequently, the herbicide effectiveness, to a significantly greater level than would a polar surfactant. Thus, a non-ionic surfactant is the ideal choice as an adjuvant.

Pesticides and herbicides are toxic chemicals. Their handling and application processes expose agricultural workers to harmful chemicals. Protective clothing is used in pesticide related applications to minimize and, hopefully, avoid dermal exposure. Several barrier materials have been used in pesticide protective clothing.

In pesticide protective clothing studies, the two aspects primarily studied are wearer comfort and the barrier effectiveness to penetration by the pesticide. Protective garments made from encapsulated rubber, neoprene, vinyl, and even certain types of Tyvek® offer the best protection against pesticide penetration but are extremely uncomfortable. These materials do not permit the evaporation (and thus the drying and subsequent cooling) of perspiration from the wearer's body, and make the wearer feel clammy and uncomfortable. Consequently, this would discourage an agricultural worker's use of protective clothing made from such materials.

Textile fabrics containing microporous materials have been developed for use in active wear. These materials have been used in research to determine their suitability for pesticide protective clothing applications. Microporous materials work by allowing the water vapor (perspiration) from a wearer's body to pass through them and evaporate on the outer fabric surface. Concurrently, they keep the larger liquid molecules from penetrating into the fabric.

Previous studies with textile fabrics, such as Gore-Tex®, containing a polytetrafluoro-ethylene (PTFE or Teflon®) microporous membrane have shown that they performed well, i.e., resisted pesticide penetration and afforded wearer comfort (Branson, Ayers, & Henry, 1986; Branson, DeJonge, & Munson, 1986; Leonas, Easter, & DeJonge, 1989). In some of these studies, fabrics made from microporous PTFE membrane were compared to cotton and spunbonded polyethylene. The penetration resistance of the test fabrics to different concentrations of pesticides was also investigated (Branson & Rajadhyaksha, 1988; Leonas et al., 1989; Shaw, 1993; Shaw & Hill, 1990). The results of these studies are not conclusive and warrant further investigation.

Research with microporous polypropylene fabrics for pesticide protective clothing has been conducted at Virginia Tech in the Department of Clothing and Textiles. One area of this research involves wearer-comfort aspects, while the other involves evaluation of barrier effectiveness to solutions of a surfactant (which represents a pesticide emulsion of a specific surface tension) following abrasion of the protective fabric.

Fabric wetting is influenced to a great extent by liquid surface free energy (surface

tension). Only liquids that have a surface free energy lower than the fabric will wet the fabric. Low surface tension of the herbicide emulsion is essential to the wetting of plant surfaces, but it presents a concomitant risk of the fabric becoming wet easily and thus failing to serve as an effective protective barrier. A surfactant solution has the lowest surface tension at its critical micelle concentration (CMC). Beyond the CMC, increased concentrations of surfactant in a solution do not reduce the surface tension. CMC can be reduced by the use of certain electrolytes (Pugh & Manev, 1991); however, reduction of the CMC by the electrolyte addition technique is beyond the scope of the present study.

Even though concentrations up to the CMC would give the lowest γ, the application of herbicides in practice involves the usage of surfactants in concentrations several magnitudes greater than the CMC (Foy, 1979-80; Foy & Smith, 1965) The higher concentrations of surfactant are claimed to enhance herbicidal penetration and phytotoxicity, thereby permitting herbicidal usage at lower dosages. Surfactant concentrations in excess of the levels required for minimum surface tension might be beneficial from the agricultural standpoint. However, the effect of such high surfactant concentrations on the barrier effectiveness of protective clothing is not known. Such knowledge would be critical for the judicious selection of protective clothing in pesticide applications.

Careful consideration of the opposing needs of increasing herbicidal phytotoxicity and efficiency versus the barrier effectiveness (non-wetting) of the protective clothing should be made. Such consideration would help in the final selection of an ideal textile

material that could perform as an effective barrier under these constraints.

Herbicide emulsions of different surface free energy levels would exhibit different wetting characteristics on solid surfaces. Because surfactants are the chemicals that influence the surface tension of the herbicide formulation (or the spray tank emulsion), water containing different concentrations of surfactant could attain different surface free energy levels, though only below the CMC, and thus, could be expected to exhibit different wetting characteristics.

Despite the extensive literature on pesticide protective clothing, the barrier effectiveness of protective material, as a function of surfactant concentration and surface tension, has not been reported. It is important to understand the influence of surface free energy and concentration of a surfactant on the liquid transport properties of microporous polypropylene fabric that may be used in pesticide protective clothing.

Knowledge of the influence of surface free energy would help in understanding the mechanisms/relations of wetting, wicking, and capillary penetration properties which, in turn, could help characterize the barrier effectiveness to pesticides. Since surfactant concentrations beyond the CMC are commonly used in herbicide formulations, the effect, if any, of increased surfactant concentration on wetting, wicking, and capillary penetration of protective clothing fabrics would help determine the threshold range of surfactant concentration beyond that for optimization of herbicidal efficacy and efficiency.

A non-ionic surfactant that has a moderately high hydrophilic-lipophilic balance (HLB) value, reduces aqueous surface tension to levels favorable for leaf surface wetting,

shows good emulsifying properties, and has wide usage as an agricultural adjuvant was suitable for the purpose of this study. Following a review of the properties of several surfactants from several sources, and considering the practical field-application requirements and constraints, Triton® X-100 (Union Carbide) was the surfactant selected.

Research Problem Statement

The purpose of this research is to evaluate the influence of the surface free energy and concentration of Triton® X-100, a non-ionic surfactant, on the barrier effectiveness of micro-porous polypropylene fabric which may be used in pesticide protective clothing. The capillary penetration, wetting, and wicking characteristics of the fabric were used to indicate its barrier effectiveness.

Aqueous solutions of different concentrations of Triton® X-100 were prepared using double distilled, de-ionized (DDDI) water. DDDI water, with a mean surface tension of 72.52 dynes/cm and a Triton® X-100 concentration = 0% w/v, was used as an additional liquid in the evaluation.

Fabric wetting was evaluated from the drop absorbency test, a modified Draves test, spreading coefficient calculations, and, by inference, the Zisman plot. The fabric's surface free energy and spreading coefficient values were determined from the immediate advancing contact angle measurements.

Chapter II

REVIEW OF LITERATURE

The purpose of this research is to evaluate the influence of the surface tension and concentration of a non-ionic surfactant on the barrier effectiveness of microporous polypropylene nonwoven fabric for pesticide protective clothing. To address the purpose of this study, it is first necessary to understand the underlying principles that would govern the performance of the fabric under the testing conditions of this research.

This chapter reviews the literature pertinent to the diverse areas that were examined to understand the influence of surface tension and concentration of a surfactant on the protective performance of the test fabric. This chapter is organized into four sections, namely,

- Wetting of Surfaces
- Pesticides
- Adjuvants
- Pesticide Protective Clothing

The review of literature on the wetting of surfaces examines the phenomenon of surface free energy, contact angle, wetting, and the role of these phenomena in pesticide application and protective clothing performance. This chapter's section on pesticides and adjuvants is truly an in-depth review of surfactants, the adjuvant that is the primary focus of this research. The section on pesticide protective clothing reviews the materials that

have been used for such clothing, and gives an introduction to microporous materials for pesticide protective clothing applications.

Wetting of Surfaces

Wetting of surfaces is a complex phenomenon influenced by several factors. Wetting involves interaction between two phases, and the term 'interface' is often used in describing wetting behavior. Several interfaces are possible, based on the three states of matter. This research and any discussion of wetting and interfaces in this research will, however, deal strictly with liquid-solid interfaces.

Depending on the surface to be wetted, factors such as a liquid's surface free energy (surface tension), a solid's surface free energy, and the solid porosity influence the possibility and the extent of wetting. In order to fully understand the phenomenon of wetting, the concepts of surface free energy and contact angle must be first understood. The following addresses these factors and their relationship to wetting.

Surface Free Energy (Surface Tension)

Surface free energy is a property exhibited by solid and liquid substances and is commonly called the surface tension of the substance. It represents the free energy of formation of an interface or the work required to increase the area of a surface by unit amount (Shaw, 1970), and is denoted by γ with units of erg/cm^2 or dyne/cm. Surface tension is dependent on temperature, and it generally decreases with increasing

temperature.

Surface free energy is also identified as the force per unit length (dyne/cm). It is a force that prevents a substance from wetting, spreading or otherwise homogeneously combining with an anisotropic material. This force could be considered to be a 'sheath' that prevents the spreading and wetting of, for instance, a liquid. A strong force implies that the 'sheath' holds the liquid together tighter (and thus limits/prevents wetting) than a weaker force. Addition of a surfactant reduces the force of the 'sheath', thereby allowing a freer flow of the liquid, and facilitating wetting.

The concept of surface free energy is often illustrated by stretching a film of soap across a wire frame. When a soap film is stretched, a force acts in the direction opposite to the direction of the applied force. The work done in extending the soap film per unit area is the surface free energy (Adamson, 1976).

If the free energy of formation of an interface is positive, then the force required to stretch the liquid film across a wire frame will be high. In such cases, the liquid will not show a tendency to continuously expand its surface region; it will try to agglomerate and form a drop that will not spread readily. If the energy of formation of an interface is negative or zero, it implies lack of resistance to expanding the surface area of the film. Under such a condition, the liquid will show a tendency to expand its surface area continuously; it will not agglomerate, but rather, it will spread and wet a surface.

Water, for instance, has a free energy of about 72 dynes/cm, and it does not spread or wet most solid surfaces. Addition of a small amount of a surfactant reduces the free

energy of water to 25-30 dynes/cm, depending on the surfactant added, which then allows water to spread more easily. Because of surfactants' ability to reduce the free energy and thereby facilitate spreading and wetting, they are common additives to pesticide application systems containing pesticide, water, and other ingredients (Foy & Smith, 1969).

As with liquids, solids also have surface free energies. Low surface free energy of a solid prevents the spreading and wetting of liquids that have free energies higher than that of the of the solid (Fox & Zisman, 1950). Surfaces of leaves are difficult to wet with herbicide emulsions due to the low surface free energy from the presence of waxes on the leaf surfaces (Foy & Takeno, 1992). Knowledge of the free energies of leaf surfaces would be helpful in tailoring a herbicide application system of specific γ to optimize the wetting of the leaf surface by the applied herbicide.

Surface free energy (γ) of liquids is determined relatively easily by several methods such as the capillary rise method, the Wilhelmy plate method, the du Noüy ring method, and the pendant drop method, to name a few. The surface free energy of solids, however, cannot be measured directly, even for smooth films of polymers. Solid surface free energy is determined indirectly by the liquid homolog method, the critical surface tension method, and other methods (Fox & Zisman, 1950; Wu, 1982).

Zisman and co-workers (Ellison & Zisman, 1954; Fox & Zisman, 1950, 1952) proposed a technique to determine surface free energy of solid polymers by using contact angle and liquid surface tension data. In their approach, a homologous series of liquids of

known surface tensions was taken and their contact angles were measured on a given polymer surface. The cosines of the contact angles were plotted on the ordinate against the surface tension of the liquids on the abscissa to give a straight-line graph. The intercept of a line drawn from the ordinate of $\cos \theta = 1.0$ (i.e., $\theta = 0°$) gives the surface free energy of the liquid in the homologous series that would just spread on the polymer surface. The surface free energy of the liquid that will just spread on the polymer surface is also the critical surface tension (γ_c) of the solid polymer.

Contact Angle

When a drop of a liquid is placed on a flat solid surface, it either spreads completely or forms a sessile drop having a definite angle of contact with the solid surface (Adamson, 1976). The angle formed between the tangent to the profile of the liquid drop at the point of contact with the solid surface is called the contact angle, and is represented by the Greek symbol theta, θ.

Contact angles are formed when the cohesive forces within a liquid are stronger than the attractive forces between a liquid and a solid surface. The formation of a contact angle implies a condition of non-wetting of the solid surface in question, although this might be a simplistic explanation. When $\theta = 0°$, the solid surface is completely wetted by the liquid, whereas a contact angle of 180° implies a condition of no wetting (Shaw, 1970).

Contact angles are measured by several techniques such as the drop-bubble

method (which includes the sessile drop method using a goniometer), the tensiometric method, and the capillary rise method. The accurate measurement of a contact angle of a liquid on a solid surface is often hindered by the lack of reproducibility or homogeneity and by the lack of smoothness of the solid surfaces (Shaw, 1970; Wu, 1982). Surface roughness normally tends to lower the contact angle, as compared to a condition of surface smoothness, with the same liquid (Fox & Zisman, 1950).

Contact angles are affected by surface contamination, which presents difficulties in their accurate measurement. In a solid-liquid system, as surface free energy (surface tension) of a liquid increases, the contact angle increases and vice versa. On the other hand, as the surface free energy of the solid surface decreases, the contact angle increases and vice versa (assuming the liquid in contact with the solid surface is the same). Non-staining carpet is an application of non-wetting (high contact angle) from a decrease in the surface free energy of the solid surface.

Work of Adhesion

The work of adhesion is the work or energy, in dynes/cm, required to separate one square centimeter of a common interface between two phases into two distinct interfaces (Adamson, 1976; Shaw, 1970). Work of adhesion, W_a, is indicative of the attraction of the solid surface to the liquid at their interface and is given by the Young-Dupré equation

$$W_a = \gamma_{LV} (1 + \cos \theta) + \pi_E$$

where γ_{LV} is the surface free energy of the liquid, θ is the contact angle for the liquid on

the solid surface, and π_E is the equilibrium spreading pressure of the adsorbed vapor on the solid surface. For a liquid like water, which has a relatively high boiling point, π_E is negligible and is eliminated from the above equation (Fox & Zisman, 1950, 1952) to give

$$W_a = \gamma_{LV} (1 + \cos \theta).$$

The application of the work of adhesion concept is in determining the wetting or spreading behavior of, for instance, a liquid over a solid surface. Good wetting of a surface is a prerequisite in pesticide application and in general adhesion-related situations. Poor wetting, on the other hand, is desirable in pesticide protective clothing applications.

Work of Cohesion

Work of cohesion (W_c) is a characteristic of a single liquid (i.e., a homogeneous system) that is indicative of how well a unit cross-sectional area of the liquid holds to itself. It is defined as the amount of work or energy, in dynes/cm, needed to pull apart a column of the liquid (Adamson, 1976; Shaw, 1970), and is determined from the surface free energy of the liquid,

$$W_c = 2\gamma_{LV}.$$

A liquid that has a high surface free energy also will have a high work of cohesion value, and will not easily spread on a given surface. Low work of cohesion (from low surface tension) values are required for good wetting of surfaces, whereas high work of cohesion (high surface tension) values are desirable for applications requiring limited or no wetting.

Wetting and Spreading

Wetting has been defined as the phenomenon resulting from the forces of adhesion at the solid-liquid interface (Ellison & Zisman, 1954). Wetting implies that the contact angle between a liquid and a solid is zero or very close to zero. Under conditions of low-to-zero contact angles, the liquid will have a tendency to spread easily over the solid surface. Spreading is the indefinite movement of the bulk liquid or a thin film (Fox & Zisman, 1950) across a surface. The two terms, wetting and spreading, are used interchangeably in the context of this research.

In order to determine whether a liquid will spread on a solid surface, a quantity called the spreading coefficient is often used. The spreading coefficient is the difference between the work of adhesion and the work of cohesion (Fox & Zisman, 1950). Thus,

$$S_c = W_a - W_c$$

where W_a is the work of adhesion, W_c is the work of cohesion and S_c is the spreading coefficient in dynes/cm. A positive S_c value implies that the liquid will spread and wet the solid surface, and a negative S_c value implies that the liquid will not spread or wet the solid surface within the time of the contact angle measurement. For all liquids, the initial spreading coefficient is negative because the contact angle is never zero at the very outset of placing the drop on the solid surface.

Since $W_a = \gamma_{LV} (1 + \cos \theta)$ and $W_c = 2\gamma_{LV}$, substituting the respective quantities for the work of adhesion and the work of cohesion, we have

$$S_c = \gamma_{LV} (1 + \cos \theta) - 2\gamma_{LV}, \text{ or}$$

$$S_c = \gamma_{LV} (\cos \theta - 1).$$

Thus, the spreading coefficient can be determined easily from the surface free energy and the contact angle of the liquid on the solid surface. In general, as the liquid surface free energy increases, the contact angle increases and the spreading coefficient decreases.

Other Mechanisms of Liquid Transport

Permeation and penetration are the two mechanisms that have been used to characterize the movement or the passage of a liquid through a material. The concept of penetration is generally used in characterizing the barrier properties of materials used in pesticide protective clothing. Liquid transport through the mechanism of penetration entails the nonmolecular-level movement of the chemical through porous materials, and/or through imperfections in a barrier material (ASTM, 1995c). Penetration itself is further categorized into four modes, viz., capillary penetration, pressure penetration, impact penetration, and evaporation-condensation penetration. In the context of this research, only capillary penetration is detailed.

Capillary penetration is a type of penetration mainly promoted by capillarity. It is dependent on several factors such as liquid surface tension and viscosity, fiber surface free energy and morphology, interaction of the fluid with the fiber surface, the size, volume and orientation of the pores in the fibrous network, and the surface density (Minor, Shwartz, Buckles, Wulkow, Marks, & Fielding, 1961).

Wicking, the migration of a liquid through the interfiber or interyarn capillaries of a

fabric, is yet another form of capillary penetration. Wicking is caused by the pressure difference across the curved surface of a given liquid meniscus, and is quantified by the Young-Laplace equation (Adamson, 1976) as

$$\Delta P = 2\,\gamma_{LV} \cos\theta / r$$

where ΔP is the pressure difference across the meniscus, γ_{LV} is the surface free energy of the liquid, θ is the contact angle, and r is the capillary radius.

The Role of Wetting in Pesticide Application

The relevance of some of the surface chemistry concepts reviewed above becomes clear in the application of pesticides, and specifically herbicides. In field applications, a vast surface area usually must be covered by the applied pesticide and any adjuvants within a very short application time. The full efficacy and efficiency of the pesticide can be realized only if the pesticide emulsion stays on the applied areas.

The epidermal wax on a plant inhibits the penetration of the applied pesticide emulsion. Contact angles as high as 145° have been reported for leaf surfaces covered with wax (Foy & Takeno, 1992). A good surfactant will reduce the contact angle and promote penetration of the pesticide into the target area.

The reduction of the surface free energy of the pesticide emulsion by the addition of a small amount of surfactant is the key to optimizing the efficiency and efficacy of the pesticide. Decrease in surface free energy decreases the contact angle of the emulsion on the leaf surface and increases the spreading coefficient, which permits greater wetting.

The contact angle cannot always be reduced to zero, even with very efficient wetting agents (McKay, Koch, & Herbert, 1987).

Effect of Wetting on Pesticide Protective Clothing

For optimal efficacy and efficiency of a pesticide's usage, conditions that promote optimal wetting are necessary. The pesticide emulsion that is applied should promote effective wetting and penetration of the applied plant surfaces. The requirement and achievement of conditions of optimized wetting of a plant surface by a pesticide emulsion are, however, in direct contrast to the conditions required for a clothing material to perform effectively as a barrier material. Low surface free energy, low contact angle, and high spreading or wetting ability of the pesticide emulsion are essential for pesticide application, but the exactly opposite conditions are desirable for effective performance of protective clothing.

Careful consideration of the opposing needs of increasing herbicidal phytotoxicity and efficiency versus maintaining the barrier effectiveness, through non-wetting, of the protective clothing should be made. The non-wetting of the permeable protective clothing material (as opposed to impervious materials) could be assured by using clothing materials of very low surface free energies. A barrier material that has a very low surface free energy would give a high contact angle, assuming the surface free energy of the solid is lower than the free energy of the liquid (pesticide emulsion).

Pesticides

The term 'pesticides' refers to chemicals that are used to combat insects, rodents, weeds, and other pests. Herbicides, insecticides, fungicides, nematicides, larvicides, and plant growth regulators are some of the chemicals called pesticides. Representing a significant portion of the chemical industry, pesticides have annual worldwide sales of $25 billion. Pesticide sales in the United States alone are $7 billion or 28 percent of worldwide sales. Of this $7 billion, herbicides account for about $4.5 billion or 65 percent of total annual sales of pesticides and plant growth regulators (Foy, 1993).

Herbicides are used in agriculture to combat weeds, insects, nematodes, and plant diseases. Nearly 50 percent of the world's annual agricultural produce is estimated to be lost to insects, weeds, and other factors. Unlike losses caused by insects and plant diseases, losses due to weeds are not readily visible. Weeds reduce agricultural yields by competing with crops for water, light, and nutrients. They also are reported to produce substances that inhibit the growth or germination of other plants (Chase, 1984). In the United States losses due to weeds, alone, are estimated at more than $18 billion annually (Foy, 1991, 1993). The sheer magnitude of these figures reflects the pivotal responsibility bestowed upon herbicides in protecting crops against undesirable elements.

Agrochemicals, which include pesticides and other chemicals, increase farm yields, lower costs, and improve the quality of farm products. A typical formulation for a herbicide, or other pesticide, that is used in agriculture contains the active ingredient and other chemicals called adjuvants.

Adjuvants

Most herbicides are insoluble or have low solubility in water and thus are usually dissolved in oils or organic solvents (Mullins, 1995). Dissolution in oil or solvent, however, renders such solutions immiscible with water, the eventual carrier of the herbicide. It is partly for this reason that a surfactant, having good emulsifying capabilities, besides other properties, is used in a herbicide formulation.

In addition to surfactants, other additives called 'adjuvants', are combined with pesticides to aid or enhance the efficacy of the pesticide. Adjuvants represent about six percent of the value of pesticide sales (Foy, 1991, 1993). Adjuvants are incorporated in the formulated product (formulation adjuvants) and/or in the spray tank (spray adjuvants). Spray adjuvants are used more commonly with herbicides than with other classes of pesticides. Reeves (1991) lists the general purposes of adjuvants: a) to improve or facilitate the physical handling characteristics of herbicides; b) to improve performance effectiveness and consistency; and c) to comply with legal requirements.

In the category of adjuvants are chemicals that have a wide range of functions, such as activators, antidrift or drift-reduction agents, antifoam agents, buffers, chelates, compatibility agents, conditioners, hygroscopic agents, penetrants, safeners, stickers, spreaders, surfactants, and wetting agents (Foy, 1989a; 1994 Weed Control Manual). Adjuvant terminology is in the relatively nascent stages, and the Weed Science Society of America, in concert with the industry and the researchers in this area, is expending efforts to standardize the terminology.

The earliest published literature on adjuvant research dates to 1888, and is attributed to Gillette who used kerosene emulsions and soap solutions to destroy insect eggs. Until the 1950s, soap solutions and other household detergents often were recommended as additives to pesticide spray solutions. Both soaps and household detergents pose limitations as adjuvants (Foy, 1989). With hard water, soaps form scums which are calcium and magnesium salts of fatty acids and which have limited surface active properties. Household detergents, albeit good wetting agents, usually contain low concentrations of surfactant and are thus expensive.

The effectiveness of the herbicide application often depends on the adjuvants. The effectiveness of adjuvants in their intended purpose is, in itself, a matter of considerable analysis and debate. It should be stressed that not all adjuvants work effectively with all herbicides.

Surfactants

Among all adjuvants used, surfactants have clearly been identified as the most important, with the bulk of the published literature in the area of adjuvants relating to them. A surfactant is a chemical that is active at surfaces (surface active agent). Even when used in extremely small concentrations, surfactants have the property to significantly modify the properties of materials at their surfaces.

