

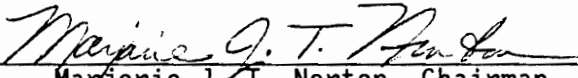
EFFECT OF COLD AMMONIA GAS PLASMA IRRADIATION ON DYEABILITY
OF POLY(M-PHENYLENE ISOPHTHALAMIDE) FIBERS WITH ACID DYES

by

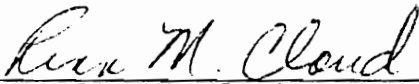
Gautam K. Mishra

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
in
Clothing and Textiles


APPROVED:



Marjorie J. T. Norton, Chairman



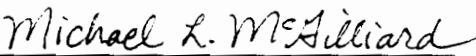
Rinn M. Cloud



Vera B. Keeble



Judy S. Riffle



Michael L. McGilliard

August, 1992

Blacksburg, Virginia

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**Committee Chairman: Marjorie J. T. Norton
Clothing and Textiles**

(ABSTRACT)

The purpose of the dissertation research was to investigate the effect of cold ammonia gas plasma irradiation on the dyeability of poly(m-phenylene isophthalamide) fibers (Nomex Type 430) with acid dyes. Unmodified Nomex filament yarns were irradiated by ammonia radio frequency glow discharge plasma with constant input power (100 W) and plasma pressure (1 torr) inside the reactor; exposure times were 60, 120 and 180 seconds. The modification in dyeability of plasma irradiated yarns was studied by dyeing with three anthraquinone based acid dyes (C.I. Acid Green 25, C.I. Acid Blue 45, and C.I. Acid Blue 80) and measuring dyebath exhaustion and color strength (K/S) of dyed yarns. The improvement in dyeability of plasma irradiated Nomex filament yarn was investigated by studying the surface chemical composition, surface amine concentration, surface topology, and wettability. Surface chemical composition was analyzed by x-ray photoelectron spectroscopy (XPS). The surface amine concentration was evaluated by studying the plasma amination kinetics through ion-exchange reactions between the ionic dye Ponceau Red 3R and Nomex filament yarn. Surface topology of

plasma irradiated filament yarns was studied with high resolution scanning electron microscopy (HR-SEM). The wettability of the irradiated Nomex filament yarns was analyzed in terms of grams of de-ionized water absorbed per gram of fiber after immersing the yarn specimens in de-ionized water for three time periods (15 s, 30 s, 60 s). The effect of irradiation on the filament yarns' tensile properties was evaluated by measuring breaking tenacity, elongation at break, and toughness. Statistical analyses of data on various parameters included analysis of variance (ANOVA), orthogonal polynomial contrasts between means, and post-hoc Newman-Keuls tests between means.

XPS spectra showed a higher concentration of both oxygen and nitrogen atoms at the Nomex filament surface after irradiation. Plasma amination kinetics indicated substantially more primary amino functional groups at the filament yarn surface after the plasma irradiation. SEM photomicrographs of plasma irradiated filament yarn indicated surface etching at low magnification (1,600 X) and surface cavitations at higher magnification (25,000 X). The wettability of irradiated Nomex filament yarns with de-ionized water was significantly higher compared to nonirradiated specimens. The dyeability of ammonia plasma irradiated Nomex filament yarns with acid dyes was improved as indicated by higher dyebath exhaustion and higher color strength. The dyebath exhaustion for the three dyes did not vary noticeably with respect to irradiation times (60 s, 120 s, 180 s). Ammonia plasma treatment adversely affected the tensile properties of Nomex filament yarn to a significant extent only after 180s. Breaking elongation and toughness were more severely affected after 180-s plasma treatment than was the breaking tenacity.

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Chapter I

Introduction

The production of synthetic fibers has grown rapidly during the last three decades, and is still growing worldwide (Simpson, 1991). Synthetic fibers maintain an important position in the multifiber industry. Synthetic fibers can be tailor-made according to requirements, and they have better ease-of-care properties and more versatility than natural fibers (Magat & Morrison, 1977). Despite their distinct advantages, synthetic fibers often are difficult to dye because of their high degree of crystallinity, marked hydrophobic character, and absence of chemical reactive groups on the surface of the fiber polymer (Peters, 1963). Several operations, such as heat setting, high-temperature/high-pressure dyeing, thermosoling, transfer printing, and solvent dyeing, were developed to improve dyeability following the introduction of synthetic fibers (Moncrieff, 1975).

Nomex^R, a member of the aramid family of fibers, was developed by DuPont for applications requiring good tensile properties, dimensional stability, and excellent heat resistance (DuPont Fibers Technical Information, 1981). Aramid fibers have rigid aromatic nuclei and highly crystalline microstructures which contribute to flame resistance and thermal stability or high strength and stiffness (Rebenfeld, 1990). Many of the unique characteristics of Nomex have been attributed to the aromatic nucleus, which causes the formation of stable hydrogen bonds

through acidic imino (N-H) groups (McCarthy, Rebenfeld, & Weigmann, 1981). The phenylene units in the Nomex polymer are in a rigidly parallel arrangement in the crystalline regions. Strong intermolecular interactions restrict torsional vibration and prevent free rotation (Frosini & Butta, 1971). The complex morphology restricts chemical modification by severely limiting accessibility and reactivity under conditions that avoid impairment of structural features and fundamental fiber properties (Bernashid & Tesoro, 1990).

Since the surface properties of solid organic polymeric materials have a strong effect on most of their practical applications, the properties and structure of an aramid fiber polymer surface are important in potential modification. Several techniques have been employed to modify the fiber surfaces to improve wettability, dyeability, and adhesion properties (Boenig, 1982). These methods include chemical treatments, corona discharge, and plasma irradiation. Plasma treatment on textiles has been shown to be one of the ideal methods for surface modification of natural and synthetic fiber polymers (Bhat & Nadiger, 1978).

The properties of Nomex resulting from its structure, particularly the high glass transition temperature ($T_g \sim 275^\circ \text{C}$), make the fiber almost impossible to dye in conventional processes (DuPont Fibers Technical Information, 1981). Only a select class of modified cationic dyes can be employed to dye fabrics into pale and medium shades and that process requires the use of concentrated carriers which are

environmentally unacceptable (Moore & Weigmann, 1986). Nomex is one of the most suitable choices for military camouflage uniforms due to its superior mechanical, chemical and flame resistant properties (Hodge & Dodgson, 1991). Dyes employed for coloration of fabrics for such uniforms are generally limited to acid dyes due to the availability of camouflage shades and ability to meet the infrared reflectance requirements (Ramsley & Bushnell, 1981). Unfortunately, Nomex has little affinity for anionic dyes including acid dyes.

Ammonia gas plasma irradiation is a process that results in the incorporation of reactive amino functional groups on the surfaces of fiber polymers (Allred, Merrill, & Roylance, 1985). The presence of functional amino groups at fiber surfaces is responsible for increasing the chemical reactivity of fibers while improving wettability and surface polarity (Zeronian & Collins, 1989). In acidic conditions amino groups can be protonated and show affinity to anionic dyes. Ammonia plasma irradiation may obviate carriers and permit the dyeing of Nomex with a range of anionic dyes to obtain more variety of shade and depth. Besides the addition of amino groups, plasma irradiation has been shown to increase fiber surface roughness without adversely affecting the fiber bulk properties (Allred, Merrill, & Roylance, 1985; Ward & Benerito, 1982). It may be that Nomex irradiated with ammonia gas plasma will develop a hydrophilic rough surface layer with amino groups attached. Fiber surface roughening through plasma irradiation may yield higher absorption of dyes.

There is relatively little information about plasma treatment on fully aromatic polyamide fibers, such as Nomex, and no research is known to have been conducted on surface modifications of Nomex fibers by ammonia glow discharge plasma irradiation. The purpose of this research is to investigate the effect of ammonia plasma irradiation on the dyeability of poly(m-phenylene isophthalamide) fiber (Nomex Type 430) with acid dyes.

Chapter II

Review of Literature

This chapter gives important background on plasma irradiation techniques and their effects on surface modification of textile fiber polymers. Literature dealing with the Nomex aramid fiber is reviewed because the research examines the potential improvement in the dyeability of Nomex with acid dyes through plasma treatment. The review of literature also discusses the broad concepts of plasma technology, plasma irradiation on the fiber phase, and the synthesis and dyeability of Nomex fiber.

Plasma Technology

Plasma Definition

Plasma is an ionized gas with essentially equal densities of positive and negative charge carriers and thus electrical neutrality of the system (Encyclopedia of Chemical Technology, 1984). The concept of plasma was introduced by Langmuir in 1926, and the first man-made plasma was observed inside a glow discharge tube (McTaggart, 1967). Plasma was later defined as a state where a significant number of atoms and/or molecules are electrically charged or ionized. Plasma, in general, refers to a gaseous state consisting of excited states of atoms, molecules, ions, metastables, and electrons such that the concentration of positively and negatively charged species is roughly the same (Ward, 1984).

Variables Affecting Plasma Characteristics

Plasmas vary greatly in many respects, depending on the parameters by which they are classified: pressure, charged particle density, and temperature (Liston, 1989). Plasma generation is achieved in the pressure range of about 0.1 to 10 torr. At very low pressures (<0.1 torr), the electron mean free path is too long for gas collisions to be significant for ionization (Boenig, 1982). At much higher pressures (>10 torr), the mean free path is very short and frequent gas collisions can generate highly ionized pathways for the conduction of current, and thus can form sparks. Plasmas, by definition, consist of ionized gases having positively and negatively charged particles. Most of the positive charges are positive ions and most of the negative charges are electrons. Because of the huge mass difference between these species, the ions are almost stationary in the plasma and the current is mainly carried by the electrons (Clark & Dilks, 1978). As a consequence, the species in a plasma may vary widely in temperature. One characteristic of plasma irradiation is that the Boltzmann temperature of the ions and molecules is roughly ambient in most cases, while that of the electrons is two orders of magnitude greater. In inert-gas plasmas, the energy distribution corresponds to a Maxwellian distribution (Boenig, 1982). The ionized gas system in plasma irradiation displays significantly different physical and chemical properties compared to the neutral condition. Plasma can be strongly influenced by electric and magnetic fields. Due to ionization in the gas, plasma can conduct electricity. Theoretically, plasma is referred to as a "fourth state of matter," and

it is characterized in terms of the average electron temperature and the charge density within the system (Clark & Dilks, 1978).

Plasma Types

The multitude of natural and synthetic plasmas is classified according to plasma temperature and charge density. Temperature is expressed in degrees Kelvin and equivalently in electron volts (ev). Densities of electrons and ions are measured by the number of charged particles per cubic centimeter (Encyclopedia of Chemical Technology, 1984). There are three distinguishable types of artificially produced plasmas: thermal plasmas, cold plasmas, and hybrid plasmas (McTaggart, 1967). In all three types, electrical neutrality is maintained so that the total number of electrons and other negatively charged particles is equal to the total number of positively charged species. The electron density is maintained between 10^9 - $10^{12}/\text{cm}^3$ to produce excitation or ionization of gas molecules. Thermal plasmas, produced by arc discharges, have temperatures ranging from several thousand degrees to over $50,000^\circ$ K. All the species (electrons, ions) in this type of plasma are in thermal equilibrium, that is, they have the same range of kinetic energies. Low electron energy plasmas are called cold plasmas. Cold plasmas are distinguished by the lack of thermal equilibrium between the neutral atoms, molecules, and free radicals and other charged species such as electrons and ions which are present. The familiar corona discharge is classed as a hybrid plasma (Riccobono, 1973). Hybrid plasmas are considered to be essentially cold plasmas

with a uniform distribution of thermal sparks that are really equivalent to miniature thermal plasmas. The sparks are small and their number and frequency of distribution are low enough that the overall temperature of the gaseous mixture is quite low.