Surfactants are crucial in diverse applications like petroleum extraction (especially in enhanced oil recovery), mining and minerals' extraction, paper, paints, textiles, inks,

adhesives, cosmetics, detergents, foods, and pesticide adjuvants. In the textile industry, surfactants are used in detergents, scouring agents, lubricants for spinning, warp sizes, defoamers, fabric softeners, biocides, etc. It is, however, their use as adjuvants with herbicides that is the focus of this research.

Before reviewing the roles of surfactants as adjuvants, some theoretical concepts relevant to the general behavior of surfactants are explained. Two basic phenomena, viz., adsorption at surfaces and micelle formation in solution, govern the behavior of surfactants and distinguish a surfactant from other chemicals. These and other characteristics of surfactants, such as their effect on aqueous surface tension and wetting, their emulsifying abilities, and their hydrophilic-lipophilic balance, are discussed below.

Adsorption

Adsorption is one of the most important characteristics of a surfactant. Adsorption is the tendency of a surfactant to have a higher concentration at the surface of a liquid than in the bulk of the liquid (Shaw, 1970). Adsorption occurs at the interfaces (boundaries) of substances that may or may not have the same physical state. Thus, adsorption occurs at the interfaces of air/liquid (e.g., foam), liquid/liquid (e.g., an emulsion), and liquid/solid (e.g., herbicide spray solution on a plant leaf surface or on a protective clothing material). The surface active effects seen in, for example, emulsification, wetting, detergency, dispersion of solids in liquids, or foaming, are caused by the adsorption of surfactants at the surfaces or interfaces.

Adsorption of surfactants occurs due to their unique molecular constitution. A surfactant molecule often is depicted with a long, straight non-polar group (tail) attached to a small, round polar group (head) as shown below:

O=^-^-^-^-^-

The non-polar tail is hydrophobic (water-hating) or lipophilic (oil-loving), and is attracted to oil-like or non-polar materials. The polar group head, on the other hand, is hydrophilic (water-loving) and is attracted to polar materials (Chow, 1984; Porter, 1991).

In a practical demonstration of the adsorption phenomenon, the intimacy and the stability of such intimacy between two immiscible liquids such as water and oil is achieved by the addition of a very small amount of surfactant. The surfactant forms a very thin monolayer at the interface of water and oil, with the polar head oriented toward the water and the non-polar tail oriented toward the oil, due to their respective attraction for these phases. Surfactant adsorption at the interface renders the two liquids miscible.

In the case of a liquid/solid system, the polarity of the solid surface governs the adsorption of a surfactant at the interface (Porter, 1991, chap. 4). Thus, polar surfactants (anionic and cationic) are adsorbed more on polar than on non-polar, or hydrophobic, surfaces. The adsorption of non-polar surfactants (non-ionics), on the other hand, is more on non-polar than on polar substances.

Micelles

Besides adsorption, the ability of a surfactant to form micelles in solution is the

other very important characteristic. Micelles are spherical assemblies of surfactant molecules, wherein the non-polar (hydrophobic or lipophilic) tails are all oriented toward the center of the spherical assembly while the polar (hydrophilic) heads are oriented away from the center and toward the aqueous phase.

Micelles form when surfactant concentration in a dilute, aqueous solution reaches saturation at the surface and further addition of surfactant would not appreciably reduce the surface tension further. Past the saturation point, additional surfactant molecules may enter the bulk of the solution and form more micelles, but their non-polar tails would still be repelled from the aqueous phase (Porter, 1991). Micelles influence the viscosity of a surfactant solution and the solubility (miscibility) of lipophilic substances (e.g., oils and organic hydrocarbons) in aqueous solution.

The number of surfactant molecules comprising a micelle gives an indication of the micelle size, and is called the 'aggregate number'. In general, aggregate numbers of non-ionics are five to twenty times larger than those of anionic and cationic surfactants. These differences in aggregate numbers magnify with increasing temperature. Because aggregate numbers are indicative of micelle size and because micelles influence solubility, non-ionics, with their relatively high aggregate numbers, are better at solubilizing (or making miscible) oils and organic hydrocarbons than are polar surfactants (Porter, 1991). This also could explain why non-ionic surfactants are used more than polar surfactants as adjuvants with herbicides that are dissolved in oils.

Critical micelle concentration. When surfactant is added to water, the surface tension (γ) of water decreases. As surfactant concentration in the aqueous solution increases, the surface tension of water keeps decreasing almost linearly until it reaches an equilibrium point after which it stays constant or nearly so. This equilibrium surface tension is the juncture at which micelles first start to form; the surfactant concentration at the equilibrium surface tension is called the critical micelle concentration (CMC).

The CMC for most surfactants is below 1.0 percent. For a surfactant to be effective in solubilizing insoluble organic substances in water, it should be used above its CMC because it is only past the CMC that micelles, which solubilize the insoluble organic substances, are formed (Shaw, 1970). In their application as herbicidal adjuvants, surfactants are used in concentrations much above their CMC (1.0, 2.0, and even 5.0 percent, w/v), in order to solubilize lipophilic materials, to enhance herbicide efficacy, and to achieve other purposes (Foy, 1991, 1992b; Foy & Smith, 1965, 1969).

The CMC of a surfactant can be altered by changing its chemical composition. Alteration of CMC without changing the surfactant composition can be accomplished by the addition of electrolytes (Pugh & Manev, 1991; Shaw, 1970). The electrolyte addition technique to reduce the CMC is more effective with polar than non-polar surfactants.

Effect of Surfactant on Surface Tension and Wetting

As mentioned earlier, surface tension (γ) is a force that prevents a liquid from wetting a surface. If the γ of the surface to be wetted is lower than that of the liquid, no

spreading or wetting will occur. Thus, water with a high γ of around 72 dynes/cm will not wet the surface of polypropylene with a surface tension around 30 dynes/cm (Wu, 1982), nor of certain plant leaves that have a surface tension of around 32 dynes/cm (Foy & Smith, 1965).

Addition of a small amount of surfactant to water reduces its γ, and when this γ declines to a level below the critical surface tension of a surface which needs to be wetted, then the aqueous solution of the surfactant will spread and wet the surface. The decrease of liquid surface tension, and the consequent increase in wetting of plant leaf surfaces, is one of the primary effects of a surfactant's use as a herbicidal adjuvant. Because γ at the CMC is the lowest attainable γ of a solution, surfactants that give the least γ at their CMC would seem ideal for optimizing wetting of leaf surfaces. However, the lowest surface tension of most non-ionics is as high as 30-32 dynes/cm at their CMC.

From a wetting standpoint, the following points need to be considered in the selection of a surfactant (Porter, 1991):

- Wetting is more when the non-polar group has a shorter, rather than longer, chain.
- Water solubility of a surfactant increases as the number of polar groups (e.g., ethylene oxide), in the surfactant increases, but the solution's wetting power decreases because the minimum γ and the CMC increase with the number of polar groups.
- Addition of electrolytes to polar surfactants decreases the γ and increases the wetting power, whereas the addition of electrolytes to non-ionic surfactants generally reduces their wetting power.

Emulsions

One of the important features of a surfactant is its ability to form an emulsion. Emulsions are intimate mixtures of immiscible liquids (e.g., water and an organic solvent or oil). By their tendency to be adsorbed at surfaces, surfactants bring the water-immiscible (or water-insoluble) substances into intimate contact with the aqueous phase. In such an emulsion, the hydrophilic part of the surfactant will be in the aqueous phase and the lipophilic part in the oily phase. The emulsion so formed should be stable, i.e., not separate upon standing.

The ability of a surfactant to form emulsions is vital in diverse industrial and domestic applications. Where herbicide application is concerned, one function of a surfactant is to serve as an emulsifier in the formation of an emulsion between oil, the solvent for the herbicide, and the aqueous medium of application.

Two types of emulsions are possible: oil-in-water (O/W), in which the oil droplets are dispersed in a continuous aqueous phase; and water-in-oil (W/O), in which the water droplets are dispersed in a continuous oil phase. A surfactant that is highly soluble in the continuous phase would allow for maximum adsorption and give stable emulsions. Since herbicide spray 'solutions' are O/W emulsions, any surfactant used as an adjuvant should have a high solubility in water.

Hydrophilic-Lipophilic Balance

A property often used in characterizing a surfactant is the hydrophilic-lipophilic

balance (HLB). The HLB value of a surfactant indicates the surfactant's emulsifying abilities as a function of its chemical structure. The HLB value, a measure first proposed by W.C. Griffin in 1949, is derived by dividing the molar percent of hydrophilic groups in a surfactant by five.

The maximum possible HLB value is 20, and represents a surfactant that is completely soluble in water. A surfactant with a low HLB value would have a low percent composition of hydrophilic groups in the structure, and thus would be difficult to dissolve in water, but easy to dissolve in oily substances. For application as herbicidal adjuvants, surfactants with a high HLB value (high solubility in water) are desirable because water is the carrier and the continuous phase of the oil-in-water (O/W) emulsion.

Classification of Surfactants

Surfactants are classified by the ionic charge of the hydrophilic group of the molecule. Classification by the ionogenic type lends the following types of surfactants (Chow, 1984; Foy 1979-80, 1989a).

Anionic surfactants. An anionic (negatively charged ion) hydrophilic group on a surfactant molecule provides the surface active properties. For example, in sodium lauryl sulfate, $C_{12}H_{25}SO_4Na$, the hydrophilic anion $(C_{12}H_{25}SO_4)^-$ provides the surface activity. Anionic surfactants are relatively cheap and found extensively in detergents. Their use as herbicide adjuvants is extant though not extensive. They are incompatible with cationic substances, and hence unusable with cationic herbicides like paraquat (Foy, 1991, 1995;

Foy & Smith, 1969).

Cationic surfactants. Cationic (positively charged ion) hydrophilic groups on a surfactant molecule provide the surface active properties. Quaternary ammonium compounds constitute many cationic surfactants. For example, dodecyl trimethyl ammonium chloride, $C_{12}H_{25}N(CH_3)_3Cl$, contains the quaternary ammonium cation $C_{12}H_{25}N(CH_3)_3^+$. Cationic surfactants are, in general, very expensive. They are incompatible with anionic surfactants and form water-insoluble complexes. Cationics find applications mainly as biocides, textile softeners and antistats, and corrosion inhibitors. They are not generally used as herbicide adjuvants because they are phytotoxic, i.e., toxic to plants (Towne, Bartles, & Hilton, 1978).

Amphoteric surfactants. These surfactants also are called ampholytic or zwitterionic surfactants. Depending on the pH, the hydrophilic group in an amphoteric surfactant has the ability to assume either a positive or negative charge and exhibit surface active properties. Amphoteric surfactants are usually blended with anionic and non-ionic surfactants for use in personal- and home-care products. Their use as herbicidal adjuvants is limited.

Non-ionic surfactants. The surface active hydrophilic group in a non-ionic surfactant (NIS) does not carry a charge and remains chemically inert. The hydrophilic group usually is a hydroxyl (R-OH) or an ether group (usually, ethoxylates from ethylene oxide, E.O.), that is attached to a hydrophobic group such as alkyl phenol, an alcohol, or a fatty acid. Triton® X-100, Turgitol® X-J, Tween® 20, and Surfactant X-77® are trade

names of some non-ionic surfactants.

Non-ionics are used extensively as herbicide adjuvants. As noted by Chow (1984) and Foy (1989a, 1991, 1995), the reasons for this are the following:

- Non-ionics are compatible with other ionogenic classes of surfactants and with all herbicides because they do not react with the active ingredient.
- They are not affected by hard water, which is especially relevant in field conditions.
- They are stable over wide pH ranges.
- On non-polar leaf surfaces, they are adsorbed significantly more than polar surfactants.
- Non-ionics are excellent at solubilizing oils and organic hydrocarbons because they have very high aggregate numbers.
- Non-ionics are soluble in water and in organic solvents.

Speciality surfactants. Most widely used surfactants give γ at CMC, or the equilibrium surface tension, in the range of 25-35 dynes/cm. Very few commonly-used surfactants give γ below 25 dynes/cm (McKay, Koch, & Herbert, 1987). Under certain conditions, and for some specific applications, surfactants that can reduce the γ below 25 dynes/cm are needed to wet surfaces of very low γ. Examples of such conditions are the wetting of Teflon® or the extinguishing of gasoline fires by the spreading of aqueous foams. For the purpose of this study, surfactants that give very low γ ($\leq$ 20 dynes/cm) are called 'speciality surfactants'. Two chemical types, viz., fluorochemical and silicone types, dominate this group of surfactants. Within each of these chemical types, there are anionics, cationics, and non-ionics. Speciality surfactants are very expensive and are used

for specific applications.

Silicone surfactants reduce the surface tension of water to 20 dynes/cm, and their use as herbicidal adjuvants has been reported in a few studies. Some polar fluorochemical surfactants reduce the liquid surface tension to as low as 17 dynes/cm at concentrations of 0.2 percent (w/w); a non-ionic fluoro-surfactant reduces it to 20 dynes/cm at only 0.01 percent (w/w) concentration. No studies involving the use of fluorochemical surfactants as herbicidal adjuvants were found.

Studies on Surfactants as Herbicidal Adjuvants

Most research on adjuvants deals with surfactants, and the surfactant class studied the most is the non-ionic, which reflects its wide use in field conditions. For instance, an agricultural bulletin from Du Pont (1995b) lists 76 NIS, representing several manufacturers and suppliers, that have been approved for use with Du Pont's herbicides. Per Du Pont's guidelines (1995a), no anionic or cationic surfactants have been recommended.

The interactions of herbicide and surfactant and the improvements in herbicidal performance by surfactants were first reported in the early 1940s. Since then, several researchers have reported the benefits of using surfactants and other adjuvants in maximizing herbicide efficacy and efficiency. For an in-depth study, the reader is directed to the extensive list of references in Foy (1989b).

As adjuvants, surfactants assume the roles of emulsifiers, dispersants, wetters,

solubilizers, spreaders, stickers, or activators (Chow, 1984; Foy, 1989a, 1991). These roles are not mutually exclusive, and a single surfactant may function in all these roles.

The plant cuticle region is a layer of cutin, composed of cross-linked hydroxy fatty acids, which is covered with a layer of wax. These and other underlying layers of a leaf resist the penetration and the wetting of the leaf surface by a herbicide. Surfactants are believed to solubilize non-polar substances in these layers and make the cuticle permeable, thus affording penetration of the herbicide to the interior cellular targets (Crafts & Foy, 1962; Chow, 1984; Foy & Takeno, 1992).

Herbicides can penetrate the leaf cells and be effective only after they first spread and wet the surface. Liquids of γ higher than those of the leaf surfaces give contact angles (θ) as high as 145° (Foy & Takeno, 1992). Surfactants reduce the γ of the herbicide emulsion and the θ at the leaf surface, thereby enhancing spreading and wetting. Enhanced wetting of the plants results in increased uptake of the herbicide from the emulsion, with consequent enhancement of the herbicidal phytoxicity.

Foy and Smith (1965) examined the influence of concentration of three non-ionic and two anionic surfactants on surface tension and contact angle. At 0.1-0.5 percent (w/v) concentration, the non-ionics reduced γ of distilled water to as low as 35 dynes/cm whereas the anionics gave the overall lowest γ of 31 dynes/cm at only 0.1 percent (w/v). Contact angles on corn leaf and paraffin wax-coated plexiglass decreased as a function of increasing surfactant concentration in distilled water. Solutions of some NIS did not wet the surfaces (θ=75-80°) at concentrations up to 1.0 percent, but an anionic surfactant

showed complete wetting ($\theta=0°$) at concentrations of 0.01 and 0.05 on paraffin wax and corn leaf, respectively.

Researchers (Foy & Smith, 1965; Roggenbuck, Rowe, Penner, Petroff, & Burow, 1990) caution that the γ reducing ability of surfactants does not necessarily translate to enhanced efficacy of the herbicides. Plant leaf-herbicide-surfactant interactions are studied extensively in weed science and should be the primary criterion in the selection of surfactants for adjuvants. Before a surfactant can qualify for use with a specific herbicide, extensive tests must be conducted to ensure its effectiveness in the intended purposes without promoting crop injury.

Several researchers have studied the effect of surfactant concentration on herbicide toxicity (efficacy). Foy and Smith (1965) concluded that surfactant concentrations up to ten times greater than those required to achieve lowest γ and θ resulted in maximum herbicidal phytotoxicity and effectiveness. Foy and Smith (1969) later showed that, when the concentration of octyl phenol- and nonyl phenol-polyoxyethylene glycol ether surfactants (both non-ionics) was increased from 0.1 percent to 1.0 percent (w/v), herbicide toxicity increased almost 100 percent. They contend that the increased concentration of the surfactant permits the adsorption of herbicide molecules into the surfactant micelles and increases the diffusion rate of the surfactant, thus the herbicide penetration, into the cuticle.

Jansen, Gentner, and Shaw (1961) showed that, as concentration of some non-ionic surfactants increased from 0.001 to 1.0 percent (w/v), the inherent phytotoxicity of

surfactants on corn and soybean increased 100-400 percent even in the absence of a herbicide. O'Sullivan, O'Donovan, and Hamman (1981) observed the effects of increasing non-ionic surfactant concentrations on glyphosate phytotoxicity on barley. They determined that three surfactants enhanced glyphosate phytotoxicity at concentrations of 0.25-2.0 percent (v/v), two showed no effect until 2.0 percent, and three others decreased phytotoxicity at 0.1-0.25 percent surfactant concentrations. Besides enhancement of herbicidal efficacy, increased surfactant concentration has been postulated to enhance or retard the movement of both herbicide and water in soils (Foy, 1992b).

The hydrophilic-lipophilic balance (HLB) value of non-ionic surfactants influences their properties. Foy and Taneko (1992) observed the influence of HLB of two non-ionic surfactants and their mixtures on the leaf surface ultrastructure, and found that decreasing HLB values increased penetration and uptake of the herbicide methazole. They cite results of other studies involving HLB values which do not indicate a consistent pattern, noting that the HLB requirement could be different for different plants and herbicides.

Different surfactants influence herbicidal efficacy in different ways. O'Sullivan et al. (1981) showed that some surfactants increased the phytotoxicity of the herbicide glyphosate while others reduced it. Jansen et al. (1961) studied the effects of 63 surfactants, representing all ionogenic classes, with four herbicides, and determined inconsistent alterations in herbicidal efficacy with different surfactants.

A few reported studies (McKay et al., 1987; Reddy & Singh, 1992; Roggenbuck et al., 1990) have involved silicone surfactants for reducing the critical rain-free period and

for improving herbicidal efficacy and rainfastness. The longer the critical rain-free period, the greater the chance of herbicide washing away from the desired target area by rain. The silicone surfactants used in these studies reduced the surface tension to 20 dynes/cm.

Besides their positive effects in emulsifying, dispersing, solubilizing, wetting, and improving the efficacy of herbicides, some surfactants exhibit deleterious characteristics. Foy (1979-1980, 1989b, 1991, 1995) reports that several surfactants themselves are phytotoxic. Some reduce the efficacy of herbicides with which they are used, others get metabolized by plant cells to herbicide-resistant simpler molecules, and others adversely affect the permeability of plant cell membranes.

Surfactants, like all other chemicals, can deliver the intended benefits when used judiciously. Surfactants allow for reduced usage of herbicides, due to the enhancement in uptake, penetration, phytotoxicity, and other properties. They are much cheaper than herbicides. Surfactants can thus help address critical environmental and economic issues.

Pesticide Protective Clothing

Exposure to pesticides causes health problems ranging from mental confusion and drowsiness to genetic mutations, birth defects, sterility, neurological problems, and cancer (Boraiko, 1980; Rucker, 1994). Dermal absorption has been identified as more common than inhalation and ingestion as a mode of pesticide entry into the body (Wolfe et al., 1976). The adverse effects of agricultural workers' exposure to pesticides may not be evident immediately, but could be long-term and are usually permanent. The need for an

effective barrier that minimizes or eliminates the transmission of chemicals to the underlying skin cannot be overstated.

The zeal to protect agricultural workers from pesticide exposure by using effective barrier materials needs to be tempered with the practical consideration of workers' preference for, acceptance of, and willingness to wear protective clothing. Rucker (1994) has reviewed several studies that examined agricultural workers' attitudes toward protective clothing and related issues.

Pesticide protective clothing is an area studied extensively. Research in this area has dealt primarily with two issues: wearer-comfort and barrier effectiveness. Traditionally, these two issues have shown an inverse relation to one another in that when the conditions for one are optimized, those for the other are usually sacrificed. However, some new materials offer hope for the concurrent optimization of both comfort and protection.

Barrier Materials

Among all barrier materials used in chemical protective clothing in the U.S., polyester and polyethylene are used the most and each had a 40 percent market share in 1994 (Strzetelski, 1995). In pesticide protective clothing, materials made of polyester, nylon, acrylic, cellulosics (cotton, viscose rayon, and wood pulp fibers), and polyethylene (PE) are the most common. These materials may be used by themselves or combined with others in different ways to form the final barrier material. Besides these,

polypropylene (PP), polytetrafluoroethylene (PTFE), rubber, neoprene, polyvinyl chloride (PVC), and others are used.

Spunbonded olefins have been used extensively in limited-use or disposable protective clothing, and DuPont's Tyvek® has been used in several studies. Tyvek® is available in several forms, but the type of Tyvek® used is not always specified in pesticide protective clothing research. It should be noted that DuPont recommends Tyvek® only for handling pesticides in the form of granules, powders, or dusts and not for liquids (DuPont, 1995c). For handling pesticides that are eventually applied as liquids, other types of protective materials are available and recommended, such as Tyvek® QC and Tyvek® laminated with Saranex® 23-P.

Tychem®10,000, a new member in DuPont's Tychem® line of chemical protective fabrics, seems to offer excellent permeation performances against a wide variety of chemicals, especially against ethyl parathion and malathion (DuPont, 1995d), and warrants evaluation for limited-use protective clothing. Sarin (1994) evaluated PP/cotton/PP trilaminate fabrics of varying fiber composition, and found that laminates did not offer enhanced protection when compared to fabrics made from 100 percent PP and Tyvek®. Overall, comfort studies in the area of pesticide protective clothing have shown that spunbonded polyolefins, and laminates thereof, are not very comfortable.

GoreTex®, a fabric made of microporous PTFE membrane sandwiched between two fabric layers, has been used in pesticide protective clothing research; however, W. L. Gore and Associates, the manufacturer, indicates that the company does not promote the

use of GoreTex® for pesticide protective clothing (W. L. Gore and Associates, personal communication, 1995).

Nonwoven fabrics containing a layer of microporous polypropylene are being evaluated in the Department of Clothing and Textiles at Virginia Tech. Microporous materials and their application in pesticide protective clothing will be reviewed separately.

Research on Types of Pesticides, Their Forms, and Methods of Exposure

In evaluating protective clothing, researchers have used different pesticides, in different forms and quantities (volumes), and under different exposure conditions to study the influence of these variables on barrier effectiveness. Pesticides such as malathion, methyl parathion, dinoseb, carbaryl, chlorpyrifos, atrazine, diazinon, guthion, and paraquat have been used. Pesticide forms used in such studies have included flowable liquids, emulsifiable concentrates, wettable powders, and encapsulated materials.

Laughlin et al. (1986) concluded that methyl parathion in the encapsulated form showed the least penetration, followed by wettable powder and then the emulsifiable concentrate. Raheel (1991a) used wettable powder and flowable liquid formulations, and found that the liquid pesticide showed penetration three to ten times as much as the wettable powder. This is to be expected because the liquid tends to flow into the capillaries and other openings, but the solid powder cannot do the so unless the particles are of a size smaller than the capillaries of the fabric.

Exposure conditions that influence pesticide penetration and have been

investigated include pesticide application method, volume of the pesticide applied, duration of exposure, and nature of the collector substrate. (The substrate is the layer showing the contamination from the pesticide that has been transported to it.)

As to pesticide protective clothing itself, the influences of the fabric characteristics of fiber content, fabric construction, and fabric finish on the effectiveness of a barrier material in preventing or minimizing pesticide transport to the skin have been studied. Based on the results of several researchers, Branson and Sweeney (1991) contend that fabric construction and fabric finish may be the most important characteristics that influence barrier performance.

Raheel and Gitz (1985) examined the influence of fabric geometry on capillary penetration (wetting and wicking) of cotton, and found high wicking rates in cotton fabrics with smaller interfiber and interyarn capillary radii (broadcloth, a plain weave) and high wetting rates in fabrics with larger interfiber and interyarn radii (twill and poplin). Leonas (1991) obtained similar results with plain weave and twill fabrics.

The barrier effectiveness of fabrics made from synthetic fibers is lower than that of fabrics made from cotton. The irregular surfaces in cotton fibers, coupled with the high polarity of cotton, allow it to absorb and hold liquids without passing them to the underlying substrate. A non-polar fiber like polyester has low absorbency and liquid-holding abilities. Thus, several studies (Leonas, 1991; Lillie, Livingstone, & Hamilton, 1981; Raheel, 1991) have found that woven fabrics made of 100 percent cotton were better barriers against pesticide penetration than fabrics made of 100 percent polyester and

polyester/cotton blends.

In comparing the penetration resistance of several fabrics to pesticides, Raheel (1991a) found that Tyvek® and fabrics with fluorochemical-repellent finishes were more effective than 100 percent cotton, blends of cotton with polyester, and synthetic fiber-based fabrics. Studies by Leonas, Easter, and DeJonge (1989) and Staiff, Davis, and Stevens (1982) showed that PE-coated and Saranex®-coated Tyvek® were better barriers than uncoated Tyvek®.

Improvements to the pesticide penetration resistance through functional finishes have been attempted. Obendorf, Kasunick, Ravichandran, Borsa, and Coffman (1991) used starch as a means to trap pesticides and limit penetration. Several researchers (Laughlin, Easley, Gold, & Hill, 1986; Leonas & DeJonge, 1986; Raheel, 1991a) have used fluorochemical (FC) finishes to alter the surface properties of treated fabrics and reduce pesticide penetration. Reusable garments treated with FC finishes have, however, shown a tendency to retain pesticides even after laundering (Branson & Rajadhyaksha, 1988; Laughlin & Gold, 1989).

Microporous Materials

A microporous material is a material having extremely small pores. These pores usually have diameters in the submicron range (0.1-3 μm), although materials having pores as big as 10 μm. also are included. A square inch of a microporous material may have seven to eleven billion pores (Gregor, Tanny, Shchori, & Kenigsberg, 1988).

Microporous materials are available in several forms, viz., membranes, films, sheets, coatings, and fibers, and are used in different applications. Their main application, so far, has been in separation technology (Mizutani, Nakamura, Kaneko, & Okamura, 1993). They perform critical functions as separators in biological separations, in desalination, in preparation of ultra-pure water, in long-lasting storage batteries for electric vehicles (e.g., electric cars), and in protective garments for medical and chemical industries (Davies & Owen, 1989; Gregor, et al., 1988; Krejčí, Vanýsek, & Trojánek, 1993).

Microporous materials made from nitrocellulose were first introduced in 1927 by Sartorius-Werkes in Germany. Currently, polymers that are used in making microporous materials include PTFE (Teflon®, as in GoreTex®), polyurethane (used in Entrant®), and polyolefins (used in fabrics from 3M and Kappler). Other polymers used are polysulfone, nylon, and cellulose (Gregor et al., 1988). Microporous materials made from these polymers vary in cost, have different properties, and are engineered for specific end applications. Microporous membranes are made by two principal methods: wet cast and biaxial stretching.

In the wet cast method, a solution of the polymer in an organic solvent is coagulated by leaching it in water (Gregor et al., 1988; Krishnan, 1992). Coagulation is effected in gel-like structures as a thin film on a conveyer belt or as a coating directly on woven or nonwoven fabrics. The organic solvent is then removed from the film by washing in water and then drying. The pore sizes obtained through this process are in the

order of 0.1-10 μm. The wet-cast method is a relatively slow and expensive process, but still widely used.

In the biaxial stretch method, a crystallizable polymer (e.g., PTFE) is stretched biaxially (in longitudinal and transverse directions) to cause extremely small tears in the material (Davies & Owen, 1989; Gregor et al., 1988). These tears, having diameters of 0.1-10 μm, are the micropores. The PTFE membrane used in GoreTex® fabrics is made by this method. This method is slow, and the onion skin-like membranes so produced are expensive.

Applications of microporous materials in clothing. The diameters in microporous materials are between 0.2-10 μm, although 0.2-3 μm is the typical range. Water droplets have a larger diameter (100 μm), and thus will not penetrate through a microporous structure. Water vapor, as from perspiration and body heat, has a smaller diameter (0.0004 μm) and can easily pass through the micropores. Based on this principle, microporous materials would allow water vapor to pass through them and concurrently keep water droplets out. Such materials thereby offer waterproof and breathable characteristics.

GoreTex® fabrics, containing a microporous PTFE membrane, were the first to be introduced for such an application (Bucheck, 1991). Several other materials are now made by different techniques to obtain the waterproof and breathable characteristics (Bucheck, 1991; Davies & Owen 1989; Krishnan 1992). Waterproof and breathable

materials find such applications as sports- and leisure-wear, workwear, rainwear, shoes, and gloves.

GoreTex® is made by laminating, between two fabric layers, a microporous PTFE membrane, the membrane having been formed by biaxial stretching. The lamination is effected by spot-bonding with adhesives. Various substrates are used to form the face and back layers, and the choice of the substrates depends on the application. The face fabric usually has a water-repellent finish to ensure minimal seepage of challenge liquids.

Microporous materials in pesticide protective clothing. Although a material like Tyvek® provides fair protection against pesticide penetration, protective clothing made from it is uncomfortable as it does not allow for the dissipation of body heat and perspiration. Fabrics containing microporous materials, that can afford the waterproof and breathable qualities, thus seem the logical choice in such applications. These materials would work by resisting penetration by liquid droplets of a pesticide emulsion, for instance, while permitting perspiration from a wearer's body to pass through them and evaporate off the fabric surface. Among all micro-porous materials found in pesticide protective clothing, microporous PTFE (as in GoreTex®) has been used the most. The following is a review of research related to the use of GoreTex® and other fabrics containing microporous PTFE.

A study by Orlando, Branson, and Ayers (1981) was among the earliest which proposed GoreTex® as an effective barrier to pesticide penetration. Branson, Ayers, and

Henry (1986) evaluated the barrier effectiveness of three fabrics made from microporous PTFE membranes to field strengths of different pesticides. Their investigation showed that all three fabrics offered significantly better protection than fabrics of spunbonded polyethylene and three different weaves of cotton.

Leonas, Easter, and DeJonge (1989), using 12 fabrics, observed the effect of fabric characteristics on pesticide penetration. They determined that GoreTex® resisted penetration to three of the four pesticides used (at 0.12% concentration). They concluded that fabric surface energy was not a determinant in the penetration of pesticide; but contrarily, they attribute the penetration of the pesticide Captan® through GoreTex® to "the nature of interaction between pesticide solution and the fabric surrounding the PTFE layer". From the published information, it appears that surface energy characteristics were not studied in a controlled manner by Leonas et al. (1989) and justify further investigation.

Through a controlled laboratory study, Branson, DeJonge, and Munson (1986) determined that GoreTex® fabrics were as comfortable as fabrics made from 100 percent cotton chambray. Polyethylene-coated Tyvek®, which was also used in the study, did not permit the dissipation of body heat and thus was perceived as uncomfortable.

Shaw and Hill (1990) observed the effect of variability in four water-repellent fabrics containing microporous PTFE on the sorption of an emulsifiable concentrate of diazinon. Diazinon was found to have sorbed to different extents between different regions in the same fabric and also into the PTFE membranes. The variability in sorption

was attributed to non-uniformity of application of water-repellent finish.

Shaw (1993) attempted to characterize the distribution patterns (sorption and penetration) of emulsifiable concentrate diazinon in layered fabrics containing microporous PTFE laminated to woven fabrics of different fineness. Penetration occurred in all the laminates, and was attributed to the contact points of the yarns with the PTFE membrane. Shaw claims that the coarser yarns caused more damage to the membranes during lamination than did the finer yarns such as found in commercial GoreTex®; thus, fabrics with coarser yarns showed greater penetration than those with finer yarns.

Fabrics made from microporous PTFE (like GoreTex®) have shown better wearer comfort and lower penetration by field-strength and full-strength pesticides as compared to other effective, but moisture-impermeable barriers. However, such fabrics have been observed to retain high amounts of pesticide in all layers of the laminate, both before and after laundering (Branson & Rajadhyaksha, 1988; Easter, 1983). Pesticide retention in GoreTex® could be a serious limitation in its use for protective clothing, especially due to its high cost and claimed reusability.

One of the biggest drawbacks in pesticide protective clothing research has been that, usually, several variables concerning fabrics, pesticides, and exposure conditions are observed and/or are operative at a time. The resulting analyses rarely establish causal relationships between these variables. In so far as fabrics containing microporous materials are concerned, such materials should, ideally, not show any liquid penetration. The study by Shaw (1993) provides some physical-mechanical explanation (damage of the

PTFE membrane by the lamination process) for the observed penetration; however, it should be noted that Shaw used two-layered laminates. No similar damage of the PTFE membrane was reported with commercial GoreTex®, a three-layer laminate.

Summary of the Literature Review

Certain additives called 'adjuvants' are blended with a herbicide, at the formulation and/or the spraying stage, so as to enhance the herbicidal efficacy, efficiency. Adjuvants are credited with the delivery, optimization, and persistence of herbicide phytotoxicity (Chow, 1984; Foy, 1989; 1991). Thus, adjuvants play a significant role in helping a herbicide realize its potential in combating weeds, insects, and other pests.

Among all adjuvants used, surfactants constitute the largest and most widely used. A surfactant is a chemical that is active at surfaces (surface active agent). Surfactants are chemicals that show significant activity at the surfaces or interfaces than in the bulk of the systems containing them. Surfactants reduce the surface free energy and contact angle of a liquid when added to it. Reduction of the surface free energy and contact angle leads to increased spreading and wetting of a solid surface by the liquid.

Of the several hundred surfactants used as adjuvants in agrochemicals, non-ionic surfactants (NIS) are used the most because they do not react with the other ingredients of a pesticide/herbicide formulation (Chow, 1984; Foy, 1979-80; 1991). Leaf surfaces of crops/plants have a layer of non polar wax on their outer, cuticular region. A non polar surfactant (a NIS) would facilitate the adsorption and, consequently, the herbicide

effectiveness, to a significantly greater level than a polar surfactant. Thus, non-ionic surfactants are used extensively as herbicidal adjuvants.

When a surfactant is added to water, the surface tension (γ) of water decreases till it reaches equilibrium. The equilibrium surface tension is the juncture at which micelles first start to form and the surfactant concentration at the equilibrium surface tension is called the critical micelle concentration (CMC). A surfactant solution has the lowest γ at its critical micelle concentration (CMC). Beyond the CMC, increased concentrations of surfactant in a solution do not reduce the γ. The CMC for most surfactants is below 1.0 percent.

For a surfactant to be effective in solubilizing insoluble organic substances in water, it should be used above its CMC because it is only past the CMC that micelles, which solubilize the insoluble organic substances, are formed (Shaw, 1970). The application of herbicides in practice involves the usage of surfactants in concentrations several magnitudes greater than the CMC (Foy 1979-80; Foy & Smith, 1965). The higher concentrations of surfactant are claimed to enhance herbicidal penetration and phytotoxicity, thereby permitting herbicidal usage at lower dosages.

Pesticides and herbicides are toxic chemicals. Their handling and application processes expose agricultural workers to harmful chemicals. Protective clothing is used in pesticide related applications to minimize and, hopefully, eliminate dermal exposure. Several barrier materials have been used in pesticide protective clothing.

In pesticide protective clothing studies, the two aspects primarily studied are

wearer comfort and the barrier effectiveness to penetration by the pesticide. Protective clothing made from encapsulated rubber, neoprene, vinyl, and even certain types of Tyvek® offer the best protection against pesticide penetration but is extremely uncomfortable. These materials do not permit the evaporation (and thus the drying and subsequent cooling) of perspiration from the wearer's body and make the wearer feel clammy and uncomfortable. Consequently, this would discourage an agricultural worker's use of protective clothing made from such materials.

Textile fabrics containing microporous materials have been used in pesticide protective clothing applications. Microporous materials work by allowing the water vapor (perspiration) from a wearer's body to pass through them and evaporate on the outer fabric surface. Concurrently, they keep the larger liquid molecules from penetrating into the fabric.

Fabric wetting is influenced to a great extent by liquid surface tension (γ). Only liquids of γ less than the fabric surface tension (or surface free energy) will wet the fabric. While low γ of the herbicide solution is essential to the wetting of plant surfaces, it presents a concomitant risk of the fabric becoming wet easily and thus failing to serve as an effective protective barrier.

Surfactant concentrations in excess of the levels required for minimum surface tension might be beneficial from the agricultural standpoint. However, the effect of such high surfactant concentrations on the barrier effectiveness of protective clothing is not known. Careful consideration of the opposing needs and demands of increasing

herbicidal phytotoxicity and efficiency versus the barrier effectiveness (non wetting) of the protective clothing should be made. Such consideration would help one select an ideal textile material that could perform as an effective barrier under these 'constraints'.

Herbicide-water emulsions of different γ levels would exhibit different wetting characteristics on solid surfaces. Because surfactants are the chemicals that influence the surface tension of the herbicide formulation (or the spray tank emulsion), water containing different concentrations of surfactant could attain different γ levels, though only below the CMC, and thus, could be expected to exhibit different wetting characteristics, too.

Despite the extensive literature in pesticide protective clothing, the barrier effectiveness of protective material, as a function of surfactant concentration and surface tension, has not yet been studied. It would be important to understand the influence of surface tension and concentration of a surfactant on the barrier effectiveness of microporous polypropylene fabric that may be used in pesticide protective clothing.

Knowledge of the surface free energy and concentration influences would help in understanding their relations to wetting, wicking, and capillary penetration properties which, in turn, could help characterize the barrier effectiveness of the microporous polypropylene fabric to pesticides. Since surfactant concentrations beyond the CMC are commonly used in herbicide formulations, the effect, if any, of increased surfactant concentration on wetting, wicking, and capillary penetration would help determine the 'threshold range' of surfactant concentration beyond that for the optimization of herbicidal efficacy and efficiency (i.e., for protective clothing).

Chapter III

SETTING OF THE PROBLEM

This chapter is organized into the following sections:

- Theoretical framework
- Definitions of major concepts
- Research problem statement
- Objectives
- Research hypotheses and rationale for the hypotheses
- Assumptions
- Limitations of scope

Theoretical Framework

Certain additives called 'adjuvants' are blended with a herbicide, at the formulation and/or the spraying stage, so as to enhance the herbicidal efficacy, efficiency. Among all adjuvants used, surfactants constitute the largest and most widely used. A surfactant is a chemical that is active at surfaces (surface active agent). Surfactants reduce the surface free energy of a liquid when added to it. Surface free energy or surface tension is a force that prevents wetting. Liquids with high surface free energies will not easily wet a solid surface. Reduction of the surface free energy leads to increased spreading and wetting of a solid surface by the liquid.

When a surfactant is added to water the surface tension (γ) of water decreases till it reaches equilibrium. The equilibrium surface tension is the juncture at which micelles first start to form and the surfactant concentration at the equilibrium surface tension is called the critical micelle concentration (CMC). A surfactant solution has the lowest γ at its critical micelle concentration (CMC). Beyond the CMC, increased concentrations of surfactant in a solution do not reduce the surface tension.

A drop of liquid in contact with a solid surface forms an angle of contact. The formation of a contact angle implies a condition of insufficient or no wetting. Liquids of high surface tension form larger contact angles than do liquids of lower surface tension. Thus, a decrease in surface tension, brought about by an increase in surfactant concentration in a system, will cause a corresponding decrease in contact angle, till the critical micelle concentration.

A plot of the cosine of contact angle and the surface tension of a homologous series of liquids is linear and is called the Zisman plot. A Zisman plot can afford the information about the surface tension of a liquid that gives a contact angle of zero (0°). A liquid that just gives a contact angle of 0° has the same surface tension as the solid surface (Ellison & Zisman, 1954; Fox & Zisman, 1950, 1952). Thus, the Zisman plot can give the surface free energy or the critical surface tension (C_{st}) of a solid surface.

Fabric wetting is influenced to a great extent by the free energies of the liquid and the fabric surface. Only liquids of γ less than the fabric surface tension (or surface free energy) will wet the fabric. Wetting is the phenomenon resulting from the forces of

adhesion at the liquid-solid interface (Ellison & Zisman, 1954). The energy that is indicative of the attraction of a solid to the liquid at their interface is called the work of adhesion and is given by the Young-Dupré equation,

$$W_a = \gamma_{LV} (1 + \cos \theta) + \pi_E$$

where, γ_{LV} is the surface free energy of the liquid, θ is the contact angle for the liquid on the solid surface, and π_E is the equilibrium spreading pressure of the adsorbed vapor on the solid surface. For a liquid like water, which has a relatively high boiling point, π_E is negligible and is eliminated from the above equation (Fox & Zisman, 1950, 1952) to give

$$W_a = \gamma_{LV} (1 + \cos \theta).$$

Work of cohesion (W_c) is another form of energy that is indicative of how well a unit cross-sectional area of the liquid holds to itself. It is determined from the surface free energy of the liquid,

$$W_c = 2\gamma_{LV}.$$

A liquid that has a high surface free energy also will have a high work of cohesion value, and will not easily spread on a given surface. Low work of cohesion (from low surface tension) values are required for good wetting of surfaces, whereas high work of cohesion (high surface tension) values are desirable for applications requiring limited or no wetting.

A quantity, called spreading coefficient, is often used to describe the wetting behavior of a liquid on a solid surface. Spreading coefficient is the difference between the work of adhesion and the work of cohesion. Thus,

$$S_c = W_a - W_c$$

where W_a is the work of adhesion, W_c is the work of cohesion and S_c, the spreading coefficient in dynes/cm. A positive S_c value implies that the liquid will spread and wet the solid surface, and a negative S_c value implies that the liquid will not spread or wet the solid surface within the time of the contact angle measurement.

Since, $W_a = \gamma_{LV} (1 + \cos \theta)$, and $W_c = 2\gamma_{LV}$, substituting the respective quantities for the work of adhesion and the work of cohesion in the spreading coefficient equation, we have, $S_c = \gamma_{LV} (\cos \theta - 1)$. In general, as the liquid surface free energy decreases, the contact angle decreases and the spreading coefficient (and consequently, the wetting) increases.

Capillary penetration is penetration promoted primarily by capillaries. It is influenced by the liquid and solid surface free energies and other factors like surface density, liquid viscosity, etc. (Minor, et al., 1961). Wicking is a concept often used in describing capillary penetration. Wicking is the migration of liquid through the interfiber and interyarn capillaries of a fabric. Based on the Young-Laplace equation, wicking occurs due to the pressure difference across the curved surface of a liquid meniscus (Adamson, 1976). Thus,

$$\Delta P = 2 \gamma_{LV} \cos \theta / r.$$

where ΔP is the pressure difference across the meniscus, γ_{LV} is the surface free energy of the liquid, θ is the contact angle, and r is the capillary radius. A liquid with a high surface tension has a high pressure difference across its surface and is wicked farther than a liquid with a lower surface tension.

Definitions of Major Concepts

Surface Free Energy

Surface free energy, often called 'surface tension', is the free energy of formation of an interface or the work required to increase the area of a surface by unit amount (Shaw, 1970). It is also identified as the force per unit length (dyne/cm) and is represented by the Greek symbol, the gamma (γ).

Contact Angle

The angle formed between the tangent to the profile of the liquid drop at the point of contact with the solid surface is called the contact angle (Adamson, 1976), and is represented by the Greek symbol, the theta (θ). The formation of a contact angle implies a condition of insufficient wetting or non wetting.

Critical Surface Tension

The surface free energy of the liquid that will just spread on the polymer surface is the critical surface tension (γ_c) of the solid polymer. Stated otherwise, critical surface tension (C_{sl}) of a solid is equal to the surface tension of a liquid which, when placed in contact with the solid surface, gives a cos θ value approaching unity (i.e., $\theta = 0°$) (Ellison & Zisman, 1954; Fox & Zisman, 1950, 1952).

Work of Adhesion

The work of adhesion is the work or energy, in dynes/cm required to separate one square centimeter of a common interface between two phases into two distinct interfaces (Adamson, 1976; Shaw, 1970). Work of adhesion, W_a, is indicative of the attraction of

the solid surface to the liquid at their interface.

Work of Cohesion

Work of cohesion (W_c) is the amount of work or energy, in dynes/cm, needed to pull apart a column of the liquid (Adamson, 1976; Shaw, 1970), and is determined from the surface free energy of the liquid ($W_c = 2\gamma_{LV}$). A liquid that has a high surface free energy also will have a high work of cohesion value, and will not easily spread on a given surface.

Wetting and Spreading

Wetting has been defined as the phenomenon resulting from the forces of adhesion at the solid-liquid interface (Ellison & Zisman, 1954). Wetting implies that the contact angle between a liquid and a solid is zero or very close to zero, because it is in such conditions that the liquid will have a tendency to spread easily over the solid surface. Spreading is the indefinite movement of the bulk liquid or a thin film (Fox & Zisman, 1950) across a surface. The two terms, wetting and spreading, are used interchangeably in the context of this research.

Spreading Coefficient

The spreading coefficient is the difference between the work of adhesion and the work of cohesion (Fox & Zisman, 1950). Thus,

$$S_c = W_a - W_c$$

Where W_a is the work of adhesion, W_c is the work of cohesion and S_c is the spreading coefficient in dynes/cm. A positive S_c value implies that the liquid will spread and wet the

solid surface, and a negative S_c value implies that the liquid will not spread or wet the solid surface within the time of the contact angle measurement.

Research Problem Statement

The purpose of this research is to evaluate the influence of the surface tension and concentration of Triton® X-100, a non-ionic surfactant, on the barrier effectiveness of micro-porous polypropylene fabric which may be used in pesticide protective clothing. The capillary penetration, wetting, and wicking characteristics of the fabric were used to indicate the barrier effectiveness.

Aqueous solutions of different concentrations of Triton® X-100 were prepared using double distilled, de-ionized (DDDI) water. DDDI water, with a mean surface tension of 72.52 dynes/cm and a Triton® X-100 concentration = 0% w/v, was used as an additional liquid in the evaluation.

Fabric wetting was evaluated from the drop absorbency test, a modified Draves test, spreading coefficient calculations, and, by inference, from the Zisman plot. The fabric's surface free energy and spreading coefficient values were determined from the immediate advancing contact angle measurements.

Objectives of the Research

The objectives of this research are as follows:

1. To determine the effect of concentration of Triton® X-100 on the surface tension

of its aqueous solutions.

2. To determine the influence of surface tension and concentration of Triton® X-100 on the capillary penetration, drop absorbency, Draves sinking, spreading coefficient, and wicking characteristics of, and the contact angles formed with, the microporous polypropylene test fabric.

3. To determine the surface free energy of the microporous polypropylene test fabric.

Research Hypotheses and Rationale

Hypothesis 1. As concentration of Triton® X-100 in the aqueous solution increases from 0.0 percent, the lowest concentration used in this study (Liquid No. 1), surface tension will decrease linearly at first and then remain steady.