Plasma treatment of most textile materials is restricted to the hybrid or cold types (Riccobono, 1973). There are few materials used in the textile field that could survive the high temperature of thermal plasmas even for a short time. Cold plasmas have moderate operational temperatures in the range of 1-10 eV, which makes them suitable for textile applications. In addition, it has been established that cold plasmas do not penetrate more than 500-1000 angstroms into the surface of a polymer (Bersin, 1972). Therefore, the plasma irradiation effect may be restricted to the surface of the fibrous polymer and may have no effect on internal fiber morphology.

Plasma Generation

Plasmas are copious sources of electromagnetic radiation, particularly in the ultraviolet (uv) region (Liston, 1989). Various techniques have been employed to produce a plasma suitable for chemical reactions, such as direct-current and low-frequency glow discharges and radio-frequency and microwave discharges (Yasuda, 1976). For organic chemical reactions, radio frequency is used most frequently in both laboratory and industrial production, chiefly because of the convenience of handling, ease of availability, and low energy requirements (Boenig, 1982). Plasma generation is strongly dependent on pressure, electrical field strength, and rate of gas flow throughout in the reactor.

Laboratory experiments are usually carried out at pressures of 0.1 to 2.0 torr, at power levels of 25 to 250 W, and at flow rates of several cubic centimeters per second (Boenig, 1982).

Due to the complexity of plasma systems, relatively little is known about the mechanism involved in plasma reactions. Plasmas are initiated and sustained by the applied electromagnetic field (Hudis, 1974). Free electrons are accelerated by the field, and they partially ionize the gas molecules through inelastic collisions. The degree of ionization is rather low, on the order of 1 in 10^4 - 10^6 mols (Chapman, 1980). Besides the relatively few ions, the plasma gas molecules exist as free radicals or as various excited-state species (Allred, Merrill, & Roylance, 1985).

Plasma Irradiation on the Fiber Phase

Low electron energy plasmas are referred to as cold plasmas and are most suitable for modifying properties of natural and synthetic fiber polymers (Bhat & Nadiger, 1978; Bradley & Fales, 1971). Cold plasmas are generated by gaseous electric discharge and encompass a low energy radiation spectrum with moderate operational temperature. They can penetrate 500-1000 angstroms into the fiber surface without affecting the fiber fundamental, or bulk, properties (Riccobono, 1973; Benerito, Ward, Soignet, & Hinjosa, 1981). Plasma irradiation induces a series of reactions in fiber polymer surfaces, involving homolytic bond cleavage, fragmentation, and the generation of free radicals resulting in crosslinking at the surface (Ward, 1984). Besides being a rich

source of active species, plasmas simultaneously create active species on polymer surfaces which can combine with the other plasma species. Since the bulk of the substrate is maintained at a low temperature and unexposed to high energy irradiation, plasmas are ideally suited for polymer surface chemical modification (Hudis, 1974). Reactive sites on the polymer surface are created by means of surface hydrogen abstraction to create free radicals (Boenig, 1982). The free-radical intensity of plasma-exposed fiber depends upon the morphology and chemical constitution of the fibers (Liston, 1989).

The nature of plasma reactions on fiber polymer surfaces is quite different from reactions induced by ionizing irradiations. Ionizing irradiations have particle or photon energies in the range of 10 kev - 100 mev, compared to 1 - 10 ev in the case of plasma irradiation (Boenig, 1982; Odian, 1981). Due to the high energies of ionizing irradiations, the interaction of these irradiations with polymeric materials involves the excitation and ionization of molecules through the ejection of electrons (Billmeyer, 1984). This does not occur in the case of plasma; furthermore the plasma irradiation effect is limited to the surface and depth of penetration is far less than for ionizing irradiations. However, the intensity at the surface is generally stronger for plasma than for the more penetrating irradiations (Yasuda, 1976).

The most outstanding and widely used effect of plasma is the surface modification of fibrous polymers, where the surface layer is altered to create chemical groups capable of interacting with adhesives

(Gregorski & Pavlath, 1980; Schonhorn & Hansen, 1967). The inherently low surface energy of untreated polymers hinders the wetting and interaction with adhesive systems. Plasma is used to add polar functional groups which dramatically increase the surface energy of fiber polymers (Brown & Swanson, 1971). Cold plasma treatment has been shown to improve the water absorbency and strength of cotton yarn (Stone & Barrett, 1962). Wettability has also been improved for tasar silk yarns and fabrics by nitrogen plasma treatment (Bhat & Nadiger, 1978). Cotton fabrics irradiated by argon plasma showed higher water absorption and more uniform dyeing by both low and higher molecular weight dyes (Jung, Ward, & Benerito, 1977). The increase in wettability and dyeability of argon-activated cotton fabrics may be explained by the modification of the cotton fiber surface and increased chemical reactivity after plasma irradiation. The plasmas based on oxidizing gases like oxygen and air are used to incorporate oxygen species in the polymer surface, whereas noble gases like argon and helium are used to generate free radicals in surfaces either to cause crosslinking or to leave active sites (Benerito, Ward, Soignet, & Hinjosa, 1981; Jung, Ward & Benerito, 1977). The active gases like ammonia leave amino groups on the surface, that are believed to react covalently with adhesives such as epoxies (Hollahan, Stafford, & Falb, 1969; Liston, 1989).

In summary, glow discharge plasmas are rich sources of active species and irradiation which can create active sites on a fiber polymer surface. The polymer surface may then be chemically modified through crosslinking or through the addition of new chemical species to the

surface atoms. The chemical effects are due to a combination of the attack by electronically-excited free radicals or atoms and by ions.

Nomex Aramid

Definition and Characteristics of Aramids

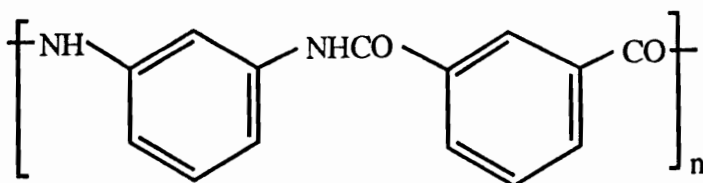
The Textile Fiber Products Identification Act defines aramid as a "manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide-linkages are attached directly to two aromatic rings" (Federal Trade Commission, 1986, p. 8).

Aromatic polyamides (aramids), which differ from aliphatic polyamides, contain aromatic carbocyclic rings as their molecular backbone. High molecular weight aromatic polyamides are characterized by an exceptionally high melting point. While aliphatic polyamides melt at a temperature below 270° C, aromatic polyamides generally melt above 300° C and in many cases above 350° C. Fibers prepared from aromatic polyamides have high strength, good recovery, and high flex life at elevated temperatures, and they are readily crystallizable. Because of excellent thermal stability, these fibers retain their strength at high temperatures for extended periods of time (Turbak & Vigo, 1991; Yang, 1989). In general, flame resistance and thermal stability occur with m-isomers, whereas high strength and stiffness are associated with p-isomers (Rebenfeld, 1990)

Aramid fibers, first developed and commercialized by E.I. DuPont de Nemours Inc. under the Kevlar trademark, represent a true milestone

in synthetic fiber technology (DuPont Fibers Technical Information, 1981). The most promising heat resistant fibers are aromatic polymers where benzene rings are linked by amide, imide, and imidazole linkages (Magat & Morrison, 1977). The major commercial aramid fiber of this type is Nomex^R which DuPont introduced commercially in 1961.

The fully aromatic polyamide polymer in Nomex fiber is poly(*m*-phenylene isophthalamide). It is a condensation product of *m*-phenylene diamine and isophthalic acid and has the following structure (O dian, 1981):



Poly (*m*-phenylene isophthalamide)

One of the first uses of Nomex was for the filtration of hot fumes emerging from steel furnaces and other metal smelters. Smelters work continuously and the temperature of the effluent may reach a peak temperature of 320° C; Nomex filter bags can sometimes last for years in such conditions (DuPont Fibers Technical Information, 1981).

Synthesis and Preparation of Nomex Fiber

The synthesis of aromatic polyamides (referred to as polyaramids) can not be carried out using diacid and diamine reactants due to the low reactivity of aromatic amines compared to aliphatic amines (O dian,

1981). The aromatic ring decreases the electron density of the amine nitrogen, therefore decreasing the nucleophilicity toward carboxyl groups. The elevated temperature needed to achieve polyamidation results in extensive side reactions and low molecular weights.

The synthesis of Nomex has not been disclosed by DuPont, but it is believed that aromatic polyamides are produced by using the faster reaction of the diamine with a diacid chloride instead of with a diacid. The polymerization reaction is shown in Figure 1. The polymerization is usually carried out in methylene chloride (CH_2Cl_2) solution, at a temperature no higher than ambient, with a base present to react with liberated hydrogen chloride (Black & Perston, 1968; Odian, 1981).

Highly polar aprotic solvents, such as dimethylacetamide (DMA), *n*-methylpyrrolidone (NMP), dimethylformamide (DMF), and hexamethylphosphoramide (HMP), have been used to prevent the growing polyamide chains from prematurely precipitating from solution. Such precipitation is a significant problem in the synthesis of aromatic polyamides since the reaction temperature is much lower than for aliphatic polyamides. The presence of lithium ions with the aprotic solvents has been found to promote polymerization by solubilizing the polymer, probably due to lithium ions coordinating with the carbonyl groups of the polyamide and/or the solvent (O dian, 1981).

End Uses

In certain end uses, flame resistance requirements are so stringent that performance needs can not be fully met by conventional

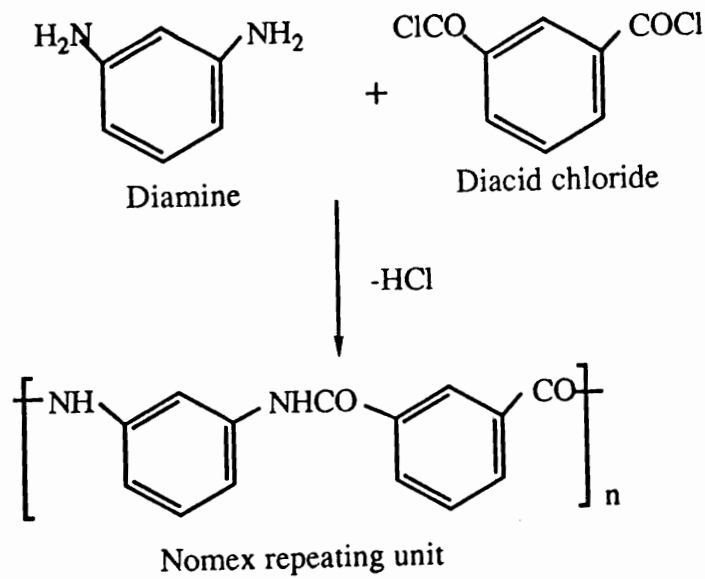


Figure 1. Possible reaction between aromatic diamine and aromatic diacid chloride for preparation of Nomex polymer

acrylic, nylon, and polyester fibers even after they are flame retarded (Magat & Morrison, 1977). These end uses dictate fibers with polymer structures which render them difficult to ignite and self extinguishing with little smoke generation. As a result of its flame resistance, Nomex is now being extensively used in protective clothing for military and industrial uses, in carpeting and upholstery in air craft, and in industrial components in electrical and electronic applications.

The primary function of thermal protective clothing is to minimize or even prevent physical harm as a result of fire. However, beyond this obvious requirement of flame protection, it is highly desirable and often necessary to provide protective clothing in various colors. The desirability of a variety of colors can be from a need for styling as with uniforms for race car drivers, or from a need for high visibility as with the outer shell of the launch and recovery suits used by the space shuttle crews (Hodge & Dodgson, 1991). Quite the opposite is required for flame resistant military camouflage, where the coloration is necessary to impart invisibility especially in infrared light.

Dyeing Behavior of Nomex

Because of the highly crystalline nature and high glass transition temperature ($T_g \sim 275^\circ \text{C}$) of aramid fibers such as Nomex, it is extremely difficult to dye aramid fabrics in conventional dyeing processes (McCarthy, Rebenfeld, & Weigmann, 1981). Colored Nomex with the best overall properties (fabric strength and color fastness) is achieved by injecting pigments into the spinning dope prior to fiber

extrusion (Hodge & Dodgson, 1991). No molecular binding of the colorant is necessary in this procedure since the colorant is physically or mechanically locked into the fiber structure.

Dyeing of Nomex in fabric form can only be achieved by using a carrier, usually a powerful organic solvent, to swell or disrupt the structure to permit dyes to migrate into the fiber (DuPont Fibers Technical Information, 1981; White, Schlaeppi, Houser, & Larkins, 1983). In dyeing there must be some sort of molecular binding of the dye to the aramid structure and only cationic dyes will bind to the polymer structure in Nomex (Ulery, 1974). Fabrics of Nomex will dye in pale to medium shades using cationic dyes (with a carrier), but will only lightly stain using acid dyes (Cook & Kleissler, 1983; Hodge & Dodgson, 1991).

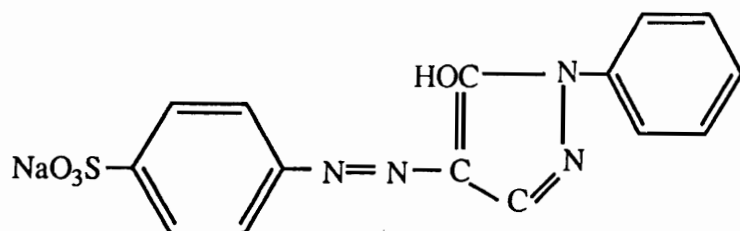
The affinity of cationic dyes for the meta aramid structure is not well understood. The most obvious bonding sites are the free carboxyl end groups. The amide groups may also play a role since amides are hybrid structures of two resonance forms resulting in the carbonyl oxygen being somewhat electronegative (Hodge & Dodgson, 1991). Van der Waals forces between the aromatic rings of the polymer and dye may also be a factor; however, this would apply equally to acid and basic dyes which have essentially no affinity for Nomex (Trotman, 1984).

For protective apparel, such as military camouflage clothing, there have been serious limitations on dyestuffs. The colors, or shades, are chosen to reduce the contrast of battle dress uniforms with the natural background. Nearly all camouflage patterns are composed of

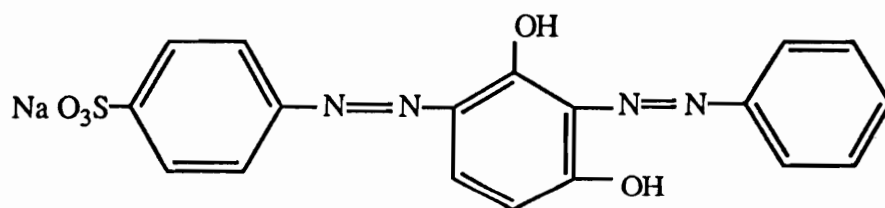
various shades of green, brown and black. There is, however, another important criterion: the shades must also minimize the contrast in the near infrared region (600-900 nm) to avoid detection by night surveillance devices. The dye classes that currently meet reflectance requirements of the military are limited to acid and vat dyes (Ramsley & Bushnell, 1981). The limitation of dyestuffs presents a unique problem for Nomex since aramids are not substantive to either of these classes of dyes.

The preferred mechanism of binding acid or basic dyes to a substrate is the formation of an ionic bond (Trotman, 1984). For example, a typical acid dye has one or more sulfonate groups, or possibly carboxylate groups, in the structure as shown in Figure 2. The sulfonate (or carboxylate) anion will be attracted by a cation that is contained in the fiber substrate. The final step in the mechanism is the formation of an ionic bond between the anionic dye and the substrate (Peters, 1963). Failure to achieve good chemical binding, or fixation, will result in wash fastness being poor or nonexistent.

In summary, the properties needed in the Nomex fiber structure to permit dyeing with acid dyes require incorporation of reactive functional groups that would facilitate the interaction between the dye and the fibers and simultaneously bonding of acid dye to the Nomex substrate.



C.I. Acid Yellow 4 : a monoazo dye



C.I. Acid Orange 25: a diazo dye

Figure 2. Structures of two common acid dyes.

Chapter III

Statement of the Problem

Theoretical Framework

Low electron energy plasmas, known as cold plasmas, are suited for surface modification of both natural and synthetic polymers. Cold plasmas are generated by gaseous electric discharge, provide a source of high energy electrons without excessive heating, and are highly reactive chemically. In contrast to thermally-induced reactions, where energy is usually equally distributed among all particles in the system, energy in cold plasma reactions is supplied principally to the free electrons. Ion and neutral molecule temperatures remain near that of the reactor vessel, hence the designation of low-temperature plasma (Ward & Benerito, 1982). Since the bulk of the substrate is maintained at a low temperature and unexposed to high-energy irradiation, plasmas are ideally suited for polymer surface chemical modification.

Plasma treatment is known to effect changes in the surface properties of polymeric materials. The extremely energetic chemical environment of the plasma has been under investigation for major improvement in fiber polymer processes that require adhesion, dyeing, and wetting properties. Therefore it is important to accumulate information regarding the change in surface chemical composition and surface topology of fibrous polymers after exposure to plasma irradiation.

Cold plasma treatment is effective in inducing polarity on fiber

surfaces, producing an enhanced hydrophilic surface layer (Byrene & Brown, 1972; Thorsen, 1974). The increase in polarity at the fiber surface is evidenced by the formation of new functional groups on natural and synthetic fiber surfaces (Ward & Benerito, 1982; Yasuda, Marsh, Brandt, & Reilley, 1977). The improvement in degree of polarity on the fiber surface is responsible for faster and more uniform wetting by water and by both low and high molecular weight dyestuffs (Jung, Ward, & Benerito, 1977). Wettability is important to the adherence of dyes and adhesives to textile fibers (Boenig, 1982).

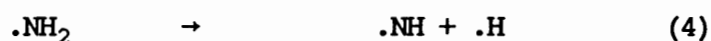
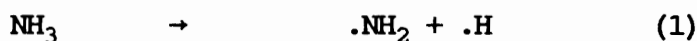
The incorporation of new functional groups on the fiber surface via plasma irradiation suggests improvement in the reactivity of the fiber surface and in its adhesion to resins (Wertheimer & Schreiber, 1981). The alteration in surface chemical composition of the fiber is due to the addition of carbon-oxygen or carbon-nitrogen functionalities (Boenig, 1982; Gregorski & Pavlath, 1980). Incorporation of nitrogen in a polymer surface occurs with the formation of carbon-nitrogen bonds (Clark, 1978). The nitrogen attachment to carbon by plasma represents the direct reaction of activated gases, whereas oxygen incorporation may be due to free-radical formation in the polymer surface followed by free-radical reaction with oxygen (Ward, 1984). Introduction of any polar atoms such as fluorine, oxygen, nitrogen, or chlorine into the surface of a nonpolar fiber is expected to enhance its chemical reactivity, wettability, adhesiveness, and dyeability (Boenig, 1982).

The introduction of amino groups on to polymer surfaces via ammonia plasma irradiation has been extensively studied (Hollahan,

Stafford, & Falb, 1969). It has been demonstrated that amine surface functionality can be introduced into a variety of aliphatic polymers by exposure to ammonia gas plasma generated by radio frequency. Hollahan et al. also indicated that surface amino groups were reactive by showing improved bonding between epoxy resin and ammonia gas-treated polytetrafluoroethylene polymer.

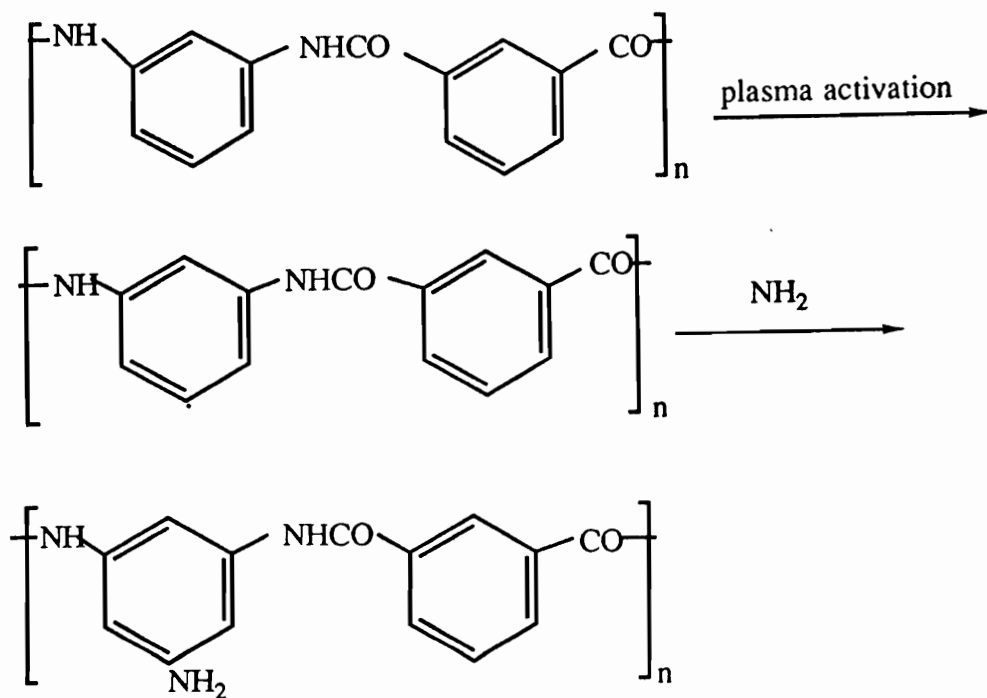
Ammonia plasma treatment on polyester filament has been found to improve adhesion to rubber (Lawton, 1974). The research suggested that ammonia plasma treatment increased adhesion without significantly affecting the bulk fiber properties. It also has been observed that introduction of amino groups to graphite yarns can be accomplished by exposure to ammonia glow discharge plasmas (Goan, 1973). Surface amination occurred very fast without any structural damage to the fundamental fiber properties.

Plasma decomposition of ammonia has been investigated (Agostino, Cramarossa, De Benedicts, & Ferraro, 1981), and has indicated that the decomposition process followed zero-order kinetics through the sequence shown below.