Rationale: Surface tension decreases with increasing concentration of a surfactant until the equilibrium surface tension point, i.e., until the critical micelle concentration (CMC). Beyond CMC, additional Triton® X-100 will not lower the surface tension any further.

Hypothesis 2: As the liquid surface tension (γ) decreases with increasing surfactant concentration in the solutions, the immediate advancing contact angles formed will decrease proportionately till CMC beyond which, they will remain constant.

Rationale: Solutions of different surface tension (γ) will form different contact angles (θ) at the fabric surface. Zisman and co-workers have shown a linear relationship between

γ and the cosine of θ for homologous series of liquids on several polymer surfaces. Surfactant solutions at different concentrations could be expected to behave like liquids in a homologous series and thus it seems rational to expect a linear relationship between cos θ and the γ of the aqueous surfactant solutions. Beyond the CMC, the γ remains constant hence the θ is expected to remain constant.

Hypothesis 3: The surface free energy or the critical surface tension (C_{ST}) of the microporous polypropylene test fabric will be the same as the surface free energy of the Triton® X-100 solution that gives a contact angle of zero.

Rationale: Critical surface tension of the solid has been shown by Zisman and co-workers (Ellison & Zisman, 1954; Fox & Zisman, 1950, 1952) to be equal to the surface tension of the liquid that gives a contact angle of zero on that solid surface. Thus, the surface free energy of the fabric will be the same as that of the solution of Triton® X-100 which gives $\theta = 0°$.

Hypothesis 4: As Triton® X-100 concentration increases and the γ of the solutions decreases, capillary penetration through the fabric will increase. The capillary penetration will increase until the critical micelle concentration (CMC). Beyond the CMC, capillary penetration will be constant.

Rationale: Capillary penetration is influenced by the surface free energies (γ) of the solid and the liquid among other factors. A liquid of high γ (like water) will not spread

easily and thus, will not wet or penetrate it appreciably. Liquids of progressively lower γ will exhibit progressively greater capillary penetration. Since capillary penetration is influenced by the γ of liquid, and since γ will remain constant beyond the CMC, it is hypothesized that capillary penetration will increase with increasing concentration until the CMC, beyond which it will stay constant. The fabric surface free energy is a constant since the fabric used is the same.

Hypothesis 5: Drop absorbency times and the Draves sinking times, two measures of wetting in this study, will show a direct relation to the surface free energy of the solutions and an inverse relation to the Triton® X-100 concentration till the CMC. Beyond the CMC, wetting, as determined from the drop absorbency and Draves sinking times will be constant.

Rationale: The drop absorbency time and the Draves sinking time are both influenced by the surface free energies of the liquid and the fabric surface. Since the surface free energy of the fabric is a constant value, changes in the concentration and surface tension of the surfactant solutions will cause corresponding changes in the wetting responses as measured by theses two tests. The wetting response times for both these tests are expected to remain constant past CMC because the surface tension of the surfactant solutions remains constant past CMC.

Hypothesis 6: As the Triton® X-100 concentration increases and the γ of the solutions

decreases till the CMC, the spreading coefficient will increase till the CMC. Beyond the CMC, the spreading coefficient will be a constant value and the liquids will not show any increased wetting/spreading.

Rationale: Spreading coefficient (S_c) is the difference between the work of adhesion and the work of cohesion and is also given by the equation,

$$S_c = \gamma_{LV} (\cos \theta - 1)$$

where γ_{LV} is the surface free energy of the surfactant solution and θ is the contact angle. With an increase in Triton® X-100 concentration and a corresponding decrease of the γ_{LV}, θ would decrease while the cosine of θ will increase till the CMC. Increase in cos θ value till the CMC will result in increased value of the S_c. Beyond CMC, γ and θ are expected to remain constant (Hypothesis No. 3, above) and hence, S_c and wetting are expected to remain constant.

Hypothesis 7: As γ of solutions decreases with increasing Triton® X-100 concentration, the solutions will exhibit a decreased tendency to be wicked through the microporous polypropylene fabric. Water that does not contain any Triton® X-100 (Triton® X-100 concentration = 0.000%) will be wicked to the greatest extent. Triton® X-100 solutions, especially at CMC and higher concentrations, will show the least wicking.

Rationale: Based on the Young-Laplace equation, wicking of a liquid through the interfiber and interyarn capillaries of a fabric occurs due to the pressure difference (ΔP) across the curved surface of a given liquid meniscus (Adamson, 1976). High ΔP values

result in increased wicking while low ΔP values result in lower wicking. With increasing Triton® X-100 concentration, the surface tension decreases and ΔP, the pressure difference across the meniscus becomes very small. Thus, it is hypothesized that as γ of a liquid decreases, the distance wicked decreases. Since 'pure' water has the highest γ (and the highest ΔP) of all the liquids tested, it should be wicked to the greatest distance. As concentration increases (and γ decreases, at least until the CMC), the pressure differential across the curved surface of a liquid meniscus decreases and the liquid will have a decreased tendency to be wicked. Because an aqueous solution of Triton® X-100 will have the least γ (and the least ΔP) at its CMC, solutions with Triton® X-100 concentrations at and greater than the CMC will be wicked the least distance.

Assumptions

1. The behavior of aqueous solutions of Triton® X-100 correctly represents the behavior of pesticide formulations of the same surface free energy (i.e., the spray tank emulsion) under normal field application conditions.
2. The surfaces of all apparati used were completely free of any contaminants that could alter the surface free energy of the liquids prepared, dispensed, and stored in them.
3. Environmental conditions (temperature and relative humidity) in the laboratories where surface free energy, contact angle, capillary penetration, wetting, and wicking were measured were very similar to one another. Differences in the environmental conditions, if any, did not appreciably influence the outcome of this research.

4. Variabilities in the manufacture of Triton® X-100 and the microporous polypropylene fabric that might cause variations in their properties are assumed to be of a random nature and not systematically affect the outcome of the research.

5. All solution and fabric preparations and measurements are precise and accurate. Errors due to operator and equipment, if any, are random and will not systematically affect the outcome of the research.

6. All equipment used affords accurate data.

Limitations of Scope

1. This study deals only with non-ionic surfactants. Anionic, cationic, and amphoteric surfactants were not used. Results are thus not generalizable to surfactants of these ionogenic classes. Even within the non-ionic class, hundreds of different surfactants are used as pesticide adjuvants. This study deals only with Triton® X-100 (an octylphenol polyether alcohol surfactant) and the results pertain strictly to that.

2. Although this study aims to evaluate protective clothing for pesticide applications, only aqueous surfactant solutions of similar γ and concentrations were used in the evaluation. The presence of pesticides, along with other adjuvants could significantly alter the behavior/response of the microporous polypropylene test fabric to the challenge liquids. Results, thus cannot be extrapolated to predict the behavior of this candidate barrier fabric to chemical environments other than those studied.

3. Under field conditions, the interactions of Triton® X-100 with a pesticide and with

other adjuvants could be significant. Such interactions, if present, could show significantly different effects on the wetting, capillary penetration, and wicking of the microporous polypropylene test fabric than those shown by only Triton® X-100 in water.

4. Results are not generalizable to other protective fabrics used in pesticide application.

5. Surface free energy is dependent upon temperature. Results of this study cannot be extrapolated to represent results at other temperatures, especially higher temperatures that may be common in field application conditions.

6. This study involves only static testing conditions in the determination of surface tension, contact angle, wetting, and capillary penetration. It should be noted that static conditions may not be a good representation of actual field spraying conditions that are more dynamic. Under dynamic conditions, pressure and impact penetration would be more relevant.

Chapter IV

PROCEDURE

The purpose of this research is to evaluate the influence of surface free energy and concentration of Triton® X-100, a non-ionic surfactant, on the barrier effectiveness of micro-porous polypropylene fabric which may be used in pesticide protective clothing applications. Barrier effectiveness was determined from the capillary penetration, wetting, and wicking characteristics.

Aqueous solutions of different concentrations of Triton® X-100 were prepared using double distilled, de-ionized (DDDI) water. Double-distilled, de-ionized water, with a mean surface tension of 72.52 dynes/cm and a Triton® X-100 concentration = 0% w/v, served, without surfactant, as the control.

Fabric wetting was evaluated from the drop absorbency test, a modified Draves test, spreading coefficient calculations, and, by inference, the Zisman plot. The fabric's surface free energy and spreading coefficient values were determined from the immediate advancing contact angle measurements.

This chapter is organized into the following sections:

- Materials
- Methods, and
- Data Analysis and Hypothesis Testing

Materials

Fabric

The fabric used in this study is a microporous polypropylene (PP) material from Kappler Safety Group, Guntersville, Alabama. The material is a two-layer composite fabric, in which a microporous PP film (the fabric face) is ultrasonically bonded at intermittent, discrete points to a spunbonded PP web layer which serves as the backing.

The microporous film has a thickness of 38 μm, weighs 0.0288 kg/m^2, and has pores 0.2 μm in diameter. A moisture vapor transmission rate (MVTR) of greater than 5,000 gm/m^2/24 hrs., at 75°F and 50 percent relative humidity, has been reported for this film (European Patent 0505027A1, Kappler Safety Group, 1992). The nonwoven PP web is the layer that lends strength to the laminate and gives the fabric a cloth-like texture. It has a thickness of 200 μm and weighs 0.0339 kg/m^2.

The microporous polypropylene fabric used in this study, hereafter called the test fabric, has been promoted for use in protective clothing for medical applications. The manufacturer has reported that the fabric is effective in preventing transmission of blood and water. The microporous layer in the test fabric laminate permits the transmission of water vapor (perspiration) from the wearer's body and thereby lends comfort to the wearer. A table in the results section lists some of the relevant characteristics of the test fabric, including data furnished by Kappler.

Substrate and Backing Materials

The substrate for the capillary penetration measurement was White AATCC Textile Blotting paper (AATCC order No. 8344), as used by Sarin (1994). Reynolds® 665 Heavy Duty Aluminium Wrap served as the backing material for the substrate.

Surfactant

Triton® X-100 (Union Carbide), used to prepare the aqueous solutions, is an alkylaryl polyether alcohol type of non-ionic surfactant; the alkylaryl group is octylphenol. Octylphenol is reacted with ethylene oxide to give the final product, in which the polyoxyethylene group may contain nine to ten moles of ethylene oxide per mole of octylphenol. The product used in this research was 'neat', i.e., 100 percent active.

Triton® X-100 is identified as an adjuvant for pesticides, that may be applied either to growing crops or in post-harvest treatments. It has been promoted as a good emulsifier for oil-in-water (o/w) systems and a surfactant that shows good wetting properties. Table 1 lists physical properties of Triton® X-100. Properties most relevant to this study are its solubility, HLB, and surface activity as to its surface- and interfacial-tension reducing abilities. The information available from Union Carbide (1995) indicates that the CMC of the surfactant is 134 ppm (0.0134 percent, w/w) and the γ at CMC is 31 dynes/cm. Additionally, data from Union Carbide reveal that, at the 0.1% concentration of Triton® X-100, the interfacial tension between water and mineral oil is reduced to 2.5 dynes/cm from 52 dynes/cm, the interfacial tension in the absence of surfactant.

Table 1

Physical Properties of Triton® X-100‡

Appearance	Clear liquid
Molecular weight (average)	624
Viscosity at 25°C	240 cP
Specific gravity 25° /25°C	1.065
pH of 5% aqueous solution	6
Cloud point (1% aqueous solution)	66°C
HLB value (calculated)	13.5
Critical micelle concentration	134 ppm (0.0134 percent, w/w)
Surface tension at CMC	31 dynes/cm
Solubility in	
Water*	Miscible
Polar organic solvents*	Miscible
Aromatic hydrocarbons*	Miscible
Aliphatic hydrocarbons	Immiscible

* Triton® X-100 is miscible in all proportions in these solvents.
‡ Source: Union Carbide, 1993 and 1995.

Methods

This section contains the following parts:

- Fabric characterization
- Preparation of aqueous surfactant solutions
- Surface tension measurement
- Contact angle measurements
- Determination of fabric surface free energy, and
- Evaluation of barrier effectiveness of the test fabric.

Fabric Characterization

The test fabric samples were conditioned for 24 hours at 21 ± 1°C and 65 ± 2 percent relative humidity. Specimens for the tests were randomly chosen after excluding 10 cm from each selvedge. Specimens were cut to the dimensions appropriate for each test, and were handled with forceps to minimize contamination or deformation (relevant, especially for contact angle measurements). The following characteristics were evaluated.

Basis Weight

The weight, in mass per unit area, of the test fabric was determined by ASTM D3776-85 Standard Test Method for Mass Per Unit Area (Weight) of Woven Fabric (Option C) (ASTM, 1995b). Three specimens, each measuring 57.76 cm^2 (9 $inch^2$), were selected from random locations in the fabric and their mass was determined. From the

mass and the area of the fabric specimens, the weight was determined and reported in units of grams/meter^2 (g/m^2).

Thickness

Thickness of the test fabric was measured with the Federal Thickness Tester (Custom Scientific, Inc.) according to ASTM D 1777-64 (1975) Standard Method for Measuring Thickness of Textile Materials (ASTM, 1995a). The area of the presser foot was one square inch. Five seconds after application of a pressure of 3.59 N/m^2 on the fabric specimen, the thickness was measured in inches and converted to the metric scale. The mean of twelve readings is reported.

Grab Tensile and Puncture/Propagation Tear Strengths

The information on the grab tensile strength and the puncture/propagation tear strength of the microporous polypropylene test fabric, as obtained from ASTM D 751 and from ASTM D 2582-93, respectively, was taken from the data furnished by Kappler (1995). The available data for machine and cross directions were converted to the metric scale and reported.

Air Permeability

ASTM D 737-75 (1980) Standard Test Method for Air Permeability of Textile Fabrics (ASTM, 1994) was used, with a U.S. Testing Air Flow Tester, Model 9025, to

determine the air permeability of the microporous polypropylene test fabric. A nozzle of size 16.0 mm and test fabric specimens of 625 cm^2 (100 $in.^2$) were used. The air permeability range for this nozzle size is 163-356 $cm^3/cm^2.sec$. The results are reported for an average of seven separate specimens in $cm^3/cm^2.sec$.

Water Repellency

In evaluating the water repellency, the static absorption method (AATCC 21-1978) was not used because it involves immersion in water; though commonly used, the method has been discontinued in the AATCC manual. Instead, the measurement was made by the spray method, using AATCC 22-1989 Water Repellency: Spray Test (AATCC, 1994) which indicates the repellency at the fabric surface. Test fabric specimens of 316.84 cm^2 (49 $in.^2$) were used. The fabric was rated using the rating chart for the spray test, and the average of three replications is reported.

Oil Repellency

The oil repellency of the microporous polypropylene test fabric was determined using AATCC Test Method 118-1992 Oil Repellency: Hydrocarbon Resistance Test (AATCC, 1994). The repellency tests were conducted with a series of eight test liquids in the Scotchgard® Textile Finishes SPS-3010 Oil Test Kit (3M Company); the surface tensions of the eight liquids range from 19.8 to 31.5 dynes/cm at 25°C. Fabric specimens of 400 cm^2 (64 $in.^2$) were used. The oil repellency rating was based on the highest-

numbered oil test liquid that would not wet the fabric within a period of 30 seconds.

Preparation of Aqueous Surfactant Solutions

Before preparation of the surfactant solutions, all glassware was thoroughly cleaned using the procedure detailed by Fisher-Scientific (1988). Glassware was cleaned with petroleum naptha followed by two washes in methyl ethyl ketone and water. It was then immersed in hot cleaning solution of chromic acid for 30 minutes, rinsed thoroughly with distilled water, and dried to room temperature before being used.

Aqueous solutions of Triton® X-100 were prepared on a w/v basis. As noted earlier, Union Carbide's technical literature identified the CMC of Triton® X-100 to be 134 ppm (0.0134 percent,w/w). A stock solution of concentration ten times greater than the CMC (0.134 percent) was first prepared and then diluted to seven, successively lower concentrations (0.0737, 0.0134, 0.00737, 0.00134, 0.000737, 0.000134, and 0.0000134 percent, w/v).

Double-distilled, deionized water (Nanopure® II, Sybron/Barnstead) was added to 1.34 gm of Triton® X-100 in a beaker, and the mixture was stirred with a glass rod. Dissolution was aided by placing the beaker in an ultrasonic shaker (Branson® Ultrasonic Cleaner, Model B-22-4, 50-60 Hz) containing water. Once dissolution was complete, the solution was transferred to a 1000-mL volumetric flask. The beaker and glass rod were thoroughly rinsed with double- distilled, deionized (DDDI) water and the rinses transferred to the volumetric flask.

Final volume was made up with DDDI water. Successive dilutions to the desired concentrations were made to 500 mL with DDDI water. In preparing the weaker solutions, a PIPETMAN™ digital pipette (Model P-1000, Rainin Instrument Company, Woburn, MA) was used to dispense out the small volumes of the stock solution. The weakest solution of Triton® X-100, at the concentration of 0.0000134 percent, was prepared by diluting 50 mL of 0.000134 solution to 500 mL with DDDI water. Solutions of 2.0 and 5.0 percent concentrations were prepared separately. These high concentrations of up to 5.0 percent represent surfactant concentrations that have been used in pesticide applications (Foy & Takeno, 1992; Ruiter et al., 1992). DDDI water, alone, was used as the control system, i.e., without any surfactant.

A total of eleven liquids formed the series of test liquids for this research. The solutions were labeled in an ascending order of Triton® X-100 concentration, with Liquid No.1 being DDDI water (Triton® X-100 concentration = 0.00 percent, i.e., no surfactant) and Liquid No. 11 being the solution of 5.0 percent concentration.

Surface Tension Measurement

Surface free energy, or the surface tension (γ), of each prepared aqueous surfactant solution and of water was measured by Method A of ASTM D 1331-89 (1995) Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface-Active Agents (ASTM, 1995c), using a FISHER Surface Tensiomat, Model 21 (Fisher-Scientific, Pittsburgh, PA). This model utilizes the principles of operation originally developed by

Pierre Lecomte du Noüy, and is called the du Noüy method.

In the du Noüy method, a platinum-iridium ring of 6.00-cm circumference is suspended from a counter-balanced lever arm. The arm is held horizontal by torsion applied to a stainless steel wire, to which the arm is clamped. Increasing the torsion in the wire raises the arm and the ring. The raised ring carries with it a film of the liquid, contained in a cylindrical glass vessel in which the ring is immersed. The force necessary to pull the test ring free from this surface film is measured. This 'apparent' surface tension is shown on a calibrated dial (Fisher-Scientific, 1988). As this research involves comparative study of the effects of γ, the 'apparent' γ values, as read from the calibrated dial, were used directly, i.e., without secondary correction to the 'absolute' values.

Before the surface tension of the first liquid was determined, the cylindrical glass vessel which holds the test liquid was cleaned in the same manner as described earlier. Surface tension measurements were made in the ascending concentration order of the test liquids, starting with Liquid No. 1. About 30 mL of the test liquid, either a surfactant solution or water, were transferred into the cylindrical glass vessel. Five readings of γ were taken for each liquid and recorded. All surface tension (γ) measurements were done at 20.5°C (69°F) and 72 percent relative humidity. The mean age of the surfaces (the time between submersion and breakaway of the ring) at the time of the surface tension measurement was 15 ± 5 seconds.

The platinum-iridium ring and the cylindrical glass vessel were cleaned after γ determination for each liquid. The ring was cleaned by dipping it in benzene, followed by

squirting acetone to remove benzene, and then flashing in an oxidizing flame of a Bunsen burner for 20 seconds to remove residual hydrocarbons and any other impurities. The glass vessel was cleaned by first rinsing it in distilled water, then with a stream of ethanol (from a can pressurized with nitrogen), followed by distilled water; the vessel was wiped clean with a lint-free tissue (KimWipes), and dried by squirting a stream of compressed nitrogen gas. The glass vessel was rinsed with the respective test liquid before it was used for surface tension determination of that liquid.

The full set of surface tension measurements was done twice in order to determine the influence of time, if any, on the surface tension of surfactant solutions. The first time was immediately after preparation of the surfactant solutions, and the second time was after a one- week storage of the prepared solutions. The data for these two determinations are reported separately. All test conditions were kept constant for both these determinations.

Contact Angle Measurement

The contact angle (θ) of a drop of a test liquid placed on a flat specimen of the test fabric was determined as the 'immediate advancing contact angle'. The instrument used was a NRL Contact Angle Goniometer (Model No. 100-00-115, Rame-Hart, Inc., Mountain Lakes, NJ),

and the manual procedure, as opposed to the automatic, was adopted to determine the θ value. The goniometer has an optical bench, an illuminator with an illuminator

control box, a three-axis specimen stage, a low-power goniometer microscope with an overall system magnification of 23X, a video camera (DAGE 650), and a 6-inch T.V. monitor (Javelin). A green filter block was used to cover the illuminator. The resultant light beam is focussed on the drop of the test liquid placed on the test fabric specimen, which itself is placed on the specimen stage. The objective lens of the microscope is aligned with the light beam and the specimen stage to produce an image of the drop silhouette. This image is transmitted through the video camera to the television monitor which shows an inverted, sharply-defined image of the sessile drop silhouette. The goniometer incorporates an internal protractor-readout which is calibrated in one-degree increments and allows for the direct reading of θ value (Rame-Hart, Inc., 1996).

In order to prepare the test specimen assembly, double stick tape (Scotch™, 3M) was stuck on a glass slide (2.5 x 7.5 cm). Specimens of the test fabric, also measuring 2.5 x 7.5 cm and having straight and smooth edges, were placed on the glass slide and carefully secured to the tape.

In conducting the actual measurement, the top surface of the substrate, at the edge closest to the microscope, was first brought into focus. A sessile drop on the substrate was formed by carefully dispensing 5 μL of the test liquid (water or surfactant solution) using a 25-μL syringe (Model 702N, Hamilton Company, Reno, NV). The microscope was refocussed and the specimen stage was adjusted to view the extreme left of the sessile drop's inverted profile. The glass reticle in the microscope, which contains the crossline that measures the contact angle, was adjusted to attain tangency with the drop profile at

the base of the drop; the θ value was read directly at the six o'clock position. A total of ten readings was taken for each test liquid within five to ten seconds of the placement of the drop on the substrate; a fresh drop and a fresh dispensing spot were taken for each reading. All measurements were made at 20 ± 1.0°C.

Determination of Fabric Surface Free Energy

Surface free energy of the microporous polypropylene test fabric was determined from the Zisman plot using the method proposed by Fox and Zisman (1950; 1952). Determination of the fabric surface free energy first required the calculation of the cosine of the mean contact angle value which had been obtained from the contact angle measurements for each test liquid. The cos θ values so obtained were plotted on the ordinate against the surface free energy (γ) of the respective liquid plotted on the abscissa.

A perpendicular was drawn to the abscissa from the point where the extrapolated graph (a straight line) intercepted the ordinate cos θ = 1.0 (i.e., when θ = 0°). The point where the perpendicular intercepts the abscissa gives the surface tension of the test liquid that just spreads on the fabric. The surface tension so obtained also represents the surface free energy or the critical surface tension of the microporous polypropylene test fabric.

Evaluation of Barrier Effectiveness

The barrier effectiveness of the microporous polypropylene test fabric was evaluated from the capillary penetration, wicking, and wetting tests. Wetting

performance was evaluated by the drop absorbency test, by an adaptation of the Draves test, and from the spreading coefficient values derived from the contact angle measurements. Wetting performance was also inferred from the Zisman plot, i.e., from the derived surface free energy of the fabric.