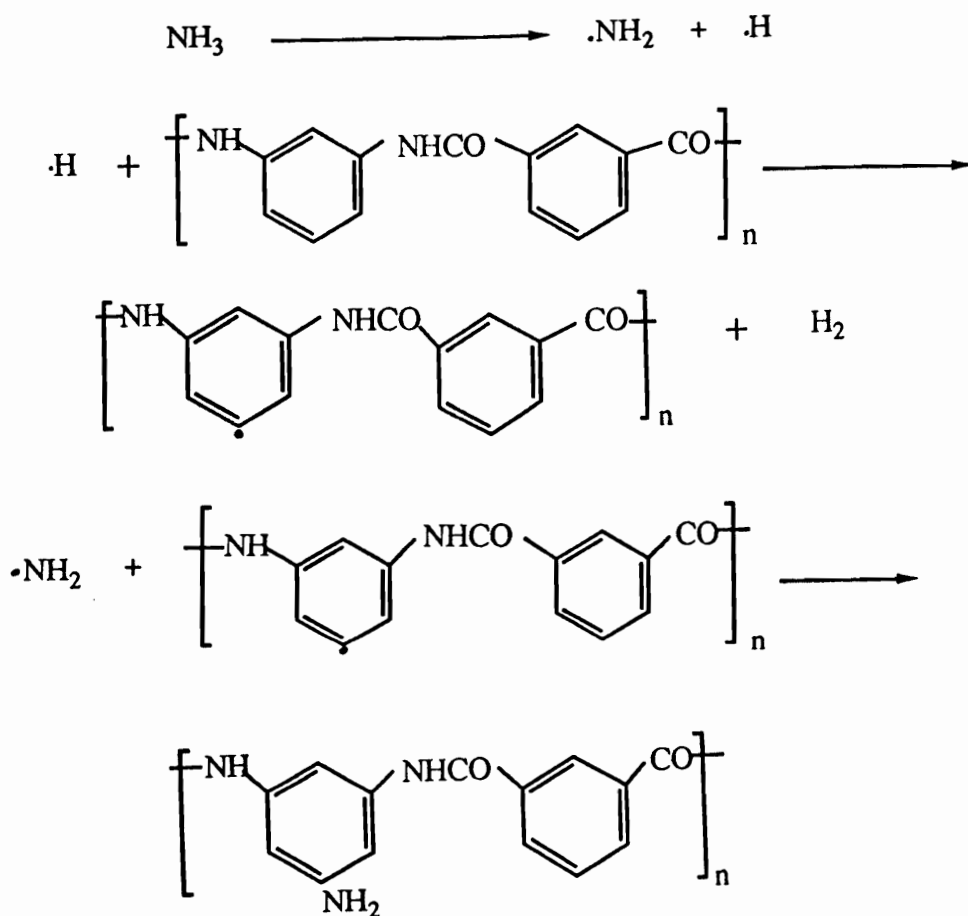
Reactions 1, 2, and 4 are nonequilibrium processes that occur through electron impact with ground state molecules, through bimolecular dissociation of vibrationally excited molecules, or through a joint vibrational impact mechanism (Capitelli & Molinari, 1980). Reaction 5 occurs very rapidly and is the main channel for $\cdot\text{NH}$ disappearance (Agostino, Cramarossa, De Benedicts, & Ferraro, 1981). $\cdot\text{NH}_2$ is the most likely species available for recombination with polymer surface radicals.

This research is based on the recombination of $\cdot\text{NH}_2$ with poly (*m*-phenylene isophthalamide) surface radicals. The surface chemistry of aramid filaments differs considerably from the bulk chemistry. The surface exists as a highly oxidized hydrocarbon layer with little nitrogen present. The poly (*m*-phenylene isophthalamide) amination reaction in an ammonia plasma may be idealized as follows:



This process is practicable for the following reasons :

1. In ammonia plasma irradiation, $\cdot\text{NH}_2$ is the most likely species available for recombination under cold plasma discharge conditions.
2. The short exposure of poly (m-phenylene isophthalamide) polymer to activated species of ammonia may result in the loss of hydrogen atoms. Subsequent reactions lead to the formation of primary amino group on the surface of the fiber, as presented below.



Radical formation is shown occurring on the fifth carbon atom because it is the most reactive site for recombination. Nitrogen species in the

plasma other than NH_2 may lead to a variety of other surface groups as would reactions with the amide group. Competing oxidizing reactions may also be expected.

Amino groups attached to polymer surfaces by ammonia plasma are confined to a thin layer of less than 1 micron (Hollahan, Stafford, & Falb, 1969). The incorporation of amino functional groups on the fiber surface increases the fiber wettability and dyeability with acid dyes, and provides sites for subsequent reaction (Zeronian & Colins, 1989). Because the reaction appears to be confined to the fiber surface, it is topochemical. Increased wettability is indicated by the reduction in the contact angle made by a water drop on the fiber surface. This could be due to increased surface roughness or pitting and to possible increase in the number of hydrophilic groups on the fiber surface caused by amination. Plasma irradiation is responsible for forming roughness at the surface of a fiber polymer due to microscopic etching (Padhye, Bhat, & Mittal, 1976). Plasma irradiation effects occur at random along the fiber. Irregularities along the surface of a synthetic fiber cause it to more strongly resemble natural fibers. Increase in porosity due to the minute cracks and pits introduced on the fiber surface significantly improves wetting, diffusion of dyes, and retention of adhesives for effective fiber bonding (Byrene & Brown, 1972). Zeronian and Colins (1989) have also reported that the presence of amino groups in polyester fiber would make it possible to dye the product with additional classes of dyes, such as acid dyes.

The surface modifications induced by plasma irradiation may not alter the bulk properties of the fibers significantly. The bulk properties of fibers may be described in terms of strength, extensibility, stiffness, elasticity, resilience, and toughness. These mechanical properties are strongly dependent upon the relative proportions of crystalline and amorphous regions in the fiber morphology and the polymer's molecular weight. Plasma irradiation effects are restricted to 500-1000 angstroms of the fiber surface. Since the plasma irradiation does not penetrate beyond the fiber surface, the irradiation effect is localized on the surface of the fibrous polymer and has possibly little effect to induce changes in its bulk properties. In summary, reactive glow discharge plasma, as with ammonia gas, can induce surface modification of fibrous polymers, where the surface layer of the irradiated fiber polymer is altered to add roughness and polar functional groups which could enhance the surface chemical reactivity, degree of wettability, and dyeability of the fibers.

Research Objectives

1. To determine the effect of ammonia plasma irradiation upon the surface chemical composition and surface topology of Nomex filament yarn (Type 430).
2. To determine the effect of ammonia plasma irradiation on the dyeability of Nomex filament yarn (Type 430) with three acid dyes, in relation to surface texture modification, wettability, and reactive amine concentration on the fiber surface.
3. To determine the effect of ammonia plasma irradiation on selected tensile properties of Nomex filament yarn, including the breaking tenacity, breaking elongation, and toughness.

Research Hypotheses

The following hypotheses are based on prior empirical results and the theoretical framework.

1. Nomex filament yarns (Type 430) after irradiation with ammonia plasma will have an altered surface chemical composition as compared to nonirradiated specimens.

Rationale: Ammonia plasma irradiation is expected to increase the surface amine concentration of Nomex filament yarns. Besides the attachment of primary amino functional groups, oxidation at the yarn surface during and after the plasma exposure is expected. Oxygen readily combines with free radicals upon exposure to air, so some oxidation at the yarn surface is expected to occur. The nitrogen and oxygen content at the yarn surface after irradiation is expected to be above that of the nonirradiated yarn indicating that amination as well as oxidation occurred due to ammonia plasma irradiation.

2. Nomex filaments (Type 430) will have a rougher surface after irradiation with ammonia gas plasma.

Rationale: Plasma irradiation is responsible for random etching of the organic polymer as well as of the fiber surface. It is expected that ammonia plasma irradiation will etch the surface of Nomex filament yarns inducing porosity due to the formation of minute cracks and pits on the fiber surface. Also the oxidation at the aromatic fiber surface will contribute to surface roughening.

3. Ammonia plasma irradiated Nomex filament yarns (Type 430) will

have a higher degree of wettability than will the nonirradiated specimens.

Rationale: It is expected that ammonia plasma irradiation will induce the incorporation of reactive amine functional groups at the surface of Nomex filament yarns. Atomic oxygen content is also expected to increase due to surface oxidation during and after irradiation.

Incorporation of electronegative atoms like nitrogen and oxygen at the fiber surface will contribute to increased polymer surface energy, which should result in improved wetting properties.

4. Nomex filament yarns (Type 430) after irradiation with ammonia gas plasma will have greater dyeability with acid dyes than will the nonirradiated specimens.

Rationale: Nomex fiber has little or no affinity for acid dyes. But after irradiation with ammonia plasma, it is expected that surface amine concentration will be increased significantly. Chemically reactive amino functional groups ($-NH_2$) can be protonated in acidic medium to form $^+NH_3$. All the dyes selected for the research are based on anthraquinone sulfonic acids. In aqueous medium, the dyes will be ionized to colored anions. Since the dye will have a negative charge and the fiber will have positively charged amino groups, electrostatic attraction between dye and fiber is expected, resulting in the formation of ionic bonds. A preliminary investigation with Acid Red 18 has shown a substantially higher color yield for ammonia plasma irradiated Nomex filament yarn compared to the nonirradiated specimens.

5. There will be no significant differences in dyeability of ammonia plasma treated Nomex filament yarn (Type 430) with respect to plasma irradiation time (60-180 seconds).

Rationale: In general, the modification in surface chemical composition and surface topology for organic polymers and fibers reaches equilibrium within the first 60 seconds of plasma irradiation. The dyeing of Nomex fiber with acid dyes is dependent on the concentration of reactive amino functional groups on the fiber surface and to some extent the surface texture. Since the surface chemical composition and texture of Nomex filament yarn are not expected to change significantly after 60 seconds of plasma irradiation, the dyeability should not be significantly different between yarns with 60-180 seconds of plasma treatment time. Preliminary investigation of ammonia plasma irradiated (60 s-180 s) Nomex filament yarn with Acid Red 18 has indicated the saturation of color yield after 60 s of plasma treatment.

6. There will be no significant differences among three selected acid dyes in terms of the dyebath exhaustion and the color strength of dyed ammonia plasma irradiated Nomex filament yarn.

Rationale: C.I. Acid Green 25, C.I. Acid Blue 45, and C.I. Acid Blue 80 are the three acid dyes selected for investigating the dyeability of Nomex filament yarns before and after the ammonia plasma irradiation. All these dyes are based on anthraquinone sulfonic acids and have two sulfonic acid groups in their molecular structure. The major difference between the three dyes is their molecular weight by virtue of somewhat different side groups. Sulfonic acid groups in a dye structure work as

binding sites for the dye molecule with the fiber. Since the three dyes have a similar chromophore (anthraquinone) with the same number of auxochromes (two sulfonic acid groups), their dyeability is not expected to differ.

7. Ammonia plasma irradiated Nomex filament yarns (Type 430) will have breaking tenacity, elongation at break, and toughness similar to those of nonirradiated Nomex yarns.

Rationale: As with all polymers, tensile properties are a function of complex molecular and supermolecular structures and of the molecular weight. The tensile properties are determined as a response to the deformation of the microfibril and surrounding matrix. Cold ammonia plasma encompasses a low energy radiation spectrum with moderate operational temperature and can penetrate only 500-1000 angstroms into the polymer surface without changing bulk properties. Since the fundamental characteristics of the Nomex yarns will remain basically the same, the tensile properties are not expected to be affected by the irradiation.

Assumptions

The following assumptions were taken into consideration for the analysis.

1. The Nomex filament yarns (Type 430) supplied by DuPont are not systematically nonuniform through the cone with respect to their fiber morphology, surface characteristics, and other fiber properties.
2. The dyeing experimental methods opted for in the research are representative of standard industrial practice in the textile industry.
3. All the instruments used for the research measurements yield reliable results.

Limitations

1. Nomex filament yarns Type 430 (200 denier/100 filaments) from DuPont were selected for the study and results refer only to such yarns.
2. Three anionic dyes (C.I. Acid Green 25, C.I. Acid Blue 45, C.I. Acid Blue 80) were used for dyeing of both plasma irradiated and nonirradiated Nomex filament specimens. The acid dye class was selected because it has the infrared reflectance characteristics to match the requirements for military camouflage uniforms. Also, military camouflage uses a green to bluish shade to blend with the background of a tropical forest.
3. Ammonia plasma irradiation upon Nomex filament yarn was employed only for three time periods from 60 to 180 seconds at each 60-second interval. It was not possible to shorten the plasma exposure to less than 60 s due to the lack of precise batch reactor control adjustments. The short plasma exposure time (60s - 180s) is used because aramid fibers, like any other synthetic fibers, are sensitive to irradiation and may degrade and lose their fundamental properties of superior strength and rigidity if exposed for long periods. Also, preliminary experiments indicated insignificant change in color strength after 60 seconds of irradiation.
5. Only the parameters of dyebath exhaustion, color strength, wettability, elemental surface atomic composition, surface roughness, surface amine concentration, and tensile properties were evaluated for both plasma irradiated and nonirradiated Nomex filament yarns. These

parameters were selected to obtain information regarding the surface modification and change in chemical composition at the filament yarn surface as they also affect the dyeability and tensile properties.

Chapter IV

Materials and Methods

This chapter is divided into three sections: (1) experimental procedure, (2) methods for testing of research specimens, and (3) data analysis and hypothesis testing. The experimental procedure included a mild scouring of Nomex filament yarn to eliminate traces of spinning oils, dust contaminants, and nonfibrous materials. The scoured Nomex filament yarn was irradiated by ammonia plasma under suitable experimental conditions. The plasma irradiated and nonirradiated scoured Nomex filament yarns were dyed according to the outlined procedure.

To evaluate the effectiveness of several types of plasma irradiation (oxygen, nitrogen, and ammonia) on the dyeability of Nomex filament yarn with acid dyes, a preliminary study was conducted. Nomex filament yarns were separately irradiated for 60 s, 120 s, and 180 s with nitrogen, oxygen and ammonia plasma. After plasma exposure, both the irradiated and nonirradiated yarn specimens were dyed with 10% on-weight-of-fiber (owf) Acid Red 18. Color strength and CIE L, a, b color coordinates were measured in the Hunter LabScan spectrophotometer under D₆₅ illuminant at 10-degree standard observation. The results and interpretation of this preliminary investigation are presented in the first section of chapter V. Due to the results, the research proceeded with only ammonia plasma irradiation.

The methods of testing the research specimens included physical

testing procedures to obtain information about the effect of ammonia plasma treatment on tensile properties of Nomex filament yarn before and after plasma irradiation. Dyeability was measured by percent of dyebath exhaustion and color strength, CIE L, a, b color coordinates, and instrumental color difference (ΔE) between dyed specimens. It was hypothesized that changes in the dyeability of Nomex filament yarn after plasma irradiation would be associated with alteration of surface texture and surface chemical composition. The filament surface topology was studied by scanning electron microscopy, and surface chemical composition was characterized by x-ray photoelectron spectroscopy (XPS). In addition, the surface amine concentration was evaluated by ion-exchange analysis with an anionic dye. Since dyeing of a fiber is dependent on its wetting properties, wettability of Nomex filament specimens was evaluated for both irradiated and nonirradiated specimens. The statistical analysis of data involved analysis of variance, orthogonal polynomial contrasts, and Newman-Keuls post hoc multiple comparisons to investigate the significant differences between means.

Experimental Procedure

Nomex filament yarns Type 430 (200 denier/100 filaments) from DuPont were used. The yarns had filaments of round cross-section with a diameter of 19 μm . Nomex filament yarns are also available in Type 430 (1200 denier/600 filaments), Type 431 (200 denier/100 filaments), Type 432 (200 denier/100 filaments), and Type 433 (200 denier/100 filaments). The Type 430 (1200 denier/600) yarn is very coarse and may not be suitable for studying plasma irradiation effects. Type 431 has an

applied electrical finish for use in electrical equipment. Types 432 and 433 are colored yarns, so they can not be included in the study.

Specimen Selection

All specimens for experiments and testing were selected in a random manner to avoid bias. The first 200 yards yarn from the cone were discarded to avoid possible environmental contaminants on the yarn surface. All specimens used for plasma irradiation were .28-.32 g weight for ease of handling and storage purposes. Specimens were cut at 15-20 ft intervals of yarn to avoid sampling from one place. A sufficient number of specimens were cut based on the coefficient of variation of breaking tenacity to obtain reliable estimates of tensile results.

Selection of Dyes

C.I. Acid Green 25, C.I. Acid Blue 45, and C.I. Acid Blue 80 were selected to investigate the dyeability of Nomex filament yarns (Type 430) before and after ammonia plasma irradiation. Predominant shades in the series of anthraquinone acid dyes are blue and green. These three dyes are based on anthraquinone sulfonic acids which constitute the most important group of acid dyes for coloring protein and polyamide fibers. Each of the dyes consists of two sulfonic acid groups in the molecule. Since sulfonic acids are polar, they increase the overall polarity of the dye molecule and make it more readily soluble in water. This allows easier preparation of dye liquors, assists in more even dye uptake by the fiber, and results in more level dyeing. Also the presence of sulfonic groups enables the formation of forces of attraction between

the dye molecules and fiber polymers. These three dyes are commercially available from the largest number of dye manufacturers and are heavily used in industry as well as in research for dyeing wool, silk, and polyamide nylon fibers. Other than the difference in molecular weight, the three dyes are similar in chemical structure and dyeing process. Three dyes were used to compare homogeneity in dyeability since results on only one dye may not be representative of other dyes.

Scouring Procedure

All specimens were scoured for 30 minutes at 60° C (140° F) in baths containing 10 g/L of AATCC Standard Detergent WOB (without optical brightener), 1 g/L of soda ash, and 0.5 g/l of Triton X-100 (Rohm and Haas) with a 30:1 liquor-to-goods ratio, then thoroughly rinsed in distilled water and air dried. Yarns were dried overnight at 110° C in a hot-air circulating oven. The dried specimens, in sealed plastic envelopes, were placed inside a desiccator to avoid contact with moisture or any contaminants prior to plasma exposure.

Plasma Irradiation Method

Ammonia plasma irradiation on Nomex filament yarns, each weighing 0.28-0.32 g, were conducted inside a plasmod reactor (March Corporation) which is designed for batch processing. The plasma reactor consisted of a cylindrical glass chamber with vacuum arrangement, and an inlet and outlet for gas. A radio-frequency (rf) oscillator was used as the source to produce the glow discharge. The operating radio frequency was set at 13.56 MHz with power input of about 100 watts. The plasma

pressure inside the reactor was maintained at 1 torr throughout the irradiation treatments. A rectangular glass frame holder was designed to introduce a yarn specimen into the plasma chamber to minimize yarn contact with the walls of the chamber and thus avoid dust contamination.

Plasma treatment consisted of pre-evacuation of the reactor for five minutes, followed by bleeding in the plasma gas for two minutes before initiating the plasma generation. Anhydrous ammonia gas of laboratory grade supplied by Matheson Gas Products (East Rutherford, NJ) was used inside the plasma reactor. Based on preliminary experiments with pressure stabilization while observing the appearance of the emitted light, the plasma reached an apparent steady state in 5-10 seconds. At low pressure of 1 torr, ammonia plasma appears light purple. Nomex filament specimens were subjected to plasma irradiation for 60, 120, and 180 s. After irradiation, the specimens were protected from contamination, moisture, and surface oxidation by placing them inside sealed plastic envelopes and storing in a desiccator until dyeing or other experiments were conducted.

Dyeing of Nomex Filament Yarns

Research grade Rico Neutral Green G (C.I. Acid Green 25), Rico Cyanine S Conc. (C.I. Acid Blue 45), and Ricoamide Blue RAWL 110% (C.I. Acid Blue 80) were the three acid dyes (Rite Industries Incorporated) selected for investigation of the dyeability of Nomex filament yarns before and after the ammonia plasma treatment. These dyes are based on anthraquinone chromophores and have two sulfonic acid groups in their molecular structure. Characteristics and molecular structures of these

dyes are presented in Table 1 and Figure 3.

The dyes were received in powder form and were made into 1% (w/v) aqueous solutions. The solutions were prepared by weighing 2.5 g of dye in a glass beaker and pasting with warm de-ionized water. Dissolved pastes were transferred into 250-ml volumetric flasks. The beakers were washed several times with de-ionized water which was then transferred into the volumetric flask to the last visible trace of dye. Finally, the volume of each dye solution was raised to 250 ml by adding de-ionized water. The dye solutions were covered with stoppers and stored in a cool, dark place to avoid adverse environmental exposure.

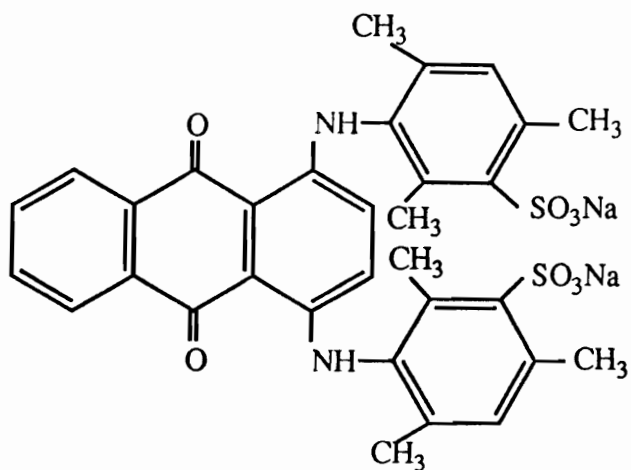
Nomex filament yarns (.28-.32 g) were dyed in beakers placed in a Fisher shaking water bath with each dye at a 40:1 liquor to goods ratio, using 10% dye on-weight-of fiber (owf) and 0.05 g/l of Triton X-100 solution. The dyebath was constantly agitated (100 cycles per minute) to facilitate uniformity in the dyeing procedure. The pH of the dyebath was maintained between 3.0 -3.5 by addition of acetic acid (80%) and sodium acetate buffer. The dyebath with Nomex filament yarn was initially set at 50° C and the temperature of the bath was raised to 90° ± 2° C (194° ± 35.6° F) in 30 min and the dyeing continued thereafter for another 60 min. Dyeing with each dye was repeated six times for both nonirradiated and irradiated (60s, 120s, 180s) Nomex specimens. After dyeing, each specimen was washed in cold de-ionized water, squeezed and air dried.

Table 1

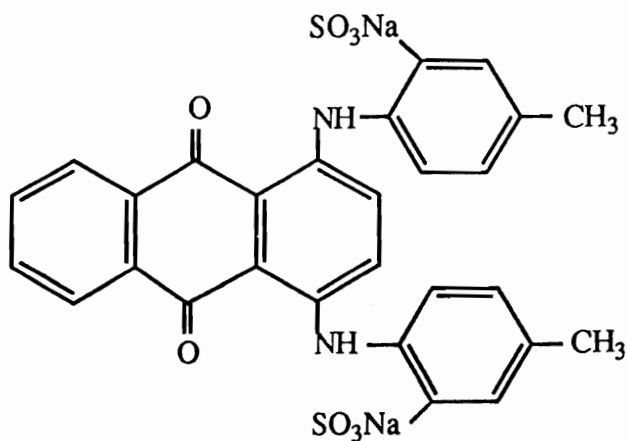
Characteristics of the Acid Dyes used in the Study

<u>Generic Name</u>	<u>Commercial Name and Manufacturer</u>	<u>Chemical Class</u>	<u>Molecular Weight</u>	<u>Wavelength of Maximum Absorbance (nm)</u>
C.I. Acid Green 25	Rico Neutral Green G (RII)*	Anthraquinone	621	640
C.I. Acid Blue 45	Rico Cyanine S Conc (RII)*	Anthraquinone	474	595
C.I. Acid Blue 80	Ricomide Blue RAWL 110% (RII)*	Anthraquinone	678	625

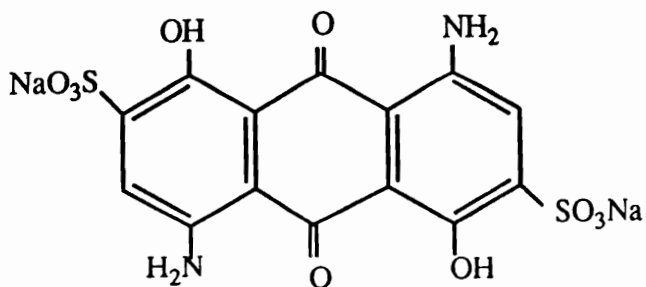
* Rite Industries Incorporated



C.I. Acid Blue 80 (61585)



C.I. Acid Green 25 (61570)



C.I. Acid Blue 45 (63010)

Figure 3. Chemical structures of C.I. Acid Green 25, C.I. Acid Blue 45, and C.I. Acid Blue 80. Chemical constitution numbers are shown in parentheses.