Capillary Penetration

Capillary penetration was determined according to the method described by Leonas (1991) and applied by Sarin (1994). The test fabric, substrate, and backing material were all cut to 7.6 x 7.6 cm. Based on the protocol adopted by Sarin (1994), the blotter paper substrate was placed on the aluminum foil backing, and the test fabric was dropped from a height of 2.5 cm. A pressure of 1 psi was applied on the assembly for 30 seconds, and the assembly was allowed to recover for another 30 seconds before it was challenged by the test liquid.

The test liquid (aqueous surfactant solution or distilled water), in the amount of 500 μL, was pipetted onto center of the test fabric/substrate assembly from a height of 1 cm, using a PIPETMAN™ digital pipette (Model P-1000). The liquid was allowed to remain on the fabric surface for 10 minutes. Excess liquid remaining on the fabric surface at the end of the 10-minute period was rolled off into a beaker. The substrate was carefully removed from the assembly and weighed immediately.

The liquid that would pass through the test fabric would penetrate and wet the underlying substrate. Thus, the change in mass of the blotter paper would represent the

capillary penetration through the fabric. A total of three replications for the change in mass were made and recorded.

Wicking Performance

The wicking of the test liquids through the test fabric was measured by the method described by Raheel and Gitz (1985). The test fabric specimen, measuring 2.5 x 15 cm, was marked at 1-cm intervals with water-soluble ink. Markings were made on the back side (the nonwoven side) of the fabric laminate, and the specimen was hung vertically above a beaker containing the test liquid. The specimen was weighted to allow an immersion of 1 cm in the liquid, and the immersion line was taken as the starting line. The distance wicked by the liquid was measured in centimeters after 1, 5, and 10 minutes, and was recorded for the test fabric in the machine and cross directions.

Wetting Performance

The wetting performance of the microporous polypropylene test fabric was evaluated by the drop absorbency test, by a modified version of the Draves test, and by deriving the spreading coefficient values from contact angle measurements.

Drop absorbency. Based on the study by Raheel and Gitz (1991), drop absorbency was measured according to AATCC 79-1992:Absorbency of Bleached Textiles (AATCC, 1994). A specimen of the test fabric, measuring 20 x 20 cm (8 x 8 in.), was held taut by an embroidery hoop (of 15.2-cm or 6-in. diameter), and a drop of

liquid was dispensed on it from a height of 1 cm. The time, in seconds, for the specular reflection of the liquid drop to disappear was measured and recorded. In the early attempts to take the drop absorbency measurements, it was found that the point of disappearance of the specular reflectance of the drop was not distinct. Therefore, the time required for the complete area of the liquid/fabric interface to become dark was noted as the drop absorbency time. Eight readings of drop absorbency were taken for each test liquid and the average was recorded as the wetting time, in seconds, for that liquid.

Modified Draves test. The Draves Wetting Test, ASTM D 2281- 68 (1992) (ASTM, 1995c) and AATCC 17-1989 (AATCC, 1994), is commonly used for the evaluation of wetting agents. The original form of the test measures the time taken by a weighted, 5-gm cotton skein to sink through a solution of a wetting agent contained in a 500-mL graduated cylinder. As such, the skein is used to standardize the testing of wetting agents; unlike in this research, the wetting of the cotton skein itself is not the point of interest. The application of the test in this research was to examine the wetting of the microporous polypropylene test fabric in different concentrations of the surfactant solutions. It was deemed necessary to modify the Draves Test in order to directly obtain the information on the wetting characteristics of the test fabric, as opposed to using a cotton skein, in a system containing a non-ionic surfactant like Triton® X-100 at different concentrations. The test, as modified, was as follows.

Samples of the test fabric were cut in dimensions of 1.5 x 1.5 cm (mean mass = 0.0160 gm). A staple (mass = 0.0330 gm) was punched diagonally through each square-

shaped fabric specimen to weight the specimen. This resulted in the test specimen having a mass of 0.0490 gm. A 50-mL graduated cylinder, with a height of 13.0 cm from its base to the 50-mL mark and an approximate open area of 8.55 cm^2 (in the direction perpendicular to the spout of the cylinder), was filled with 50 mL of the appropriate test liquid.

The protocol established to effect immersion of the test specimen through the height of the test liquid was as follows. A forcep was used to drop a fabric specimen, prepared as above, from a height of 5 cm above the liquid level. The specimen was then gently pushed to just below the liquid surface by means of a glass rod using a pressure of 1 psi. The time taken by each specimen to completely sink to the bottom of the cylinder was measured in seconds. Ten such readings, with newly prepared specimens, were taken for each test liquid.

Spreading coefficient. In order to understand the wetting behavior of the microporous polypropylene test fabric when challenged by test liquids of different surface tensions, the spreading coefficient (S_c) values were determined by the method of Fox and Zisman (1950). Since,

$$S_c = W_a - W_c$$

where W_a is the work of adhesion and W_c is the work of cohesion, the values of W_a and W_c were first calculated. The work of cohesion, W_c, was calculated by using each liquid's measured surface tension, γ_{LV}, as shown below:

$$W_c = 2\gamma_{LV}.$$

The Young-Dupré equation for calculating the work of adhesion, W_a, is shown below:

$$W_a = \gamma_{LV} (1 + \cos \theta) + \pi_E$$

where θ represents the contact angle of the liquid with the fabric, and π_E represents the equilibrium spreading pressure of the adsorbed vapor of the respective liquid on the solid surface. For liquids like water and aqueous Triton® X-100 solutions, that have fairly high boiling points as compared to some volatile organic solvents, the value of π_E would be negligible and is thus eliminated from the Young-Dupré equation above to give

$$W_a = \gamma_{LV} (1 + \cos \theta).$$

A positive S_c value for a test liquid indicates that the liquid will spread on, and wet, the fabric surface. A negative S_c value, on the other hand, indicates that the liquid will neither spread on, nor wet, the fabric surface within the time of the contact angle measurement. For protective clothing applications, and at a specific liquid surface tension value, a negative S_c value is necessary to ensure protective performance.

Effect of Time on Surface Tension

Pesticide formulations are usually stored for some time before they are finally applied. The effect of storage on the surface tension of these formulations has not been reported. The surfactant used in a pesticide formulation influences the formulation's surface tension. This study used only a surfactant in lieu of a pesticide emulsion. Thus, the effect, if any, of time on the surface tension of aqueous surfactant solutions would

represent the effect of storage of the pesticide formulation and emulsion on its surface tension and wetting properties. Data about the effect of storage on surface tension of surfactant solutions have not been reported in the literature.

After their preparation and use for surface tension measurements (measured immediately after preparation), the prepared surfactant solutions were stored at room temperature (20 ±1.0°C) for a period of seven days. Surface tension of each test liquid was determined seven days after its preparation. Statistical analysis was done to assess any significant differences between the surface tensions of the different concentrations of the liquids as a factor of storage time.

Data Analysis and Hypothesis Testing

Data analysis was done from graphs of the dependent and independent variables. Where necessary, the logarithm of the values of the variables were used to plot the graphs. The independent variables were plotted on the X-axis and the dependent variables were plotted on the Y-axis. No statistical analysis for the effect of surfactant concentration on the spreading coefficient characteristics have been given since only the means of surface tension and contact angle were used in the spreading coefficient calculations.

Statistical Tests of Hypotheses

Null hypotheses were developed for the statistical tests of the research hypotheses. The statistical analysis was conducted using the Number Cruncher Statistical System,

version 5.03, developed by NCSS, Kaysville, UT. Analysis of variance (ANOVA) was done to test whether the measured parameters differed between the concentration levels. Post-hoc analyses were done by Duncan's multiple comparison test to determine the effect of surfactant concentration on the test variable. A significance level of .05 was used in all statistical tests. The null hypotheses that were developed are listed below.

NH1: There is no significant difference between the surface tensions of the liquids containing different concentrations of Triton® X-100. Statistical analysis was done using one-way ANOVA. The independent variable was the Triton® X-100 concentration, and the dependent variable was the surface tension.

NH2: There is no significant difference in the contact angles formed by the liquids at different Triton® X-100 concentrations. Statistical analysis was done by one-way ANOVA. Triton® X-100 concentration was the independent variable, and contact angle was the dependent variable.

NH3: There is no significant difference in the capillary penetration of the test fabric with different Triton® X-100 concentrations of the test liquids. Statistical analysis was done using one-way ANOVA. The independent variable was Triton® X-100 concentration, and the dependent variable was capillary penetration.

NH4: In the evaluation of wetting by the drop absorbency method, there is no significant difference in the fabric/liquid interface-darkening time for liquids with different Triton® X-100 concentrations. Statistical analysis was performed with one-way ANOVA. The independent variable was the Triton® X-100 concentration, and the dependent variable was the interface- darkening time.

NH5: In the evaluation of wetting by the modified Draves test, there is no significant difference in the sinking times for the fabric through the liquids at different Triton® X-100 concentrations. Statistical analysis was done using one-way ANOVA. The independent variable was Triton® X-100 concentration, and the dependent variable, the sinking time.

NH6: There is no significant difference in the calculated spreading coefficients of liquids having different Triton® X-100 concentrations. Statistical analysis was done by one-way ANOVA. Triton® X-100 concentration is the independent variable, and the spreading coefficient is the dependent variable.

NH7: There is no significant difference in the distance wicked by the liquids in the machine or cross directions (fabric position), at different Triton® X-100 concentrations, and after 1, 5, and 10 minutes. Statistical analysis was done using three-way ANOVA. The independent variables were fabric position, Triton® X-100 concentration, and time, and the dependent variable was the distance wicked.

Chapter V

RESULTS AND DISCUSSION

This chapter is organized into the following four parts:

- Results of fabric characterization
- Results of surface tension and contact angle measurements
- Results of fabric surface free energy determination
- Results of barrier-effectiveness tests.

The results of the appropriate statistical tests are incorporated within the parts of the chapter. Discussion of obtained results follows the description of each portion.

Fabric Characterization

Results

The results of the various fabric characterization tests are summarized in Table 2. The data on the grab tensile strength and puncture/propagation tear strength in the machine and cross directions, are from Kappler (1995). The air permeability values were not within the detectable range for an orifice of 16.0 mm. Water repellency rating was based on the AATCC spray test rating chart for the test. The evaluation of the oil repellency showed that, when the fabric was challenged by the standard test liquids, the fabric-liquid interface became dark within 30 seconds with the liquid number 3, and, with the liquid number 2, the interface took longer than 30 seconds to become dark.

Table 2

Results of Fabric Characterization

Fabric Property	Results (Value)	No. of Observations
Basis weight	59.64 g/m^2	3
Thickness	514 μm	12
Grab tensile strength	MD 15.42 kg ; CD 14.06 kg	*
Puncture/Propagation tear	MD 2.90 kg ; CD 3.85 kg	*
Air permeability	- ‡	7
Water repellency	100 (ISO 5)	3
Oil repellency	2	3

* Data furnished by Kappler (1995)

‡ Results were not in the air permeability range for the 16.0-mm orifice.

Discussion of the Results on Fabric Characterization

Of the seven fabric characteristics reported in Table 2, the two that are most relevant, and which would help fortify the conclusions of the study, are the water repellency and the oil repellency. The discussion of the fabric characterization results will address these two characteristics.

A water repellency rating of 100 indicates that there was no wetting of the microporous polypropylene test fabric by water. Surface tension of water is around 72 dynes/cm. Water will not adhere to nor wet a material that has a surface free energy (surface tension) lower than itself. Thus, a high water repellency, as evidenced by the highest possible rating of water repellency on the AATCC spray test, indicates that the surface free energy of the test fabric is below 72 dynes/cm, the surface tension of water.

According to the oil repellency test, the fabric-liquid interface became dark within 30 seconds when the fabric was challenged by Oil Test Liquid No. 3 but did not darken by Oil Test Liquid No. 2 within the same time. Oil Test Liquid No. 3 is n-hexadecane (γ = 29.6 dynes/cm at 25°C) and Oil Test Liquid No. 2 is a 65/35 v/v mixture, at 21°C, of Kaydol® white mineral oil and n-hexadecane (γ = 27.3 dynes/cm at 25°C). In this case, if 'wetting' were to be defined as the wetting that would happen in 30 seconds, and knowing that a liquid will spread and wet only a surface which has a surface free energy greater than itself (the liquid), then an oil repellency rating of 2 indicates that the surface free energy of the fabric is greater than the surface free energy of Oil Test Liquid No. 2 but lower than that of Oil Test Liquid No. 3, i.e., between 27.3 and 29.6 dynes/cm.

The test fabric in this research has a microporous layer of polypropylene laminated to a layer of nonwoven polypropylene (the 'backing'). The results of the oil repellency test indicate that the surface free energy of the polypropylene test fabric is between 27.3 and 29.6 dynes/cm. Based on the results of two studies, Wu (1982) has reported two values for the surface free energy of polypropylene, 30.1 and 32 dynes/cm.

It should be noted that the oil repellency test affords a relative-to-approximate, as opposed to an absolute, inference of the fabric surface free energy. The oil repellency rating of 2 for the test fabric is in the range reported by Wu (1982), and thus gives a good approximation of the fabric surface free energy for the test fabric of about 30 dynes/cm.

Surface Tension Measurement

Surface tension measurements of the liquids were made after the preparation of the surfactant solutions. Measurements were made at 20.5°C (reported as 20 ± 1.0°C). The eleven test liquids were assigned numbers in the increasing order of concentration, and are referred to by their respective liquid numbers. The concentrations were converted to the log scale to simplify plotting of the results against the dependent variables. Table 4 lists the mean surface tension values for five observations at each concentration level.

Results of the surface tension determination, for the ten solutions at different concentrations (log C) and for DDDI water show that as the surfactant concentration increases, surface tension decreases almost linearly (see Figure 1). Liquid No. 2 (Triton® X-100 concentration = 0.0000134%, log C = -4.8729) contains a negligible amount of

Table 3

Analysis of Variance of Surface Tension by Concentration

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	10	12,593.24	1,259.324	37,952.26 *
Within conc.	44	1.459999	0.03318	
Total (Adj)	54	12,594.7		

* $p < .05$.

Table 4

Duncan's Multiple Comparison of Surface Tension as a Factor of Triton® X-100 Concentration

Liquid Number	Triton® X-100 Conc. (% w/v)	Log Triton® X-100 Conc. (log of % w/v)	Mean Surface Tension (dynes/cm)
1	0.0000000 ‡	-	72.52 [a]
2	0.0000134	- 4.8729	70.52 [b]
3	0.000134	- 3.8729	62.44 [c]
4	0.000737	- 3.1325	53.68 [d]
5	0.00134	- 2.8729	50.60 [e]
6	0.00737	- 2.1235	38.88 [f]
7	0.0134	- 1.8729	32.84 [i, j]
8	0.0737	- 1.1325	32.68 [j]
9	0.134	- 0.8729	32.98 [i]
10	2.0	0.3010	33.60 [h]
11	5.0	0.6989	33.92 [g]

Note. The mean of five observations for surface tension at 20 ± 1.0°C and relative humidity= 72%. All concentrations in weight/volume.

‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 % (No logarithmic value is reported).

Means with the same superscript are not significantly different at $p < .05$

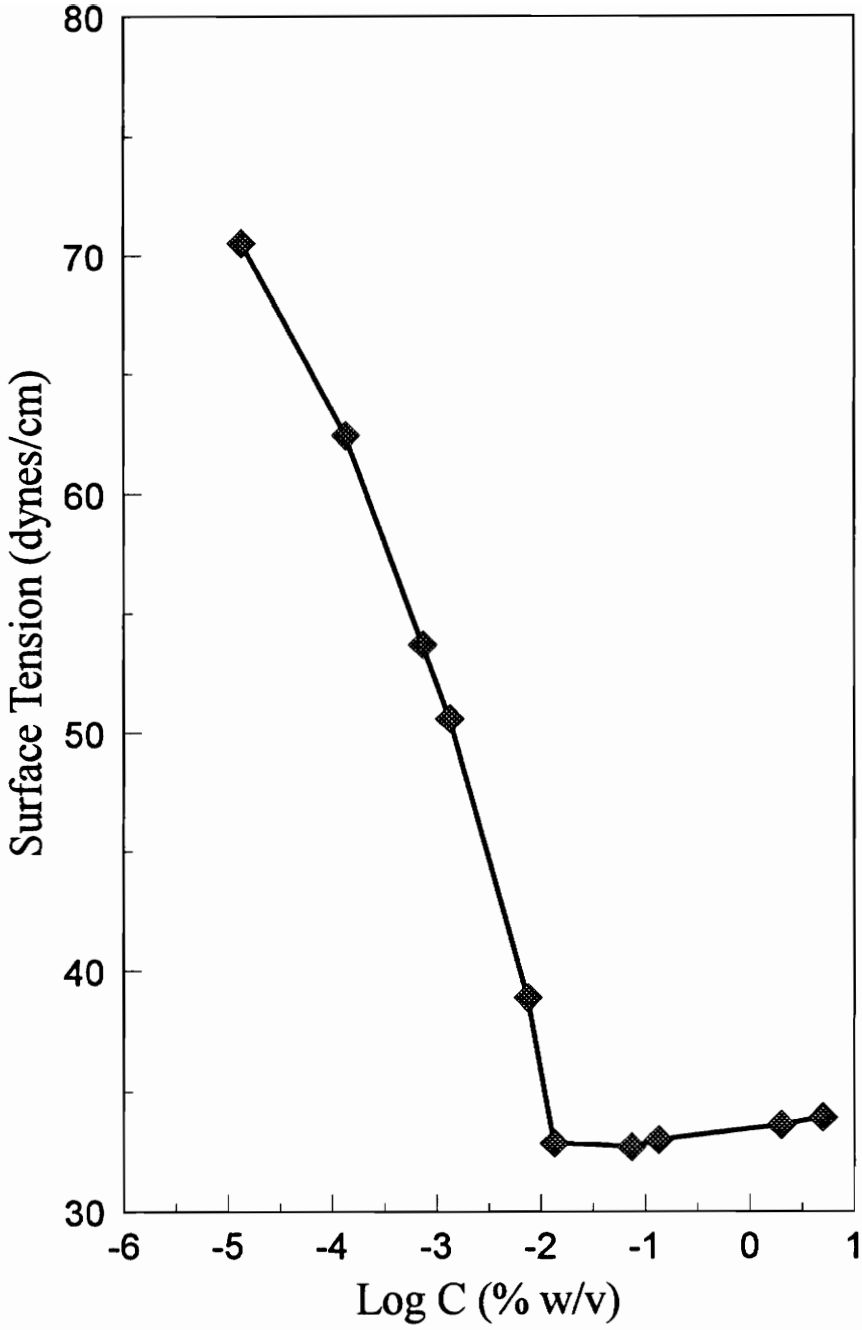


Figure 1. Effect of Triton X-100® Concentration (log C) on Surface Tension.

surfactant and has a surface tension of 70.52 dynes/cm (almost the same as the γ of DDDI water at 72.52 dynes/cm, though not on the graph). At the concentration of 0.0134% (Liquid No. 7), the γ value obtained was the lowest (32.84 dynes/cm) and the graph shows a distinct inflection at this point Surface tension remains relatively steady past this point even as the surfactant concentration increases to levels as high as 5.0%. The 0.0134% concentration point (log C = -1.8729 and γ = 32.84 dynes/cm) is the critical micelle concentration of Triton® X-100.

The results of the one-way analysis of variance (ANOVA) of surface tension by concentration are given in Table 3. The results showed a significant difference between the surface tension of the liquids by Triton® X-100 concentration. Post-hoc analysis by Duncan's multiple comparison showed that there were significant differences between the mean surface tension values between all concentrations, with only some similarities noted beyond the CMC of the surfactant. The results of the Duncan's multiple comparison are also shown in Tables 4.

Discussion of the Results of Surface Tension Measurements

As seen in Table 4 and in Figure 1, with increasing surfactant concentration, surface tension decreased linearly from a high value of 72.52 dynes/cm for Liquid No. 1 (water) to the low value of 32.84 dynes/cm for Liquid No. 7 (Triton® X-100 concentration = 0.0134 percent, the CMC of the surfactant). Triton® X-100 concentration (log C), the independent variable, is represented on the X-axis and surface tension, the dependent

variable, on the Y-axis (Figure 1).

Null hypothesis No. 1 stated that there is no significant difference between the surface tension of liquids containing different concentrations of Triton® X-100. Results of the ANOVA (Table 3), however, show a significant difference ($F = 37{,}952.26$, $df = 10/44$, $\alpha = .05$) between the surface tension of liquids containing different concentrations of Triton® X-100; the null hypothesis is thus rejected. The results of the post-hoc analysis (Table 4) placed the mean surface tension values in different groups.

Figure 1 shows the decrease in surface tension as the surfactant concentration increases. Liquid No. 7 has the concentration at CMC, and it is seen as the critical point beyond which surface tension remains relatively steady. The slight increases in surface tension beyond the CMC, though statistically significant, could be attributed to errors in the experiment, emanating either from preparation of the surfactant solutions or from the precision of the Tensiomat.

The research hypothesis for the effect of concentration on surface tension was supported. As surfactant concentration in the system increases, surface tension decreases until the CMC, after which the surface tension levels off. Increased levels of surfactant in the solution beyond the CMC do not alter the surface tension appreciably, despite the different groupings seen from the post-hoc test.

Results of Contact Angle Measurements

Table 5 shows the results of the one-way ANOVA for the influence of surfactant

Table 5

Analysis of Variance of Contact Angle (θ) by Triton® X-100 Concentration

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	10	44,704.02	4,470.402	217.62 *
Within conc.	99	2,033.7	20.54242	
Total (Adj)	109	46,737.72		

* $p < .05$.

concentration on the contact angles formed. A total of ten observations was made of contact angle (θ) for each test liquid on the test fabric. Table 6 reports the mean of these ten observations for the respective concentration.

Figure 2 shows the effect of concentration (log C) on the contact angle made by the test liquid. As concentration increases from 0.0000134 (log C = - 4.8729) to 0.000737 percent (log C = - 3.1325), θ decreases, albeit only gradually, from 80.5° to 74.4°. Beyond 74.4°, the decrease of the contact angle is sharp until 32.2° for Liquid No. 9 which has a surfactant concentration of 0.134 percent (log C = - 0.8729). The solution with log C = -1.8729 (θ = 59.9°) represents the solution at the critical micelle concentration (0.0134 percent) of Triton® X-100. The marginal increase in θ from 77.0° for log C = - 2.8729 from Liquid No. 4 (θ = 74.4°) is probably due to experimental error.

Results of one-way ANOVA of contact angle by concentration, as shown in Table 5, indicate the significant F-ratio of 217.62. Post-hoc analysis was done by Duncan's multiple comparison and the results of the comparison are given in Table 6. Duncan's comparison indicates that the mean θ value remains relatively steady at lower concentrations. As the concentration increases, the mean θ value decreases, even beyond the CMC, to as low as 29.9° with Liquid No. 10.

Discussion of the Results of the Contact Angle Measurements

Table 6 and Figure 2 show the results of the immediate (< 10 seconds) advancing contact angle measurements as a factor of Triton® X-100 concentration. As surfactant

Table 6

Duncan's Multiple Comparison of Contact Angles as a Factor of Triton® X-100 Concentration

Liquid No.	Triton® X-100 Concentration (% w/v)	Log Conc. (log of % w/v)	Mean Surface Tension (dynes/cm)	Mean θ
1	0.0000000 ‡	-	72.52	81.6 [a]
2	0.0000134	- 4.8729	70.52	80.5 [a,b]
3	0.000134	- 3.8729	62.44	77.8 [a,b,c]
4	0.000737	- 3.1325	53.68	74.4 [a,b,c]
5	0.00134	- 2.8729	50.60	77.0 [a,b,c]
6	0.00737	- 2.1235	38.88	64.4 [d]
7	0.0134	- 1.8729	32.84	59.9 [e]
8	0.0737	- 1.1325	32.68	44.1 [f]
9	0.134	- 0.8729	32.98	32.2 [g]
10	2.0	0.3010	33.60	29.9 [g]
11	5.0	0.6989	33.92	31.3 [g]

Note.
The mean of ten observations for surface tension and contact angle at 20 ± 1.0°C. All concentrations in weight/volume.
‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this 'liquid' = 0 % (no logarithm value).
Means with the same superscript are not significantly different at $p < .05$

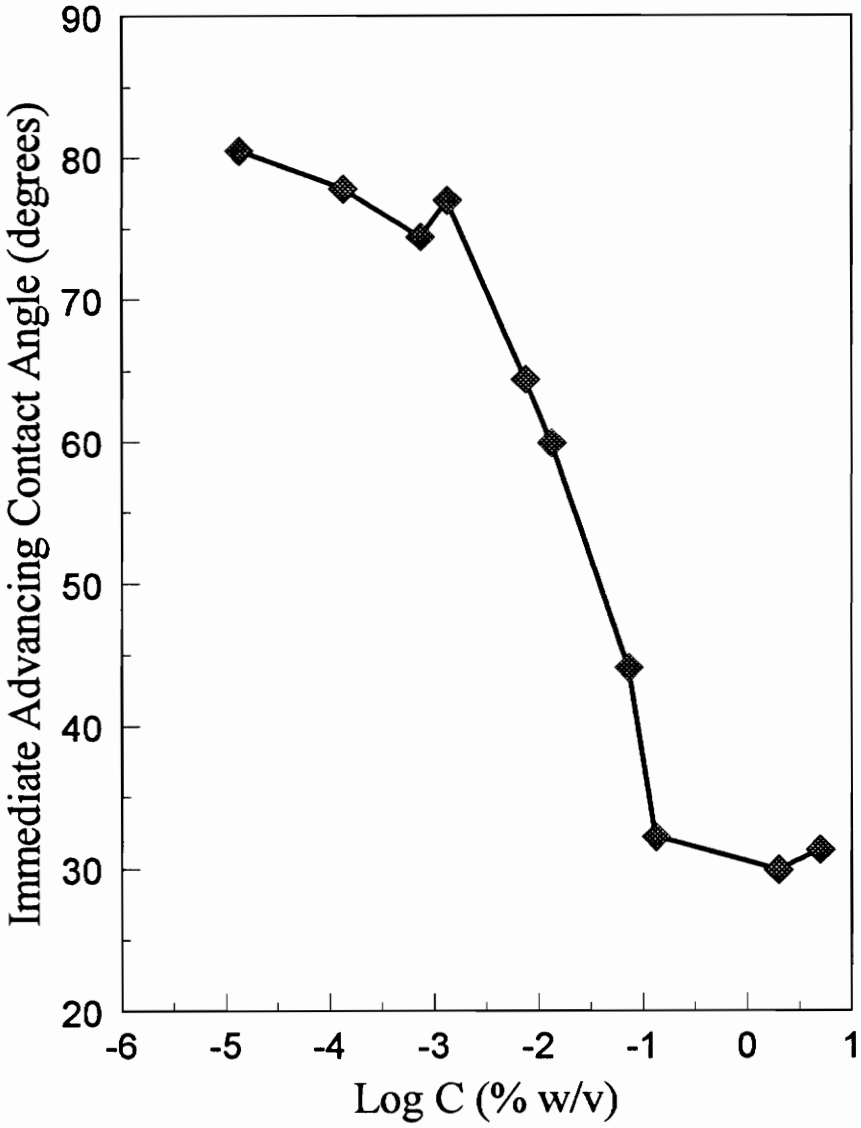


Figure 2. Effect of Triton X-100® concentration (log C) on contact angles formed.

concentration increases, the contact angle θ decreases. The decrease in θ from 77.0° for a solution with a surfactant concentration of 0.00134 percent (log C = - 2.8729) to 64.4° for Triton® X-100 concentration = 0.00737 percent (log C = - 2.1235) is precipitous, and the θ value decreases steadily beyond this point. It is important to note that the contact angle decreases even beyond the CMC (log C = - 1.8729, Liquid No. 7) of Triton® X-100.

Null hypothesis No. 2, that there is no significant difference in the contact angles formed at different concentration levels, is not rejected completely. The contact angles decrease gradually, but statistically significantly, until the CMC and beyond. However, as seen by the Duncan's multiple groupings (Table 6), there is no statistically significant difference in the contact angles formed at concentrations of 0.134 percent and beyond (Liquids 9, 10, and 11).

The contact angle formed by a drop of a liquid on a substrate is dependent on the surface tension of the liquid and other variables. As seen in Table 6 and Figure 2, surface tension decreases with increasing concentration of surfactant but remains relatively constant beyond the CMC of the surfactant. If surface tension remains constant beyond the CMC, then a similar behavior (i.e., of θ values that do not decrease appreciably past the CMC) should be seen in the contact angle measurements with solutions of Triton® X-100 concentration greater than CMC.

An important observation is the decrease in θ even beyond the CMC (log C = -1.8729, Liquid No. 7) of Triton® X-100 of 0.0134 percent. It is only past a

concentration which is ten times the CMC of Triton® X-100, that the value of the contact angle became constant. Research hypothesis No. 2, which stated that the contact angles would decrease until critical micelle concentration (CMC) and remain constant past the CMC, is thus partially supported.

Free energy relationships, that are normally used to describe the phenomenon of wetting and spreading, may not in themselves explain wetting. The results of the contact angle measurements therefore imply that drop spreading and consequently, fabric wetting, are both enhanced at higher surfactant concentrations even though the surface tension remains constant.

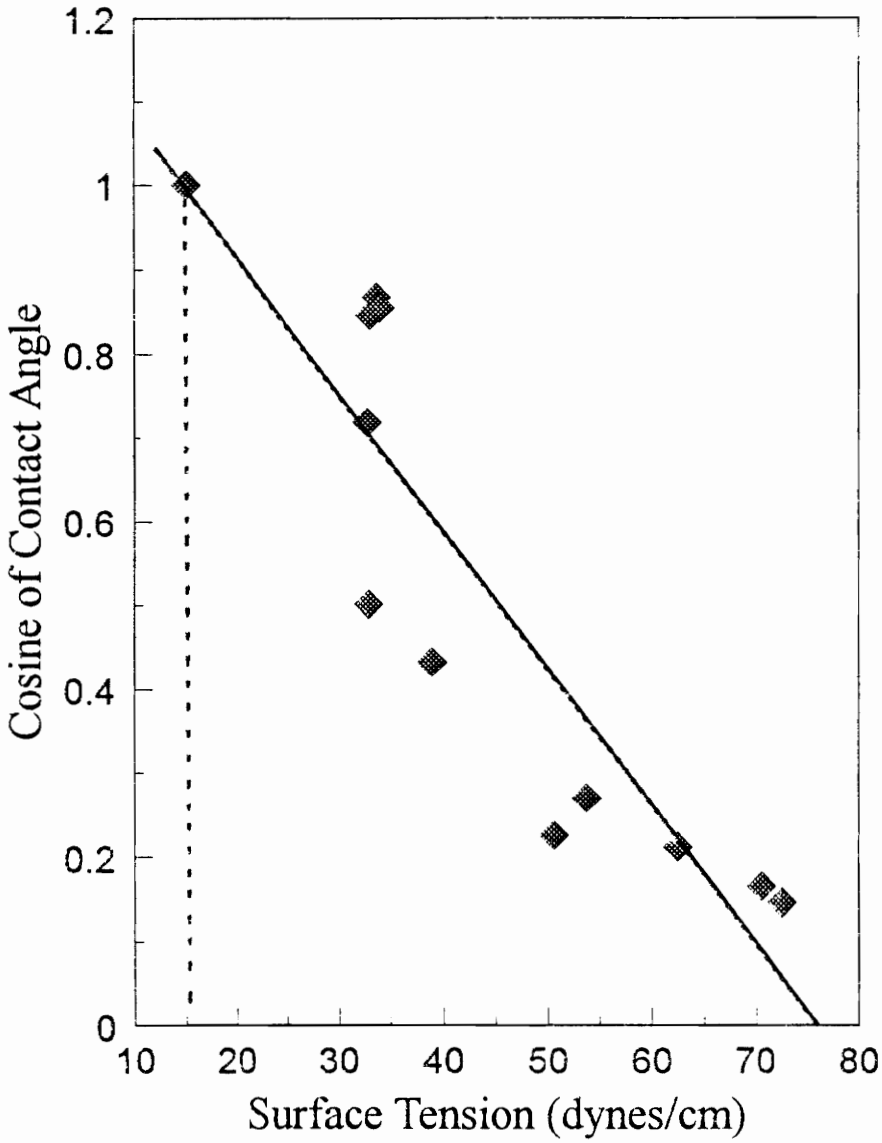
Results of Fabric Surface Free Energy Determination

Fabric surface free energy was determined from Zisman plots by plotting the cosine of the contact angle (from the contact angle measurement) on the ordinate against the surface tension of the liquids on the abscissa. Table 7 and Figure 3 show the cosines of the contact angles for the surface tension of the liquids at different surfactant concentrations. The perpendicular drawn to the abscissa from the point on the extrapolated graph at ordinate $\cos \theta = 1.0$ (i.e., $\theta = 0°$) intersects the abscissa at a surface tension value of 15 dynes/cm. Thus, the Zisman plot for this study (Figure 3) gives a fabric surface free energy value (C_{st}) of 15 dynes/cm for the microporous polypropylene test fabric.

Table 7

Surface Tension versus the Cosine of Contact Angle of Liquid on the Fabric Surface

Liquid Number	Mean Surface Tension (dynes/cm)	Cosine θ
1	72.52	0.1461
2	70.52	0.1651
3	62.44	0.2113
4	53.68	0.2689
5	50.60	0.2250
6	38.88	0.4321
7	32.84	0.5015
8	32.68	0.7181
9	32.98	0.8462
10	33.60	0.8669
11	33.92	0.8545



C.S.T. of Fabric = Surface tension at cos theta value of 1.0
= 15 dynes/cm

Figure 3. Zisman plot for determining critical surface tension of test fabric.

Discussion of the Results of Fabric Surface Free Energy Determination

The value of fabric surface free energy obtained from the Zisman plot should be considered in conjunction with the inference of the same from the oil-repellency test, which indicated that the fabric surface free energy is between 27.3 and 29.6 dynes/cm. A value of 15 dynes/cm for the C_{st} of the polypropylene test fabric is extremely low and questionable because polypropylene has been reported to have a surface free energy around 30 dynes/cm (Wu, 1982).

The derivation of surface free energy (C_{st}) from Zisman plots is a good method; however, it assumes very accurate measurement of contact angles on very smooth surfaces. The test fabric, with its microporous surface, would preclude the attainment or the presence of such a smooth surface and would thus introduce errors in the accurate measurement of contact angle. For this reason, the Zisman linear extrapolation cannot be relied upon to afford an accurate derivation of the C_{st} of the microporous polypropylene test fabric (Wightman, J.P., personal communication, April 26, 1996).

Research hypothesis No. 3 stated that the surface free energy of the test fabric will be equal to the γ of the surfactant solution that gives a contact angle of zero. The hypothesis is supported theoretically. However, the practical realities that preclude an accurate determination of the fabric surface free energy do not lend credence to the support of the research hypothesis.

Results of Barrier Effectiveness Tests

The section on the results of the barrier effectiveness of the microporous polypropylene test fabric is organized by each test that was conducted to obtain the information about this characteristic. The following details the results and discussion for each test.

Capillary Penetration

Results. The change in the mass of the substrate, in grams, was taken to represent the capillary penetration. The one-way ANOVA for capillary penetration by Triton® X-100 concentration (see Table 8) shows that concentration was a significant factor (F-ratio = 82.61, df = 10/22, α = .05). Post-hoc analysis was done by Duncan's multiple comparison, and the results of the grouping for the mean capillary penetration are shown in Table 9 along with the logarithm of the surfactant concentrations. The results also are plotted on a graph against the logarithm of the surfactant concentration (see Figure 4).

Besides DDDI water (Liquid No. 1), four concentrations below the CMC gave mean mass change values that were negative and the values for them could be attributed to experimental error. Overall, it was seen that as Triton® X-100 concentration increased, capillary penetration increased, especially with the high concentrations of 2.0 and 5.0%.

Discussion of the results of capillary penetration. Figure 4 is a graph of the capillary penetration (in grams) versus the logarithm of the Triton® X-100 concentration.

Table 8

Analysis of Variance of Capillary Penetration by Triton® X-100 Concentration

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	10	9.156×10^{-4}	9.156×10^{-5}	82.61 *
Within conc.	22	2.438×10^{-5}	1.108×10^{-6}	
Total (Adj)	32	9.400×10^{-4}		

* $p < .05$.

Table 9

Duncan's Multiple Comparison of Capillary Penetration as a Factor of Triton® X-100 Concentration

Liquid Number	Triton® X-100 Conc. (% w/v)	Log Triton® X-100 Conc. (log of % w/v)	Mean Capillary Penetration (gm)
1	0.0000000 ‡	-	-4.33×10^{-4}
2	0.0000134	- 4.8729	-5.0×10^{-4}
3	0.000134	- 3.8729	-1.76×10^{-3}
4	0.000737	- 3.1325	3.33×10^{-3}
5	0.00134	- 2.8729	-4.0×10^{-4}
6	0.00737	- 2.1235	-6.0×10^{-4}
7	0.0134	- 1.8729	7.4×10^{-3}
8	0.0737	- 1.1325	6.8×10^{-3}
9	0.134	- 0.8729	7.2×10^{-3}
10	2.0	0.3010	1.21×10^{-2}
11	5.0	0.6989	1.436×10^{-2}

Notes.
- The mean of three observations for capillary penetration in grams is reported. All concentrations in weight/volume.
- Means with the same superscript are not significantly different at $p < .05$

‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 %

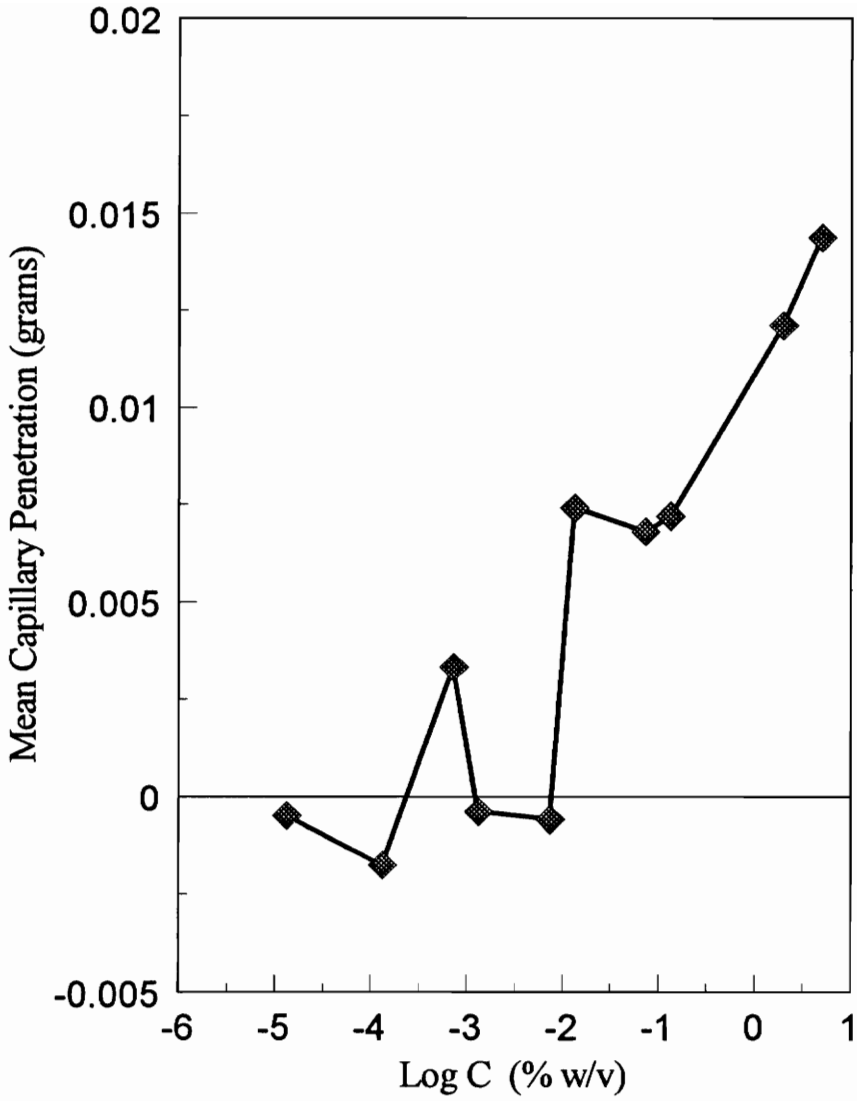


Figure 4. Effect of Triton X-100® Concentration (log C) on Capillary Penetration.

The graph shows no significant penetration at lower concentrations. The capillary penetration of 0.00333 gm for Liquid No. 4 (log C = -3.1325) is probably due to experimental error. Capillary penetration is noticeable at the CMC (log C = -1.8729) and remains steady, before increasing sharply for the surfactant concentrations of 2.0 and 5.0%. Thus, research hypothesis No. 4, which stated that capillary penetration would increase until the CMC and would remain constant past it, is only partially supported.

Capillary penetration is dependent upon several factors such as liquid surface tension, fiber surface free energy and morphology, interaction of the fluid with the fiber surface, the size, volume and orientation of the pores in the fibrous network, and the surface density (Minor et al., 1961). While surfactant surface tension and fiber surface free energy remain constant (past the CMC for the solutions) and other parameters remain unchanged, the higher surfactant concentrations at and beyond the CMC would tend to increase the viscosity and consequently the surface density, even for the same volume of liquid. The increased surface density might explain the increased capillary penetration at higher surfactant concentration levels.

Null hypothesis No. 3 stated that there would be no significant difference in capillary penetration with increasing surfactant concentration. The results of the test show that, at lower concentrations, this holds true. At concentrations of 2.0 and 5.0 percent, concentrations that are significantly higher than the CMC, the capillary penetration is significantly higher than that at CMC and around it. As applied to the two highest concentrations, 2.0 and 5.0 percent, the null hypothesis is rejected.

Drop Absorbency Test

Results. In evaluating the drop absorbency characteristics of the test fabric, it was found that the disappearance of the specular reflectance was not a sharp end-point. Solutions of Triton® X-100 at concentrations higher than the CMC spread more easily than others but still showed some specular reflectance well past 600 seconds. Therefore, instead of the disappearance of specular reflectance, the fabric-liquid interface darkening time was measured.

Liquids 1 through 6 (all below CMC) gave drops having sharply-defined profiles and did not spread on the fabric surface. The drop profiles became flatter beginning with Liquid No. 6, and the drops spread easily with increasing concentration. However, the interface became dark within 600 seconds only for Liquids 10 and 11 at 2.0 and 5.0 percent concentration, respectively. One-way ANOVA was performed to see if surfactant concentration was a significant factor in the drop absorbency times. Results of the ANOVA, given in Table 10, indicate significant differences in drop absorbency times as a factor of concentration (F-ratio = 758,691.19, df = 10/77, α = .05).

The results of the post-hoc analysis, done by Duncan's multiple comparison (see Table 11), indicate that Liquids 1-9 had interface-darkening times greater than 600 seconds (taken as 600 seconds for statistical analysis). The higher surfactant concentrations of 2.0 and 5.0 percent showed significantly lower interface-darkening times of 92 and 14 seconds, respectively. The fabric-liquid interface darkening times for Liquids 10 and 11 are significantly lower than the corresponding time for liquids at lower

Table 10

Analysis of Variance of Drop Absorbency Time by Triton® X-100 Concentration

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	10	3,941,253	394,125.3	758,691.19 *
Within conc.	77	40	0.519481	
Total (Adj)	87	3,941,293		

* $p < .05$.

Table 11

Duncan's Multiple Comparison for Drop Absorbency Time as a Factor of Triton® X-100 Concentration

Liquid No.	Triton® X-100 Conc. (% w/v)	Log Triton® X-100 Conc. (log of % w/v)	Drop Absorbency Time (seconds)	Log Drop Absorbency Time (sec.)
1	0.00000 ‡	-	> 600 [a]	2.7782
2	0.0000134	- 4.8729	> 600 [a]	2.7782
3	0.000134	- 3.8729	> 600 [a]	2.7782
4	0.000737	- 3.1325	> 600 [a]	2.7782
5	0.00134	- 2.8729	> 600 [a]	2.7782
6	0.00737	- 2.1235	> 600 [a]	2.7782
7	0.0134	- 1.8729	> 600 [a]	2.7782
8	0.0737	- 1.1325	> 600 [a]	2.7782
9	0.134	- 0.8729	> 600 [a]	2.7782
10	2.0	0.3010	92 [b]	1.9638
11	5.0	0.6989	14 [c]	1.1461

Note.
- The mean of eight observations for the drop absorbency time (interface-darkening time) in seconds is reported. All concentrations in weight/volume.
‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 %
- Means with the same superscript are not significantly different at $p < .05$

concentrations of Triton® X-100 (see Figure 5).

Discussion of the results of the drop absorbency test. Figure 5 is a graph of the logarithm of the surfactant concentration versus the drop absorbency times measured in seconds. Drop absorbency time (D.A.T.), as inferred by the interface-darkening time, was greater than 600 seconds (log D.A.T. = 2.7782) for Triton® X-100 concentrations as high as ten times the CMC. It was only with the very high Triton® X-100 concentrations of 2.0 and 5.0 percent that the drop absorbency was noticeable in the 10-minute evaluation period (92 and 14 seconds, or log D.A.T. = 1.9638 and 1.1461, respectively).

Research hypothesis No.5 stated that drop absorbency times would decrease with increasing concentration of Triton® X-100 and would remain constant past the CMC. Drop absorbency is a measure of the wettability of the fabric. Wetting is influenced, to a large extent, by the surface free energies of the solution and the fabric, besides other variables. Given that the fabric surface free energy is constant and knowing that the surface tension of the solutions remains constant past the CMC (and as shown in Figure 1), the drop absorbency times should be similar for Triton® X-100 solutions at CMC and beyond.

The drop absorbency times for the 2.0 and the 5.0 percent concentrations are, however, dramatically lower than the other solutions. This observation is strange and can only be attributable to the increased concentration of Triton® X-100 past the CMC. Research hypothesis No. 5 is thus not supported. The higher concentrations of 2.0 and 5.0 percent appear to exert the observed influence due to increased surface density.