Methods for Testing of Research Specimens

Surface Analysis by X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful technique for the surface analysis of solids and the analysis of gas. It is possible to determine the relative atomic ratio of atoms on the surface easily within 2% for elements above 1% concentration and much more precisely for some elements whose sensitivity for detection is higher. Since information can be obtained for a few hundred angstroms from the surface of a solid, this technique is natural for the surface analysis of textile fibers (Millard, 1977). XPS, also known as electron spectroscopy for chemical analysis (ESCA), has become recognized as a sensitive analytical method for investigation of polymer surfaces.

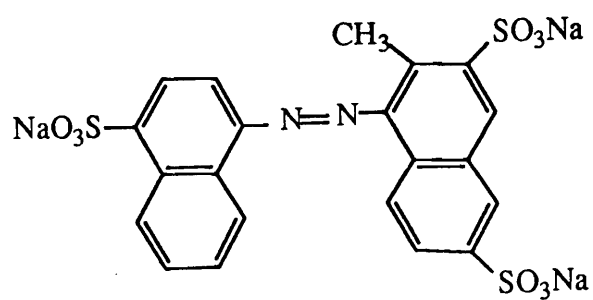
XPS analysis of Nomex filament yarn was performed to determine the change in chemical composition at the filament surface before and after the ammonia plasma irradiation. The XPS analysis was performed on a Kratos XSAM 800 spectrometer employing a $MgK\alpha$ (1253.6 eV) achromatic x-ray source operated at 13 keV and filament current of 20 mA. Nomex filament yarns were analyzed by XPS immediately upon removal from the plasma reactor. Nomex filament yarns of approximately 20 cm were wound around the sample probe using doubleback tape and were several times held under a vacuum of 10^{-6} torr during analysis. The N_{1s} , C_{1s} , and O_{1s} spectra from the surface of Nomex specimens were obtained to present the electron binding energies, peak areas, and full width at half height (FWHM). From the peak areas, the elemental surface atomic composition

of nitrogen, carbon, and oxygen was calculated and expressed in percentage.

Measurement of Amine Concentration by Ion Exchange

The procedure used for determining the amine concentration of irradiated filaments by ion exchange was originally developed to measure primary amine groups on proteins absorbed on membranes (Allred, Merrill, & Roylance, 1985; Bernashid & Tesoro, 1990). The technique has proven to be quantitative by comparisons with isotope labeling experiments, and has been extensively used for quantification of primary amino functional groups on surfaces of polymeric materials including fibers. The procedure had eight steps:

1. Three 0.32-g yarn specimens from the irradiation exposure times (60 s, 120 s, 180 s) were grouped separately for each exposure time and soaked overnight in 1.0 N hydrochloric acid (HCl) to protonate the amine groups.
2. The HCl was drained off and the specimens were covered with a 20-mg/ml solution of Ponceau 3R dye in water for one hour. Figure 4 shows the structure of the dye. The solutions were agitated occasionally to prevent a stagnation layer from forming near the reaction zone.
3. After draining off the Ponceau 3R dye, the yarns were thoroughly rinsed with 0.1 N acetic acid. Rinsing with acetic acid was to remove most of the unreacted dye, and was followed by agitation in a series of 0.1 N acetic acid solutions to remove dye entrapped between the filaments.
4. The yarns were then blotted dry and covered overnight with a



Ponceau Red 3R

Figure 4. Structure of Ponceau Red 3R

solution of 0.1 N sodium hydroxide (NaOH). After soaking, the yarns were individually rinsed with 0.1 N NaOH, followed by distilled water to remove dye entrapped in the yarn structure. A total combined effluent volume of about 40 ml resulted from the soaking and rinsing steps for each group of three yarn specimens.

5. The dye-containing effluent was concentrated by heating the solution in an oven at 75° C yielding a volume near 20 ml. The effluent was then filtered under vacuum through a fritted glass funnel to remove loose fibrils which would influence the visible absorption measurement. After filtering, the frit was washed with 0.1 N NaOH and distilled water. The combined effluent (about 40 ml) was concentrated at 75°C to 5-7 ml and cooled to room temperature. The concentrated solution was then acidified with 0.5 ml of 12.0 N HCl and diluted to 10 ml with distilled water in a volumetric flask.

6. Absorption of the solution was measured at 499 nm in a Spectronic 2000 uv-vis spectrophotometer with distilled water in the reference cell.

7. The yarns were dried overnight at 110° C, cooled, and weighed on an analytical balance.

8. Amine concentration was then calculated from the specimen optical density, the Ponceau 3R calibration correction factor (0.005), a conversion factor (1.114 g/sq. angstroms) and the filament surface area of 0.3 sq. inch, (DuPont Research Laboratory, Richmond, Virginia) by using the following formula:

$$\frac{\text{NH}_2}{100 \text{ \AA}^2} = \frac{\text{O.D} - 0.005}{W} \times 1.114$$

Where:

$\frac{\text{NH}_2}{100 \text{ \AA}^2}$ = number of amino groups per square nanometer

W = weight of Nomex yarn in grams

\AA^2 = area of Nomex yarn in square angstroms

O.D = optical density

Surface Analysis by Scanning Electron Microscopy

The surface topology of both irradiated and nonirradiated undyed Nomex filaments was visually analyzed by high resolution scanning electron microscopy (HR-SEM) with a Philips 420T Scanning Transmission Electron Microscope (STEM). Specimens were coated with 100% gold by means of a high resolution sputter coater to avoid the adverse effect of charging by the electron beam. Any roughening of the filament surface, as a result of etching during irradiation, was visually evaluated through comparison of the photomicrographs of irradiated and nonirradiated yarns. Photomicrographs were obtained at both low (1,600 X) and high (25,000 X) magnifications.

Measurement of Degree of Wettability

Wettability of both irradiated and nonirradiated Nomex filament yarn specimens was evaluated by a procedure developed by Bhat and Nadiger (1978) and Jung, Ward, and Benerito (1977). The wettability of a yarn was measured by the relative weight of water absorbed per gram of the yarn after immersion in de-ionized water for specified time periods.

All specimens were kept inside a desiccator and checked for their equilibrium dry weight before immersion. After immersing in water for 15, 30 and 60 seconds separately, specimens were removed from water and placed on a glass frame to drain for one minute. Then the specimens were reweighed to determine the amount of water absorbed by using the following equation:

$$D = C/A$$

where:

D = weight of water per gram of yarn specimen

C = B - A , weight of the water absorbed by the specimen, in grams

A = equilibrium dry weight of the yarn specimen, in grams

B = weight of the same specimen after draining for 1 minute, in grams

The relative weight of water absorbed for both nonirradiated and irradiated (60s, 120s, 180s) Nomex yarn specimens at each immersion time (15s, 30s, 60s) was taken as the average of 15 measurements.

Degree of wettability can also be evaluated by contact angle measurement. The contact angle formed by a liquid on a solid surface provides information about wettability of the solid surface. Therefore, contact angle measurements are often used to assess hydrophilic surface modification of hydrophobic polymers. The contact angle measurement procedure requires the fiber to touch the liquid surface at a perpendicular position. Since Nomex filament yarn has slight twist in it, a rigid straight fiber was difficult to obtain. Slightly twisted filaments could not be easily mounted for measurement of contact angle

because they float and do not penetrate the liquid phase.

Measurement of Dyeability

The dyeability of plasma irradiated and nonirradiated specimens with acid dyes was evaluated by measuring dyebath exhaustion, color strength, CIE L, a, b color coordinates, and instrumental color difference. Measurement of the dyebath exhaustion percent requires the absorbance peak wavelength and the absorbance versus concentration curve. A Spectronic 2000 uv-vis (Bausch and Lomb) spectrophotometer was used for obtaining the peak wavelength corresponding to maximum absorption of dye. For measurement of dyebath exhaustion, the absorbance peak wavelength was evaluated by taking 1 ml of the 1% dyebath solution and diluting it with 10 ml of de-ionized water. The colored dyebath specimen was scanned from 400 nm to 700 nm, with de-ionized water in the reference cell. The absorbance peak wavelengths for Acid Green 25, Acid Blue 45, and Acid Blue 80 were obtained at 640 nm, 596 nm, and 625 nm respectively.

The next step was to make the absorbance versus concentration curves by taking various known concentration solutions of the dyes mixed with de-ionized water and making spectrophotometric measurements. First, 10 ml of dyebath solution (1%) were taken in a 250-ml volumetric flask and diluted to 250 ml by adding de-ionized water to make the stock solution of dyes with a concentration of 0.4 mg/ml. The concentrations of dye used to make a curve were: 0.02 mg/ml (5 ml of stock solution in 100 ml of de-ionized water); 0.04 mg/ml (10 ml of stock solution in 100 ml of de-ionized water); 0.08 mg/ml (20 ml of stock solution in 100 ml

of de-ionized water); 0.10 mg/ml (25 ml of stock solution in 100 ml of de-ionized water); 0.12 mg/ml (30 ml of stock solution in 100 ml of de-ionized water); and 0.14 mg/ml (35 ml of stock solution in 100 ml of de-ionized water). The absorbance for each of these concentrations was measured at peak wavelength and then plotted with fitted regression curves shown in Figures 5 through 7.

Measurement of Dyebath Exhaustion

Dyebath exhaustion was measured by taking a 1-ml aliquot of dye solution at the end of the dye cycle, then diluting with 4 ml of de-ionized water and placing in the spectrometer. At the peak wavelength of respective individual dyes, maximum absorbance was read and the corresponding concentration was obtained directly from the regression equation generated from the known concentration vs absorbance data. The concentration was multiplied by 5 to give the correct concentration since the dye solution had been diluted. Percent exhaustion was obtained using the formula: $100 \times (\text{original concentration} - \text{final concentration}) / \text{original concentration}$. The dyebath exhaustion percent value of both nonirradiated and irradiated (60s, 120s, 180s) Nomex yarn specimens was taken as the average of six measurements.