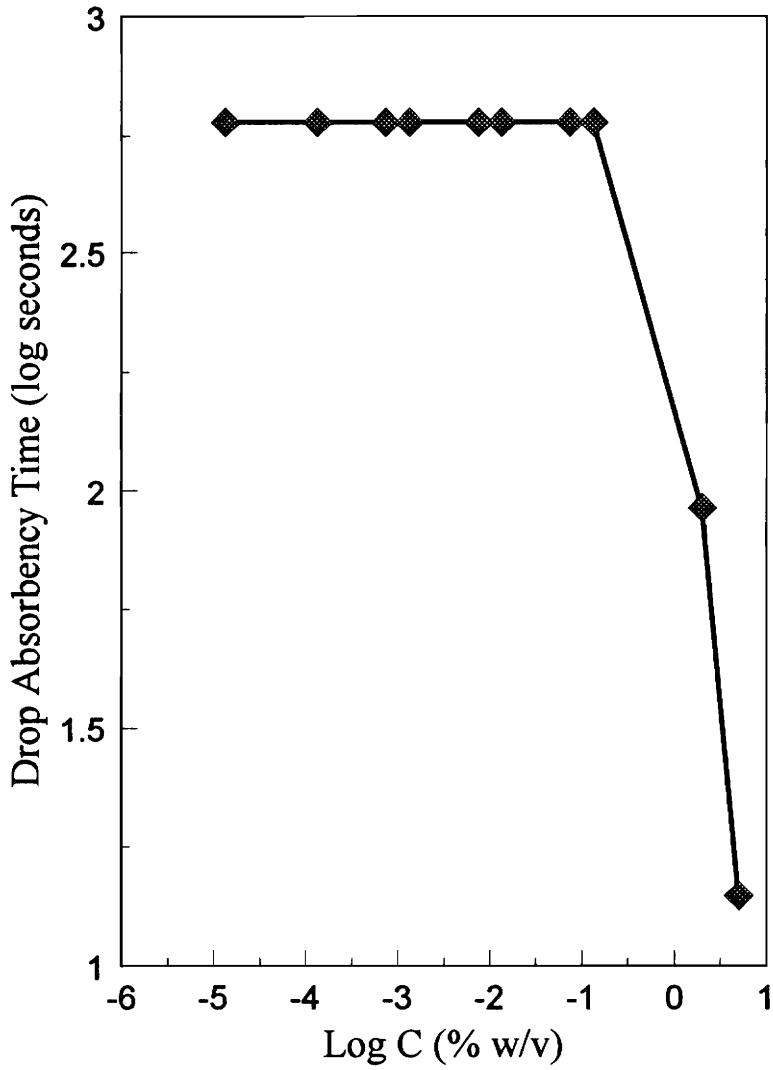


Figure 5. Effect of Triton X-100® concentration (log C) on drop absorbency time.

Null hypothesis No. 4 stated that there would be no significant difference in the drop absorbency times with different Triton® X-100 concentrations. Based on the results, the null hypothesis is rejected, at least with respect to the two concentrations of 2.0 and 5.0 percent.

Modified Draves Test

Results. The time for the fabric specimen to sink through all liquids with Triton® X-100 concentrations lower than the CMC was greater than 600 seconds. The sinking time of 600 seconds was taken for the liquids below CMC in the statistical analysis. For Liquids 1 through 4, the fabric specimen did not sink or even move downward through the liquid surface well beyond 600 seconds. Beyond the CMC, there was a significant and perceptible decrease in the sinking time as compared to the more dilute Triton® X-100 solutions below the CMC.

Results of the one-way ANOVA for sinking time by Triton® X-100 concentration, shown in Table 12, indicate that concentration is a significant factor (F-ratio = 13,923.03, df = 10/99, α = .05) in the time taken by the fabric specimen to sink through the height of the cylinder. Table 13 shows the results of post-hoc analysis, by Duncan's multiple comparison, which was done to determine which means were significantly different from one another.

The results of the sinking times, reported as log D.S.T. for 'Draves Sinking Time', from the modified Draves test were plotted against the surfactant concentration

Table 12

Analysis of Variance of Draves Sinking Time by Triton® X-100 Concentration

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	10	8,717,971	871,797.1	13,923.03 *
Within conc.	99	6,198.93	62.61546	
Total (Adj)	109	8,724,170		

* $p < .05$.

Table 13

Duncan's Multiple Comparison for Draves Sinking Time as a Factor of Triton® X-100 Concentration

Liquid No.	Triton® X-100 Conc. (% w/v)	Log Triton® X-100 Conc. (log of % w/v)	Draves Sinking Time (seconds)	Log D.S.T. (sec.)
1	0.0000000 ‡	-	> 600 [a]	2.7782
2	0.0000134	- 4.8729	> 600 [a]	2.7782
3	0.000134	- 3.8729	> 600 [a]	2.7782
4	0.000737	- 3.1325	> 600 [a]	2.7782
5	0.00134	- 2.8729	> 600 [a]	2.7782
6	0.00737	- 2.1235	> 600 [a]	2.7782
7	0.0134	- 1.8729	487 [b]	2.6875
8	0.0737	- 1.1325	3.15 [c]	0.4983
9	0.134	- 0.8729	2.72 [c]	0.4346
10	2.0	0.3010	1.95 [c]	0.2900
11	5.0	0.6989	1.44 [c]	0.1584

Note. The mean of ten observations for the modified Draves wetting test in seconds is reported. All concentrations in weight/volume.
‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 %
Means with the same superscript are not significantly different at $p < .05$

(see Figure 6). The specimens did not sink, for the 600-second time periods of observation, through liquids with surfactant concentrations up to the CMC. Liquid No. 7, the solution of the surfactant at CMC (C = 0.0134 percent, log C = -1.8729), gave a D.S.T. of 487 seconds, and it is seen as the point beyond which the sinking time drops precipitously to as low as 1.4 seconds for a solution with Triton® X-100 concentration at 5.0 percent.

Discussion of the results of the modified Draves test. Figure 6 is a graph of the logarithm of the surfactant concentration versus the logarithm of the Draves sinking times (D.S.T.). The graph is dramatic, in that it shows a precipitous and unexpected drop in the time taken by the specimen to sink through the column of the liquid. Research hypothesis No. 6 stated that the Draves sinking time would show an inverse relation to the concentration and would remain constant past the CMC of Triton® X-100. The sinking time for all liquids below the CMC of Triton® X-100 was greater than 600 seconds (reported as 600 seconds) and declined to 487 seconds (log D.S.T. = 2.6875). Beyond the CMC, the sinking times were expected to remain the same as for the solution at CMC; however, the sinking times declined further and the research hypothesis is thus supported only partially.

An earlier inference for the increased capillary penetration past the CMC (see Figure 4) was attributed to the increased surface density due to increased solution viscosity at higher surfactant concentrations. If the higher viscosity was indeed the underlying reason for the increased capillary penetration, then the higher viscosity should have adversely

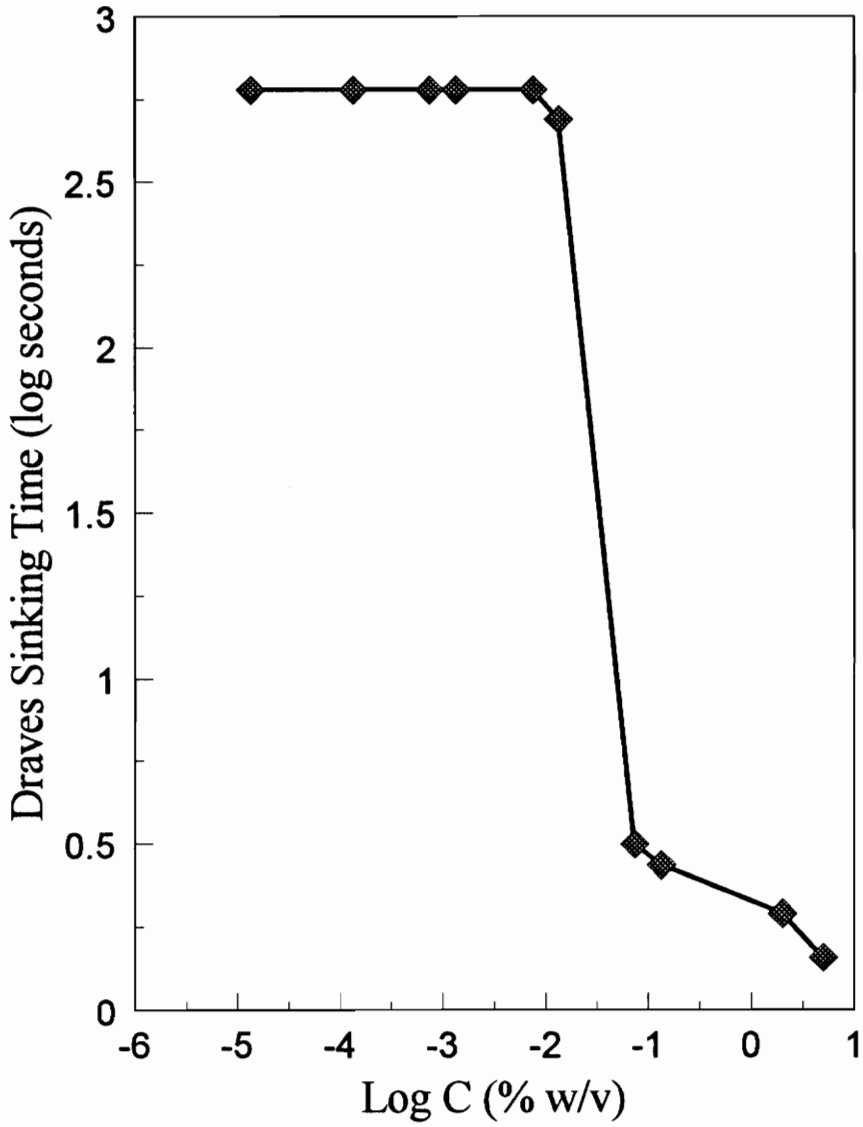


Figure 6. Effect of Triton X-100® concentration (log C) on Draves wetting (sinking) time.

impacted the sinking of the specimens through the column of the liquid in the modified Draves test. Thus, the sinking times for the specimens through the more viscous solutions of higher Triton® X-100 concentrations should have been greater than for the solutions at lower concentrations. This not being the case, viscosity is ruled out as a variable in the wetting of the specimen with respect to this modified test. Additionally, since the surface free energies of the fabric and the liquid past CMC are constant, other variable(s), such as surfactant concentration and its interactions with the fiber surface could possibly explain the increased wetting beyond the critical micelle concentration of the surfactant.

Null hypothesis No. 5, which stated that there would be no significant difference for the sinking times for liquids at different Triton® X-100 concentrations, holds true for the liquids tested below the CMC of Triton® X-100. However, there is a significant difference for the solution at CMC and for the four concentrations past the CMC when compared to the dilute solutions; the null hypothesis is thus rejected.

Spreading Coefficient

Results. The spreading coefficient values were calculated for the eleven test liquids by first deriving the work of adhesion and work of cohesion from the mean surface tension (γ) values of the solutions and the cosine of the mean contact angle (θ) values. The spreading coefficient values for all liquids were negative, i.e, less than zero, for the immediate advancing contact angles measured.

Table 14 and Figure 7 show that, as Triton® X-100 concentration increases, the spreading coefficient increases correspondingly. The spreading coefficient increases from a low value of -58.88 dynes/cm for Liquid No.2 (C = 0.0000134 percent, log C= - 4.8729) to a high value of -4.47 dynes/cm for Liquid No.10 (C = 2.0 percent, log C = -0.3010).

Discussion of the results of the spreading coefficient calculations. Research hypothesis No. 7 stated that the spreading coefficient value would increase with increasing surfactant concentration until the CMC and then remain constant. As seen in Figure 7, the spreading coefficient value increases with increasing surfactant concentration; however, the spreading coefficient value increases even past the CMC of Triton® X-100. Thus, the research hypothesis is only partially supported.

A point of interest is the increase in spreading coefficient value even past the CMC, the concentration at the equilibrium surface tension of the surfactant. This is strange since the surface tension of the liquids remains constant past the CMC. However, this observation is not completely surprising because the results of the measurements of contact angle, a quantity used in calculating the spreading coefficient value, showed a similar trend; i.e., contact angles decreased with increasing Triton® X-100 concentration, even though the surface tension of the liquids remained the same (see Table 6 and Figure 2).

Wetting has been defined as the phenomenon resulting from the forces of adhesion at the solid-liquid interface (Ellison & Zisman, 1954). Since the forces of adhesion are dependent on the surface tension and the contact angle formed by the liquid in contact

Table 14

Derivation of Spreading Coefficient (S_c) Values for Triton® X-100 Solutions at Different Concentrations

Triton® X-100 conc. (% w/v)	Log conc. (Log % w/v)	W_{coh} (dynes/ cm)	Cosine θ	W_{adh} (dynes/ cm)	S_c (dynes/ cm)
0.0 ‡	-	145.04	0.1461	83.12	- 61.92
0.0000134	- 4.8729	141.04	0.1651	82.16	- 58.88
0.000134	- 3.8729	124.88	0.2113	75.63	- 49.25
0.000737	- 3.1325	107.36	0.2689	68.11	- 39.25
0.00134	- 2.8729	101.20	0.2250	61.98	- 39.22
0.00737	- 2.1235	77.76	0.4321	55.68	- 22.08
0.0134	- 1.8729	65.68	0.5015	49.31	- 16.37
0.0737	- 1.1325	65.36	0.7181	56.15	- 9.21
0.134	- 0.8729	65.96	0.8462	60.89	- 5.07
2.0	0.3010	67.20	0.8669	62.73	- 4.47
5.0	0.6989	67.84	0.8545	62.90	- 4.94

Note. The mean γ from the as-prepared solutions and the cosine of the mean θ from the immediate advancing contact angle measurements are used.

‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 %

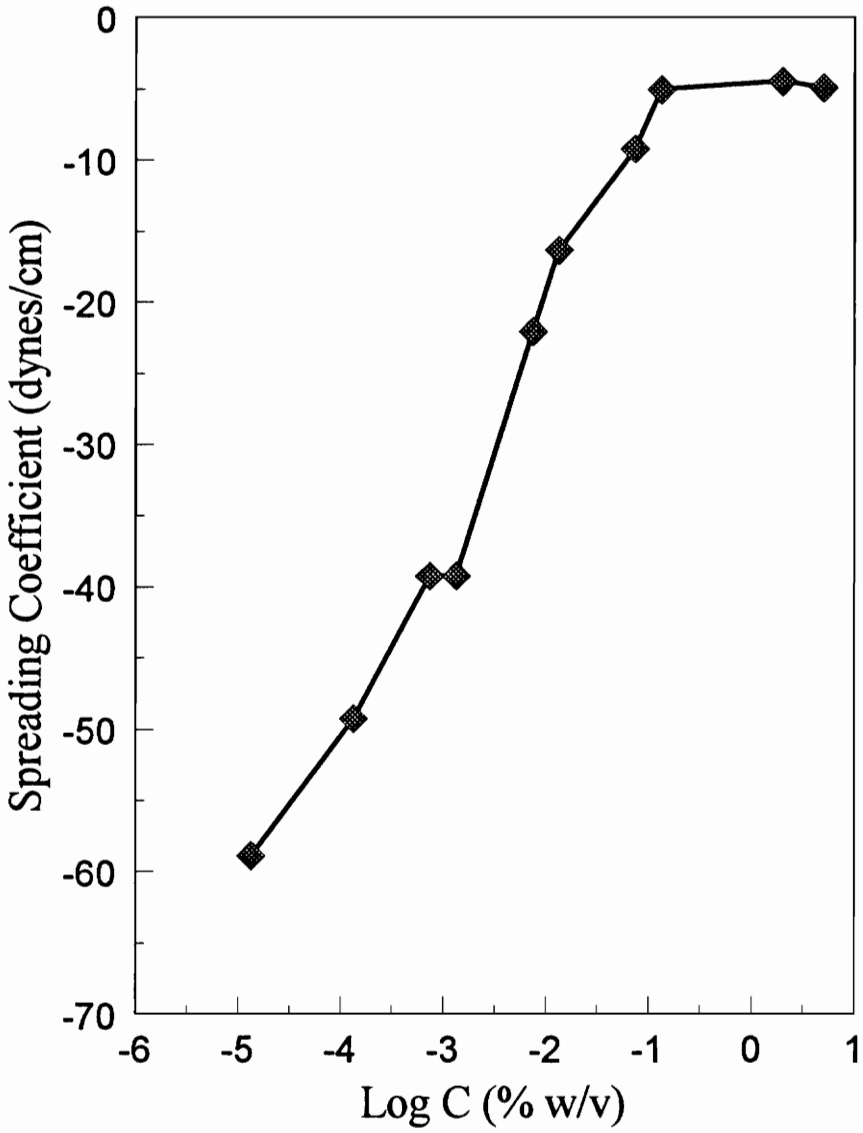


Figure 7. Effect of Triton X-100® concentration (log C) on spreading coefficients.

with a solid surface, i.e., on the free energies of the fabric surface and the liquid that challenges the fabric surface, it follows that variables which alter the free energies and the contact angle would similarly affect wetting.

Since surface tension of the surfactant solutions, the surface free energy of the fabric surface, and all other conditions are constant beyond the critical micelle concentration of Triton® X-100, surfactant concentration, the only variable that is changing, seems to be the only attributable cause for the increased wetting, as inferred from the spreading coefficient values.

Wicking

Results. There was no wicking for all three measurement times in both fabric directions for all liquids with Triton® X-100 concentrations at 0.00134 percent and lower. Additionally, there was only marginal wicking (0.23 cm for machine and 0.2 for cross directions, respectively) at a concentration of 0.00737 percent after 10 minutes.

As the concentration of the surfactant increased to its CMC of 0.0134 percent and beyond, the distance wicked increased significantly. For the measurement period of ten minutes, the distance wicked by Liquid No. 11, with surfactant concentration of 5.0 percent, was 4.4 cm in both fabric directions. Increased time of submersion in the test liquids increased the distance wicked within each concentration level past the critical micelle concentration.

Results of the one-way ANOVA (see Table 15) indicate that the concentration of

Table 15

Analysis of Variance of Wicking Distance by Triton® X-100 Concentration

In Machine Direction of Fabric

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	17	105.2926	6.19368	99.84 *
Within conc.	36	2.2333	0.06203	
Total (Adj)	53	107.5259		

* $p < .05$.

In Cross Direction of Fabric

Source	DF	Sum of Squares	Mean Square	F-Ratio
Between conc.	17	102.4081	6.02400	264.47 *
Within conc.	36	0.8200	0.02277	
Total (Adj)	53	103.2281		

* $p < .05$.

Triton® X-100 was a significant factor in determining the distance wicked after one, five, and ten minutes for both fabric directions. Post-hoc analyses were done by Duncan's multiple comparison and the results for the two fabric directions are shown in Tables 16 and 17. Liquids No. 1 through 5 did not show any wicking response for all three measurement times, and therefore were not included in the statistical analyses.

Discussion of the results of the wicking test. Figure 8 shows the influence of surfactant concentration on the distance wicked in the machine direction. The graph shows that, as surfactant concentration and the dwell time of the fabric specimen in the test liquid increase, the distance wicked increases. Research hypothesis No. 7 stated that, as the surface tension of solutions decreases with increasing Triton® X-100 concentration, the solutions would exhibit a decreased tendency to be wicked through the microporous polypropylene fabric and that water (Liquid No. 1) would be wicked to the greatest extent. Triton® X-100 solutions, especially at CMC and higher concentrations, were hypothesized to show the least wicking.

Based on the Young-Laplace equation, wicking of a liquid through the interfiber and interyarn capillaries of a fabric occurs due to the pressure difference (ΔP) across the curved surface of a given liquid meniscus (Adamson, 1976). With increasing Triton® X-100 concentration, the surface tension decreases and ΔP, the pressure difference across the meniscus, becomes very small. Smaller ΔP values should have led to smaller wicking distances.

The results of the wicking test, however, show that the distance wicked increased

Table 16

Duncan's Multiple Comparison for Wicking Distance by Triton® X-100 Concentration After 1, 5, and 10 Minutes Immersion Time

In Machine Direction

Liquid No.	Triton® X-100 Conc.	Log conc. (Log % w/v)	Liquid γ (dynes/cm)	Distance Wicked (cm) > Time of (mins.) 1	5	10
1	0.0 ‡	-	72.52	0	0	0
2	0.0000134	- 4.8729	70.52	0	0	0
3	0.000134	- 3.8729	62.44	0	0	0
4	0.000737	- 3.1325	53.68	0	0	0
5	0.00134	- 2.8729	50.60	0	0	0
6	0.00737	- 2.1235	38.88	0.03[a]	0.1[a]	0.23[a]
7	0.0134	- 1.8729	32.84	1.0[b]	1.36[c,d]	1.63[d]
8	0.0737	- 1.1325	32.68	1.2[b,c]	1.96[e]	2.2[f]
9	0.134	- 0.8729	32.98	2.1[e,f]	2.6[g]	2.9[h]
10	2.0	0.3010	33.60	3.36[i]	3.86[j,k]	3.9[k,l]
11	5.0	0.6989	33.92	3.5[j]	4.3[l]	4.4[m]

Note. The mean of three observations for distance wicked after 1, 5, and 10 minutes. All concentrations in weight/ volume. Liquids 1 through 5 were not included in the statistical analysis.
‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 %
Means with the same superscript are not significantly different at $p < .05$

Table 17

Duncan's Multiple Comparison for Wicking Distance by Triton® X-100 Concentration After 1, 5, and 10 Minutes Immersion Time

In Cross Direction

Liquid No.	Triton® X-100 Conc.	Log conc. (Log % w/v)	Liquid γ (dynes/cm)	Distance Wicked (cm) > Time of (mins.) 1	5	10
1	0.0 ‡	-	72.52	0	0	0
2	0.0000134	- 4.8729	70.52	0	0	0
3	0.000134	- 3.8729	62.44	0	0	0
4	0.000737	- 3.1325	53.68	0	0	0
5	0.00134	- 2.8729	50.60	0	0	0
6	0.00737	- 2.1235	38.88	0.03	0.1	0.2
7	0.0134	- 1.8729	32.84	0.73	1.5	1.8
8	0.0737	- 1.1325	32.68	1.2	1.67	1.83
9	0.134	- 0.8729	32.98	2.1	2.6	2.8
10	2.0	0.3010	33.60	3.2	3.7	4.1
11	5.0	0.6989	33.92	3.47	3.87	4.4

Note. The mean of three observations for distance wicked after 1, 5, and 10 minutes. All concentrations in weight/ volume. Liquids 1 through 5 were not included in the statistical analysis.
‡ Liquid No. 1 is Water, i.e., Triton® X-100 concentration in this liquid = 0 %
Means with the same superscript are not significantly different at $p < .05$

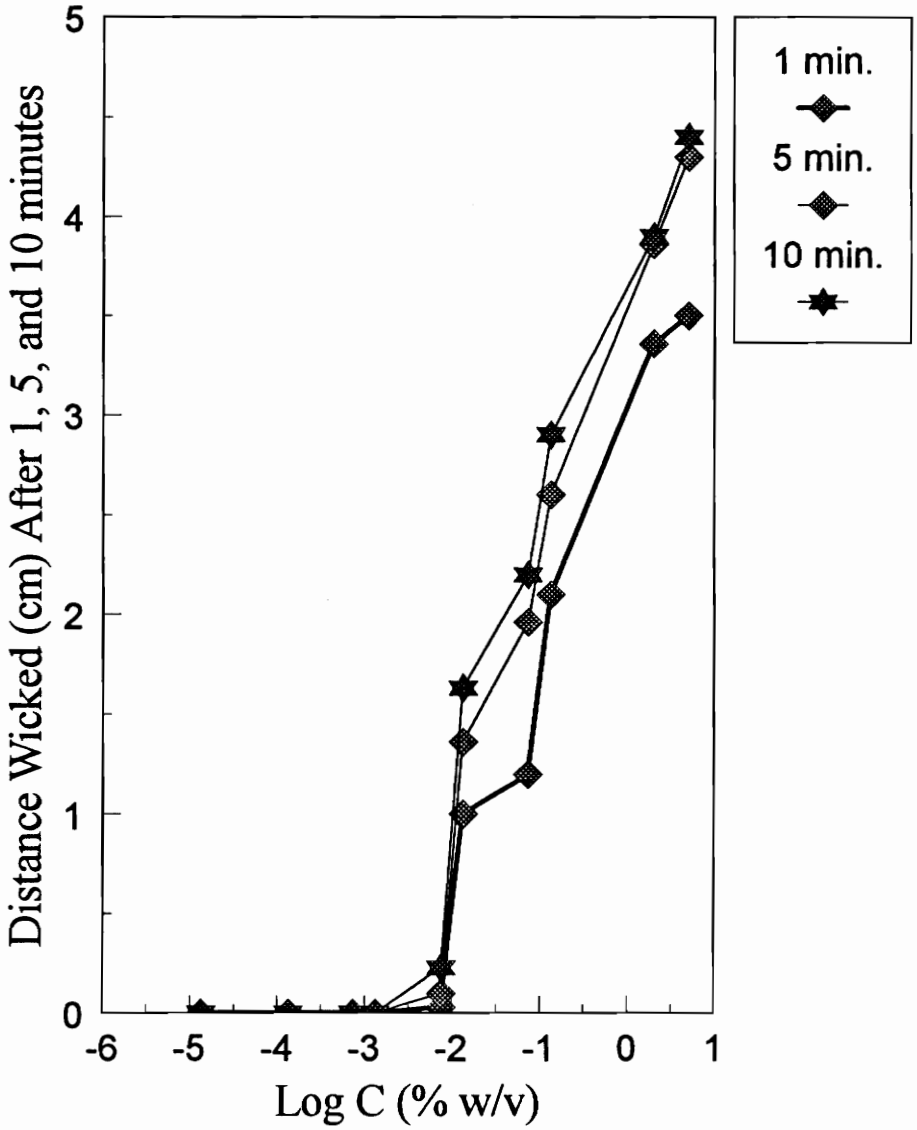


Figure 8. Effect of Triton X-100® concentration (log C) on wicking (machine direction).

with increasing surfactant concentration and decreasing surface tension. This held true, i.e., wicking distance increased, especially past the CMC of Triton® X-100 for both the machine and cross directions of the fabric. The wicking behavior for the cross direction was similar to the machine direction of the fabric. Thus, a graph for only the machine direction is provided.

The wicking behavior observed is similar to that observed by Sarin (1994), in that wicking distance increased inversely to the surface tension. The research hypothesis is thus not supported. The results of the wicking behavior cannot be explained in the context of the Young-Laplace relationship, i.e., surface free energy relations are not sufficient in explaining increased wicking, and consequently lower barrier effectiveness.

Chapter VI

SUMMARY AND CONCLUSIONS

SURFACTANT CONCENTRATION EFFECTS ON PROTECTIVE PERFORMANCE OF POLYPROPYLENE FABRIC

Manuscript

SURFACTANT CONCENTRATION EFFECTS ON PROTECTIVE PERFORMANCE OF POLYPROPYLENE FABRIC

Introduction

Surfactants are among the most common additives in the application of pesticides. Surfactants are usually used in concentrations significantly higher than the concentration that gives the lowest surface tension for that surfactant, its critical micelle concentration (CMC). Such high concentrations have been demonstrated to increase the efficacy and the efficiency of the applied pesticides through improved wetting [1]. While the high surfactant concentrations enhance the performance of the pesticide, the effect of such high surfactant concentrations on the protective performance of pesticide protective fabric and clothing is not known.

This research evaluated the effect of concentration of Triton X-100®, a non-ionic surfactant, and the surface tension (γ) on the performance of microporous polypropylene nonwoven fabric for pesticide protective clothing. Surface tension of the surfactant solutions and the contact angles formed for a drop of the liquid in contact with the test fabric, at various concentrations, were measured. Protective performance was evaluated from the capillary penetration, wetting, and wicking characteristics. Wetting was evaluated by the drop absorbency test, by a modified Draves test, and from the calculation of the spreading coefficient values.

Experimental Procedure

Materials

Surfactant

Non-ionic surfactants are the most commonly used surfactants in the application of pesticides because they do not react with the active ingredient. Triton X-100®, a non-ionic surfactant (Union Carbide), was the surfactant selected for the study. Ten solutions, with Triton X-100® concentrations ranging from 0.0000134 to 5.0% (w/v), were prepared in double distilled deionized (DDDI) water. A stock solution of 0.134% concentration (w/v) was first prepared, and this was successively diluted with DDDI water to concentrations as low as 0.0000134%. The 2.0 and 5.0% solutions were prepared separately. DDDI water served as the control for the experiment.

Fabric

Fabrics made of microporous materials have waterproof-but-breathable characteristics. These materials have small micropores that keep out large water droplets but allow the much smaller sized water vapor molecules (from perspiration) to pass through. Such properties are desirable in field application conditions.

The fabric selected for the study was a two-layer composite fabric, comprised of a microporous polypropylene (PP) film (the 'face') bonded to a spunbonded PP web layer that served as the backing. The laminate was available from the supplier and was used directly. Fabric specimens were cut to different dimensions for the different tests,

conditioned for 24 hours in a standard environment at 21± 1°C and 65±2% relative humidity.

Table 2 lists some of the characteristics of the selected fabric. The microporous film had pores 0.2 μm in diameter. A moisture vapor transmission rate (MVTR) greater than 5,000 gm/m^2/24 hr., at 75° F and 50% relative humidity, has been reported for this film. The nonwoven PP web was the layer that gave strength to the laminate and gave the fabric a cloth-like texture.

Method

Measurement of Surface Tension

Surface tension (γ) of each prepared surfactant solution and of DDDI water was determined by the Method A (the du Noüy ring method) of the ASTM D 1331-89 (1995) Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents [2] using a FISHER Surface Tensiomat, Model 21. The 'apparent' γ values, as read from the calibrated dial, were used directly. All measurements were done at 20 ±1.0°C (69°F) and 72% relative humidity.

Measurement of Immediate Advancing Contact Angle

The immediate advancing contact angles for each concentration of the prepared surfactant solution and the DDDI water were measured with a Rame-Hart NRL Contact Angle Goniometer (model No. 100-00-115). Fabric specimens, measuring 2.5 x 7.5 cm,

were placed and secured on double stick tape which itself was stuck to a glass slide. A 5 μL sessile drop was dispensed on the fabric surface. The θ value was read directly at the six o'clock position immediately after (within 10 seconds) the crossline attained tangency with the drop profile at the base of the drop. All measurements were done at 20 ±1.0°C (69°F) and 72% relative humidity.

Evaluation of Protective Performance of the Test Fabric

The protective performance of the test fabric was evaluated by the capillary penetration, wetting, and wicking tests. Wetting performance was evaluated by an adaptation of the Draves wetting test and by the drop absorbency test.

Capillary Penetration

Capillary penetration was determined according to the method applied by Sarin [3]. The test fabric, substrate, and backing material were all cut to 7.6 x 7.6 cm. The test liquid (aqueous surfactant solution or distilled water), in the amount of 500 μL, was pipetted on to center of the test fabric/substrate assembly. The liquid that would pass through the test fabric would penetrate and wet the underlying substrate. Thus, the change in mass of the blotter paper (the substrate) would represent the capillary penetration through the fabric. Three replications for the change in mass were made and recorded.

Wetting Performance

The wetting performance of the test fabric was evaluated by the drop absorbency test and by a modified version of the Draves test.

Drop absorbency. Drop absorbency was measured using AATCC 79-1992: Absorbency of Bleached Textiles standard test method [4]. A specimen of the test fabric, measuring 20 x 20 cm (8 x 8 in.), was used for this test. In the early attempts to take the drop absorbency measurements, it was found that the point of disappearance of the specular reflectance of the drop was not distinct. Therefore, the time required for the complete area of the liquid/fabric interface to become dark was taken as the drop absorbency time. Eight readings of drop absorbency were made and averaged, and the results were recorded as the wetting time (in seconds) for each liquid tested.

Modified Draves wetting test. The Draves Wetting Test, ASTM D 2281- 68 (1992) [2] and AATCC 17-1989 [4], is commonly used for the evaluation of wetting agents. The application of the test in this research was to examine the wetting of the microporous PP test fabric in different concentrations of the surfactant solutions. The Draves test was modified in order to directly obtain the information on the wetting characteristics of the test fabric (as opposed to using a cotton skein) in a system containing a non-ionic surfactant like Triton® X-100 at different concentrations.

Samples of the test fabric were cut in dimensions of 1.5 x 1.5 cm (mean mass = 0.0160 gm). A staple (mass = 0.0330 gm) was punched diagonally through each square-shaped fabric specimen to weight the specimen. This resulted in the test specimen having

a mass of 0.0490 gm. A 50-mL graduated cylinder, with a height of 13.0 cm from its base to the 50-mL mark, was filled with 50 mL of the appropriate test liquid (surfactant solution). To effect immersion of the test specimen through the height of the liquid, the specimen was dropped from height of 5 cm above the liquid level and gently pushed to just below the liquid surface by means of a glass rod using a pressure of 1 psi. The time taken for each specimen to completely sink to the bottom of the cylinder was measured in seconds. Ten such readings of sinking time, with newly prepared specimens, were taken and averaged for each test liquid.

Spreading coefficient. The spreading coefficient value (S_c)for each concentration of Triton X-100® and for DDDI water was calculated from the values of the surface tension (γ) and the cosine of contact angle (θ), for that concentration, using the equation,

$$S_c = \gamma (\cos \theta - 1)$$

A positive value of the spreading coefficient implies that the liquid will spread and wet the fabric surface, i.e., fail to serve as an effective barrier in pesticide protective clothing applications.

Wicking Performance

The wicking of the test liquids through the test fabric was measured by the method described by Raheel and Gitz [5]. The test fabric specimen, measuring 2.5 x 15 cm, was marked at 1-cm intervals with a water soluble ink. The specimen was hung vertically above a beaker containing the test liquid and weighted to allow an immersion of 1 cm in

the liquid. The immersion line was taken as the starting line. The distance wicked by the liquid was measured in centimeters after 1, 5, and 10 minutes and was recorded for the test fabric in the machine direction.

Results and Discussion

The results of the tests are reported in Table 18. The figures for the Triton X-100® percent concentration (w/v), the independent variable, were first converted to the log scale to simplify the plotting of the results against the dependent variables. Similarly, values of the drop absorbency time (D.A.T.) and the Draves sinking time (D.S.T.) were converted to the logarithmic scale. Figures 1-8 are graphic depictions of the influence of surfactant concentration on the different variables studied.

Results of the surface tension determination, of the 10 solutions at different concentrations and of DDDI water (see Table 18 and Figure 1), show that as surfactant concentration increases, γ decreases almost linearly. Liquid No. 2 (Triton® X-100 concentration = 0.0000134%) contains a negligible amount of surfactant and has a γ of 70.52 dynes/cm (almost the same as γ of DDDI water at 72.52 dynes/cm, though not on the graph). At the concentration of 0.0134 % (Liquid No. 7), the γ value obtained was the lowest (32.84 dynes/cm) and the graph shows a distinct inflection at this point. Surface tension remains relatively steady past this point even as the surfactant concentration increases to levels as high as 5.0%. The 0.0134% concentration point (log C= -1.8729) is the critical micelle concentration (CMC) of the surfactant.

Table 18

Results of Protective Performance Tests as a Function of Triton X-100® Concentration and Surface Tension

Liq. No.	Conc. (% w/v)	Log Conc.	γ (dynes/cm)	Mean θ	Cosine θ	S_c (dynes/cm)	Mean Cap.Pen. (gm)	Log D.A.T. (sec.)	Log D.S.T. (sec.)	W.D. (cm.) After (minutes) 1	5	10
1	0.0	-	72.52	81.6	0.1461	- 61.92	-0.00043	2.7782	2.7782	0	0	0
2	0.0000134	- 4.8729	70.52	80.5	0.1651	- 58.88	-0.0005	2.7782	2.7782	0	0	0
3	0.000134	- 3.8729	62.44	77.8	0.2113	- 49.25	-0.00176	2.7782	2.7782	0	0	0
4	0.000737	- 3.1325	53.68	74.4	0.2689	- 39.25	0.00333	2.7782	2.7782	0	0	0
5	0.00134	- 2.8729	50.60	77.0	0.2250	- 39.22	-0.0004	2.7782	2.7782	0	0	0
6	0.0073	- 2.1235	38.88	64.4	0.4321	- 22.08	-0.0006	2.7782	2.7782	0.03	0.1	0.23
7	0.0134	- 1.8729	32.84	59.9	0.5015	- 16.37	0.0074	2.7782	2.6875	1.0	1.36	1.63
8	0.0737	- 1.1325	32.68	44.1	0.7181	- 9.21	0.0068	2.7782	0.4983	1.2	1.96	2.2
9	0.134	- 0.8729	32.98	32.2	0.8462	- 5.07	0.0072	2.7782	0.4346	2.1	2.6	2.9
10	2.0	0.3010	33.60	29.9	0.8669	- 4.47	0.0121	1.9638	0.2900	3.36	3.86	3.9
11	5.0	0.6989	33.92	31.3	0.8545	- 4.94	0.01436	1.1461	0.1584	3.5	4.3	4.4

Note. All concentrations in percent weight/volume. Liquid No. 1 is DDDI Water (Triton X-100® concentration = 0.0 %.)

- Surface tension (γ) and contact angle (θ) measured at 20 ± 1.0°C and relative humidity= 72%. Mean of five and 10 readings, respectively, reported.
- Mean of three readings showing the change in mass (gm) is shown for capillary penetration.
- The logarithm of the mean of eight and ten readings, measured in seconds, for the Drop Absorbency Time (D.A.T.) and the Draves Sinking Time (D.S.T.), respectively, is reported.
- The mean of five readings for the wicking distance (W.D.) after 1, 5, and 10 minutes in machine direction is reported in cm.
- The calculated value for the spreading coefficient, S_c, is reported. $S_c = \gamma (\cos \theta - 1)$. The mean values of γ and θ were used in calculating spreading coefficient.

The measurement of the immediate advancing contact angles for the liquids on the microporous polypropylene fabric showed that as the surfactant concentration increased, the contact angles decreased. The decrease in the contact angle value paralleled the decrease of surface tension. This was expected, since the contact angle on a surface is dependent on the surface free energies of the liquid and the solid surface that it is in contact with (solid surface free energy remains constant since it is the same solid surface). The contact angle for DDDI water was 81.6° while that for the solution at CMC was 59.9°. However, as the concentration increases to greater than the CMC, the contact angle becomes smaller, then remains constant for solutions with surfactant concentrations of 0.134, 2.0, and 5.0 percent.

The graph of the mean capillary penetration plotted against the concentration (see Figure 4) shows no significant penetration at lower concentrations. The capillary penetration of 0.00333 gm for Liquid No. 4 (log C = -3.1325) is probably due to experimental error. Capillary penetration is noticeable at the CMC (log C = -1.8729) and remains steady, before increasing sharply for the surfactant concentrations of 2.0 and 5.0 percent.

Capillary penetration is dependent upon several factors such as liquid surface tension and viscosity, fiber surface free energy and morphology, interaction of the fluid with the fiber surface and the size, volume and orientation of the pores in the fibrous network, and the surface density (of liquid on fabric) [6]. While surfactant surface tension and fiber surface free energy remain constant (past the CMC for the solutions) and

other parameters remain unchanged, the higher surfactant concentrations at and beyond the CMC would tend to increase the viscosity and consequently the surface density (even for the same volume of the liquid). The increased viscosity might explain the increased capillary penetration at higher surfactant concentration levels.

Results of the drop absorbency test (see Table 18 and Figure 5) show that the liquid/fabric interface did not darken in the 10-minute time frame observed for each liquid. The drop absorbency time was greater than 600 seconds (log 't' approximately = 2.7782) for all liquids even up to concentrations of 0.134% (10 times the CMC). Drop absorbency times showed a dramatic decline at a concentration of 2.0% (92 seconds, or log 92 = 1.9638) and further for 5.0% (14 seconds, or log 14 = 1.1461). Since all parameters mentioned above (for capillary penetration) remain unchanged, it appears that higher surface density, at the higher surfactant concentrations, might be the variable exerting the influence observed.

The specimen sinking time (D.S.T.), as measured through the modified Draves test, showed results somewhat similar to those obtained from the drop absorbency test. The specimens did not sink, for the 600-sec. time periods of observation, through liquids with surfactant concentrations up to and just above the CMC. Immediately above the CMC (0.0737% or log C= -1.1325), the sinking time decreased precipitously from a high of 487 seconds for the solution at CMC to about 3 seconds for Liquid No. 8. Further decline in the sinking time was observed; however, this does not seem to be significantly different from the sinking time for Liquid No. 8.

Based on our earlier hypothesis that solution viscosity might be influencing the liquid transport properties (as in capillary penetration and drop absorbency), the Draves sinking time should also have been impacted, but inversely. Thus, the Draves sinking time should be greater for liquids with greater surfactant concentration since they would be more viscous than the more dilute solutions and since the test fabric specimen would need to travel through the viscous liquid column to sink. However, sinking times were very short at concentrations beyond the CMC even though liquid surface tension remained steady.

The results from the wicking test indicated that fabric orientation (i.e., machine or cross direction) was not a significant determinant in the wicking behavior after the 1, 5, and 10-minute periods. The results are thus reported (see Table 18) as the distance wicked in only the machine direction. There was no perceptible wicking for solutions with Triton® X-100 concentrations up to the CMC. Beyond CMC, the wicking distance increased steadily and dramatically for all concentrations, though not appreciably with time for the same concentration.

Based on the Young-Laplace equation, the wicking distance increases with increasing surface tension because of the higher pressure difference across the surface of a liquid meniscus than in a liquid of lower surface tension. Thus, the wicking distance should decrease with increasing surfactant concentration and decreasing surface tension. However, the results show that wicking distance increases with increasing surfactant concentration, even past the CMC.

All the tests in this study that were performed to evaluate the effectiveness of the microporous PP test fabric for pesticide protective clothing indicate that surfactant concentration plays a significant role in determining its effectiveness. Past the CMC, even though the surface tension remains relatively unchanged, there still seem to be some factor(s) that influence the liquid transport and ultimately the protective performance of the polypropylene fabric.

Summary and Conclusions

High concentrations of surfactants are routinely used in pesticide application [1]. The effect of high surfactant concentrations on the protective performance of pesticide protective fabric and clothing is not known. This research evaluated the effects of surfactant concentration on the protective performance of microporous polypropylene fabric.

If wetting, wicking and other modes of liquid transport were considered to be dependent on the surface tension (among other variables, at least for static conditions and without any applied pressure), then it would seem plausible that wetting, and hence the protective performance, would be unchanged in systems containing surfactant concentrations greater than the CMC of the surfactant. However, the results of the various tests in this research suggest that surfactant concentration and the surface tension of the resulting solution, though influenced by each other, are mutually exclusive in their effects, especially at concentrations greater than the critical micelle concentration.

Consequently, the results imply that the fabric may not offer the same protection to the wearer in dealing with pesticide systems containing high concentrations of surfactants as with lower concentrations (below CMC).

Research involving surfactant concentration as a factor in the protective performance of pesticide protective clothing has not been reported extensively. Additional research is warranted to corroborate the results obtained in the present study. Studies using pesticides in conjunction with surfactant(s), other fabrics, and with performance evaluation through other techniques need to be done to assess if our observations are supported across these and related variables.

Acknowledgments

Samples of surfactants were provided by Union Carbide. Microporous polypropylene fabric samples were provided by Kappler Safety Group.

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Chapter VII

Implications

In research pertaining to pesticide protective clothing, surface tension of the pesticide system, when and where reported, is done in a manner which might make it appear that the liquid transport characteristics (and from there, the barrier effectiveness of the protective clothing) remain unaffected past the point of the attainment of the equilibrium surface tension. The subtle implication made is that the observations for the barrier effectiveness, made at a certain surface tension (at or past the CMC), would apply to all conditions if the surface tension were kept constant.

The results of this research, however, clearly show that barrier effectiveness, as evaluated from the capillary penetration, wetting, and wicking characteristics, decreases significantly with increasing surfactant concentration, even though the surface tension remains constant past the CMC. The results further imply that a 'protective' clothing material may not offer the same protection against pesticide penetration in a system containing high concentrations of a surfactant as compared to that with lower concentrations. The specification and recommendation of a certain surface tension level of the pesticide system may thus not be sufficient in selecting a material for pesticide protective clothing which would resist penetration by the pesticide emulsion that contains a high concentration of surfactant.

Information on the concentration of surfactant in a pesticide which would optimize

the pesticide's biological effectiveness and yet allow the protective fabric to resist penetration would help in pesticide formulation and application. The divergent demands on and the effects brought about by surfactants should be thoroughly understood in the study, design, and application of pesticide protective clothing and its barrier effectiveness properties.

Suggestions for Future Research

Research involving surfactant concentration as a factor in evaluating the barrier effectiveness of pesticide protective clothing has not been reported extensively. Additional research is warranted to corroborate the results obtained in the present study. The following lists some suggestions for future research.

1. Studies using pesticides in conjunction with surfactant(s), other fabrics, and with performance evaluation through other techniques (pressure and impact penetration, for instance) need to be done to assess if our observations are supported across these and related variables.

2. In the present study, concentration levels were chosen to afford a 'broad spread' of concentrations below and above the CMC of the selected surfactant. These concentration levels, however, did not afford the needed sensitivity to precisely determine the 'point of failure', at higher surfactant concentrations, in the test fabric's ability to serve as an effective barrier. Future studies could evaluate barrier effectiveness from concentrations starting at the CMC.

3. In most field conditions, the pesticide 'solution' would have a prolonged exposure to the clothing surface. It would thus be helpful to understand the spreading behavior of the surfactant solution or the pesticide emulsion after longer exposure times, i.e., may employ longer time intervals instead of the 10-second intervals in measuring the contact angles.

4. For re-usable garments that have a fluorochemical soil-repellent finish on them, an attempt could be made to decontaminate the clothing by laundering it in oil (instead of water) containing a surfactant of low HLB value. Since oils are normally the solvents for pesticides, any residual pesticide from the clothing would dissolve in the oil and then be carried away by the surfactant. This technique could have applications in the decontamination of garments containing PTFE membranes or finishes since PTFE shows excellent oily-soil repellency.

5. Pesticides containing surfactants as adjuvants may be stored for a long time before being used. The effect of storage time on the surface tension of the pesticide system (or of a surfactant solution) is not known. Such information would be helpful in determining the wettability, and the hazards, if any, posed by exposure of clothing materials to such pesticide systems.

6. The results of this study imply that there might be a possibility of enhanced wetting, and other benefits brought about by such enhanced wetting, in applications of surfactants other than as herbicidal adjuvants (for instance, in textile processing and other engineering applications) at concentrations much greater than the CMC.

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Vita

Santosh Shankar Padki, the son of Uma S. Padki and the late Shankar Trimbak Padki, was born on October 23, 1966, in Bombay, India. After completing his schooling at Airport High School in Bombay in 1982, Santosh started his undergraduate studies at Victoria Jubilee Technical Institute (V.J.T.I.) in Bombay. He graduated with distinction from V.J.T.I. in June 1986 with a Licentiate in Technical Chemistry, specializing in Textile Chemistry. He was a recipient of merit scholarship for three years and a medal for academic achievement at V.J.T.I.

Santosh was a co-op student during his undergraduate program and underwent in-plant training in textile processing and management at Orkay Silk Mills and Empire Ind. in Bombay. He worked for a year as a Supervisor of chemical processing at Paragon Textile Mills in Bombay and then as an Assistant to the Chief Executive Officer of Mahajan Textiles in Bombay.

Santosh came to the Virginia Polytechnic Institute and State University (Virginia Tech) in Blacksburg, Virginia, U.S.A., to pursue his graduate studies in Textile Science. He completed the course work requirements toward an M.S. degree in June 1994.

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