Measurement of Color Strength

Color strength (K/S) values have been most frequently used for textiles to define the relationship between the reflectance of a dyed material and the concentration of dyes present in the substrate. The higher the K/S value the greater the color strength of the dyed material. The color strength of the dyed filament yarns was evaluated

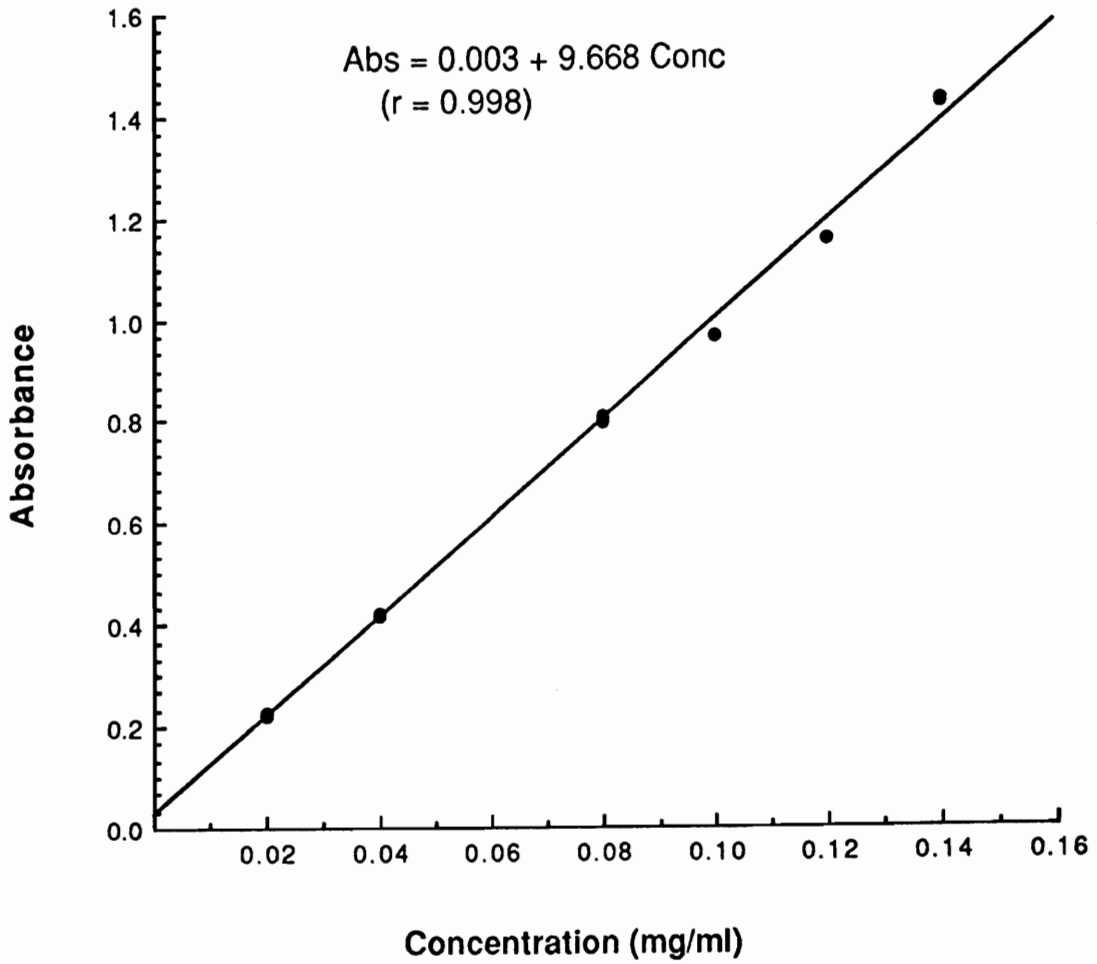


Figure 5. Absorbance vs Concentration Curve of C.I. Acid Green 25 at 640 nm.

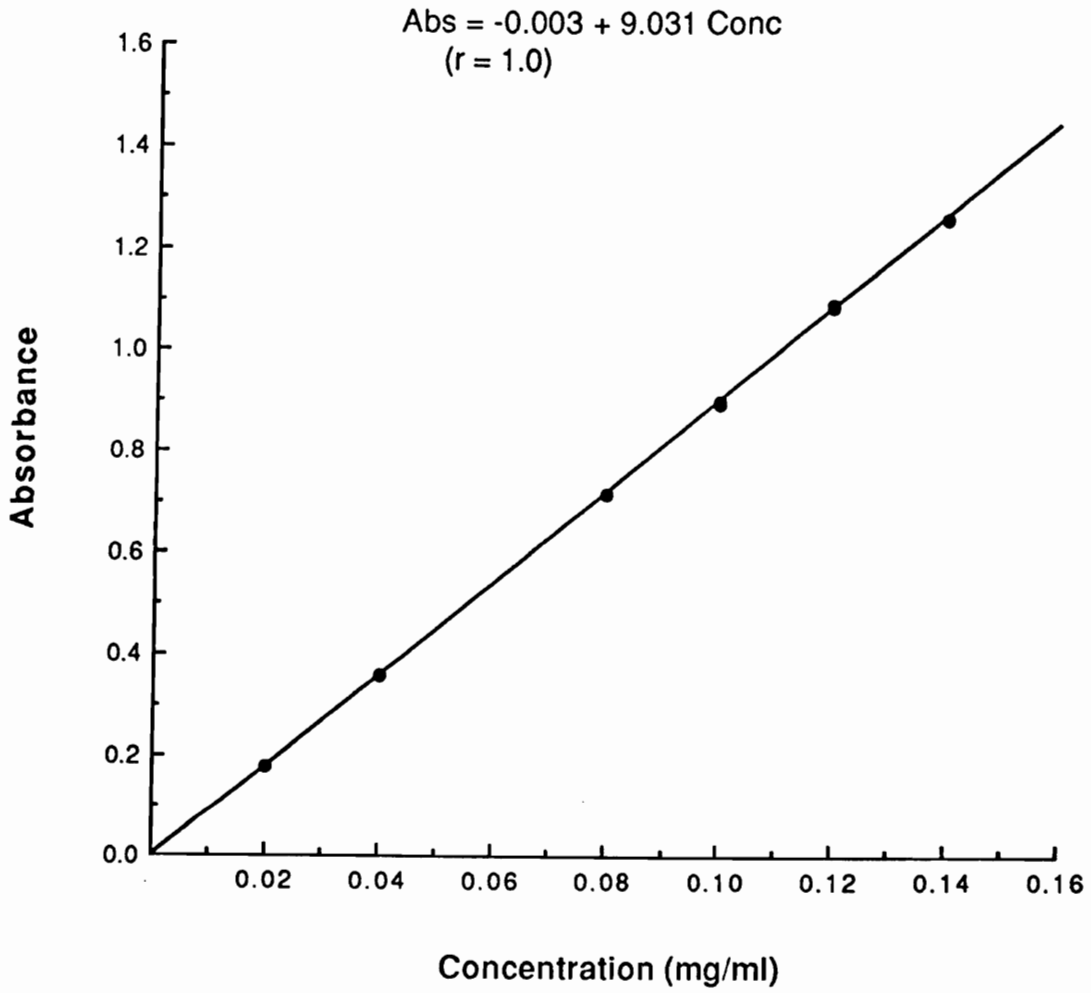


Figure 6. Absorbance vs Concentration Curve of C.I. Acid Blue 45 at 595 nm.

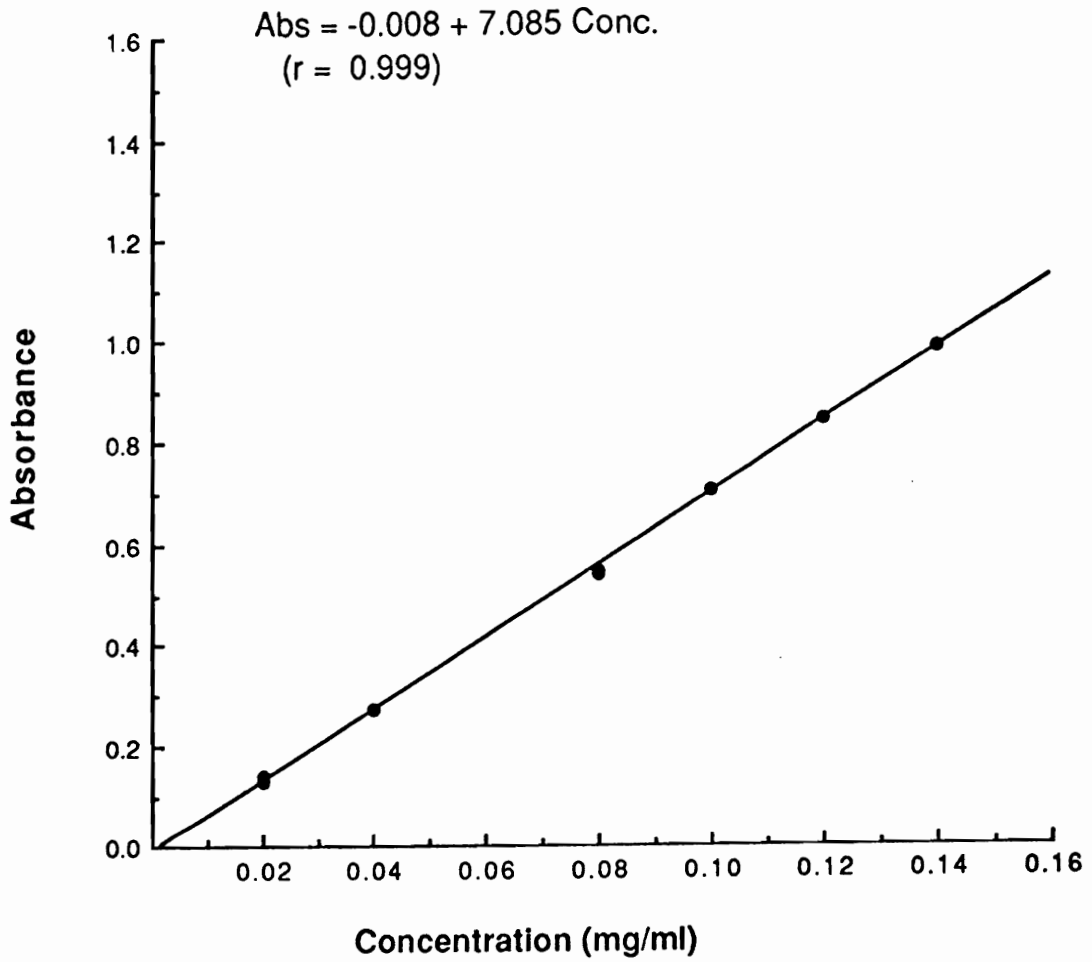


Figure 7. Absorbance vs Concentration Curve of C.I. Acid Blue 80 at 625 nm.

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by using the Kubelka-Munk equation: K/S (color strength) = $(1-R^2)/2R$

where:

R = fraction of light reflected

K = absorption coefficient

S = scattering coefficient

K/S values were measured at the wavelength of maximum absorbance for each dyed specimen by using the Hunter LabScan spectrophotometer. The Nomex filament yarn specimens were cut into appropriate sizes and wound around the 1 square inch cardboard replicas for taking the measurements. The reflectance (R) value of each specimen was taken as the average of three measurements obtained by switching the sides and position of the cardboard specimen holder.

The color strength (K/S) measurement was preferred over the dye concentration measurement on the fibers for the following reasons. There is no known solvent which could completely solubilize the Nomex fiber. Dimethylacetamide (DMAC) is used at a very high temperature to dissolve Nomex fiber to some extent. Since acid dyes are not capable of withstanding high temperatures, DMAC solubilizing methods can not be utilized in this study. Therefore K/S measurement provides a suitable alternative for measuring the color strength of the fibers from the reflectance values of dyed specimens at the wavelength of maximum absorbance.

Measurement of CIE L, a, b Color Coordinates and Instrumental

Measurement of Color Difference

The Hunter LabScan spectrophotometer was used to measure the CIE L, a, b color coordinates and color difference (ΔE) between the irradiated and nonirradiated dyed specimens. Total color difference, $\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$ was calculated from the tristimulus values (X, Y, Z) which were transformed into the uniform color system L, a, b. The L scale runs from 0 (black) to 100 (white); the higher the L value reading, the lighter the shade. The a and b readings indicate the dominant hue and degree of saturation or chroma of the shade. The a-scale measures the red (+) to green (-) component and the b scale measures the yellow (+) to blue (-) component.

Yarn Tensile Testing

All plasma irradiated and nonirradiated specimens used for tensile testing were conditioned at least 24 hours in standard atmospheric conditions of $70^\circ \pm 2^\circ$ F and relative humidity of $65 \pm 2\%$.

Yarn tensile properties of both irradiated and nonirradiated yarns were evaluated by measuring their breaking tenacity and elongation at break according to the following equations suggested in ASTM D.2256 Standard Test Method (American Society for Testing and Materials, 1990).

Breaking Tenacity: $B = F/T$

where:

B = breaking tenacity, in gf per denier

F = breaking force, in gf

T = linear density, in denier

Breaking Elongation Percent: $E_p = (E \times R \times 100) / (C \times L_g)$

where:

E_p = elongation percent

E = yarn breaking elongation in cm (final length - initial length)

R = testing speed rate, in inches/minute

C = recording chart speed, in inches/minute

L_g = nominal gage length, in inches

Toughness was measured indirectly by the area under the stress-strain curve. The area bounded by the stress-strain curve was cut from the graph and weighed on an analytical balance. The weight of a square inch of the graph paper was measured on the same balance. The area under the stress-strain curve was calculated by the following formula:

$$C = A/B$$

where:

C = area under stress strain curve, in square inches

A = weight of the area under stress-strain curve, in grams

B = weight of 1 square inch of graph paper, in grams/square inch

For evaluating tensile strength properties, an Instron Tensile Tester (Table Model 1130) fitted with special clamps for holding an individual yarn was used. A load cell of 5,000 g and load capacity setting of 2,000 g, was used along with a crosshead speed of 12 in/min, chart speed of 12 in/min, and gage length of 10 in. Breaking tenacity, breaking elongation, and toughness values for both nonirradiated and

irradiated (60s, 120s, 180s) Nomex yarn specimens were taken as the average of 25 test measurements. Before doing the actual testing, the machine was calibrated according to the manufacturer's specifications and several trial specimens were evaluated to check the consistency of the test results.

Data Analysis and Hypothesis Testing

The methods of statistically analyzing the test data included analysis of variance (ANOVA) between the means of nonirradiated and irradiated specimens, orthogonal polynomial contrasts only determined between the means for different irradiation times (60 s, 120 s, 180 s) and immersion times (15 s, 30 s, 60 s) and post hoc Newman-Keuls tests of differences between the means of nonirradiated and 60-s irradiated specimens as well as the multiple comparisons between the dye types. Orthogonal polynomial contrasts between irradiation times were used because equally spaced treatments were designed to investigate linear responses. Also, interpolations are often applied to intermediate treatment times. Newman-Keuls tests of difference between the means of nonirradiated and the 60-s were used because 60-s irradiation treatment has a physical reason for not being expected to fall between 0 and 120-s treatments in response. Characterization of surface chemical composition by XPS and surface topology by SEM were not analyzed statistically. All statistical analyses on the research data were determined at 0.05 level of significance.

Hypothesis Testing

Hypothesis 1. Nomex filament yarns (Type 430) after irradiation with ammonia plasma will have an altered surface chemical composition as compared to nonirradiated specimens.

Testing of Hypothesis 1. The alteration in surface chemical composition was expected to include an increase in the primary amino group concentration and possibly in the oxygen content at the yarn surface. The following analytical techniques were used to evaluate the surface chemical composition of Nomex filament yarn :

1. x-ray photoelectron spectroscopy for examining the elemental atomic composition at the surface before and after the irradiation.
2. plasma amination kinetics, measured by dyeing Nomex yarn with an anionic dye (Ponceau 3R) and calculating primary amine concentrations at the yarn surface based on the specimen optical density, Ponceau 3R calibration factor, and the filament yarn surface area.

Hypothesis 2. Nomex filaments (Type 430) will have a rougher surface after irradiation with the ammonia gas plasma.

Testing of Hypotheses 2. The surface morphology of both irradiated and nonirradiated undyed specimens was investigated by means of scanning electron microscopy. The roughening at the Nomex yarn surface was evaluated with respect to irradiation exposure at 1,600 X and 25,000 X magnification. The degree of roughening at the yarn surface was compared visually.

Hypothesis 3. Ammonia plasma irradiated Nomex filament yarns (Type 430) will have a higher degree of wettability than will the

nonirradiated specimens.

Testing of Hypotheses 3. Wettability of the filament yarns was measured in terms of grams of water absorbed per gram of yarn. Two-way analysis of variance was used to evaluate the difference in means of wettability between the irradiated and nonirradiated Nomex specimens with respect to irradiation times and the immersion periods. Orthogonal polynomial contrasts were made between the irradiation times to determine the trend in wettability with increased irradiation time. Post hoc Newman-Keuls multiple comparison tests were performed to identify the differences between the individual means.

Hypothesis 4. Nomex filament yarns (Type 430) after irradiation with ammonia gas plasma will have greater dyeability with the acid dyes C.I. Acid Green 25, C.I. Acid Blue 45, and C.I. Acid Blue 80 than will the nonirradiated specimens.

Testing of Hypothesis 4. The dyeability of both irradiated and nonirradiated specimens was evaluated by measuring the percent of dyebath exhaustion, color strength (K/S), CIE L, a, b color coordinates, and instrumental color difference (ΔE). The population consisted of nonirradiated and irradiated Nomex filament yarns. Two-way analysis of variance (ANOVA) was used to evaluate the difference on dyebath exhaustion percent as well as on the color strength between irradiated and nonirradiated dyed Nomex filament yarns. Orthogonal polynomial contrasts were calculated between the means of irradiation times for both the dyebath exhaustion percent and the color yield. Newman-Keuls pairwise comparison test was conducted between the means of

nonirradiated specimens and 60-s irradiated specimens for the dyebath exhaustion percent and the color yield. Comparisons of CIE L, a, b color coordinates and color differences between the nonirradiated and irradiated specimens were made to evaluate the degree of color saturation.

Hypotheses 5. There will be no significant differences in dyeability of ammonia plasma treated Nomex filament yarn (Type 430) with respect to plasma irradiation time (60-180 seconds).

Testing of Hypothesis 5. Two-way of analysis of variance was used to evaluate the difference in dyebath exhaustion percent and color strength between irradiated Nomex filament yarns with respect to the response variable irradiation time. Orthogonal polynomial contrasts were calculated between the dyebath exhaustion percents and between color strength with respect to the irradiation time (60 s - 180 s). Newman-Keuls post hoc multiple comparisons were done where ANOVA indicated a significant difference. CIE L, a, b color coordinates between the different irradiation time groups were compared to evaluate the relative saturation of color.

Hypothesis 6. There will be no significant differences among three selected acid dyes in terms of the dyebath exhaustion and the color strength of dyed ammonia plasma irradiated Nomex filament yarn.

Testing of Hypothesis 6. Two-way analysis of variance was used to indicate the difference in dyebath exhaustion and color strength between the dyed Nomex specimens with respect to the response variable dye types. Post hoc Newman-Keuls multiple comparisons between the

individual dye types were performed where ANOVA indicated a significant difference between the dyes.

Hypothesis 7. Ammonia plasma irradiated Nomex filament yarns (Type 430) will have breaking tenacity, elongation at break, and toughness similar to the nonirradiated Nomex yarns.

Testing of Hypothesis 7. Breaking tenacity, breaking elongation, and area under the stress-strain curve data for both nonirradiated and irradiated specimens were analyzed statistically by using one-way ANOVA and Newman-Keuls multiple comparison tests. Orthogonal polynomial contrasts between the irradiation times were done to check the effect of increase in irradiation dose on these tensile properties. The combination of the two statistical analysis techniques assisted in categorizing the means and examining the statistical differences among the means of individual groups.

Chapter V

Results and Discussion

The results of this research are presented and discussed in four sections. The first section is on the preliminary experiments which determined the type of plasma irradiation treatment to be used in the research. The second section entails the effect of ammonia plasma irradiation on surface chemical composition, surface amination kinetics, and surface texture of the Nomex filament yarns. The third section covers the effect of ammonia plasma treatment on wettability and dyeability of Nomex filament yarns. The final section covers the effect of ammonia plasma irradiation on the selected tensile properties (breaking tenacity, breaking elongation, and toughness) of the yarn.

Preliminary Results on Effects of Nitrogen, Oxygen, and Ammonia Plasma on Dyeability of Nomex Yarn with C.I. Acid Red 18

Various types of artificial plasma could be generated depending on the types of gas used. Oxygen, nitrogen, air, argon and ammonia induced plasma are used primarily to modify organic polymer surfaces. Since very little is known about the effect of plasma irradiation on the dyeability of aramid fibers, the effects of oxygen, nitrogen, and ammonia gas plasma irradiation were examined in a preliminary investigation on the dyeability of Nomex filament yarn with C.I Acid Red 18. C.I Acid Red 18 has a monoazo chromophore and sulfonate groups as the binding sites. Acid Red 18 is widely used for dyeing of polyamide fibers for its good affinity and exhaustion with the fiber. Nomex filament yarns were irradiated by oxygen, nitrogen and ammonia gas

plasma, each for three time periods of 60 s, 120 s, and 180 s. Dyeability of plasma irradiated and nonirradiated specimens was evaluated in terms of color strength (K/S), CIE L, a, b color coordinates, and instrumental color difference (ΔE). The results of the preliminary experiments are presented in Table 2.

The results indicated that both nitrogen and oxygen plasma irradiation had very little influence on dyeability of Nomex filament yarn with Acid Red 18. The color strength values (K/S) of the nitrogen and oxygen irradiated specimens were close to the K/S values of the nonirradiated specimens. The color coordinates L (lightness-darkness) and a red-green component of dyed specimens did not change much, which was evidenced by a low color difference (ΔE) for the oxygen and nitrogen irradiated and nonirradiated specimens. However, ammonia plasma irradiated specimens showed much greater color differences and color strengths even for a short treatment period of 60 s. The ammonia plasma treated specimens were dyed darker and much redder as indicated by low "L", and a high "a" value respectively. The color differences (ΔE) were substantially higher for the ammonia plasma irradiated specimens relative to the color differences found for the oxygen and nitrogen plasma irradiated specimens.

The dyeability of ammonia plasma irradiated Nomex filament yarn with Acid Red 18 did not change very much with increased irradiation time. The larger color difference was between the nonirradiated and 60-s plasma irradiated specimens. Further increase in irradiation time lowered "L" and increased the "a" value, but to a very small extent.

Table 2

Summary of Preliminary Results of
Dyeing with 10% owf C.I. Acid Red 18*

	<u>L</u>	<u>a</u>	<u>b</u>	<u>ΔE</u>	<u>K/S</u>
Nonirradiated	79.12	+5.15	+3.79	-	0.10
Oxygen, 60 s	77.53	+5.31	+3.73	1.60	0.13
Oxygen, 120 s	78.10	+5.29	+3.71	1.03	0.14
Oxygen, 180 s	78.50	+4.79	+4.86	1.29	0.12
Nitrogen, 60 s	78.90	+5.57	+3.70	0.48	0.14
Nitrogen, 120 s	77.65	+5.78	+3.83	1.60	0.15
Nitrogen, 180 s	76.30	+5.98	+3.92	2.94	0.18
Ammonia, 60 s	67.94	+13.24	+6.68	14.10	0.43
Ammonia, 120 s	68.97	+15.36	+7.15	14.78	0.50
Ammonia, 180 s	65.87	+15.82	+6.49	17.22	0.52

* Each value is the average of three measurements.

L = Lightness-darkness component, 0 = black, 100 = white

a = Red (+) to green (-) component

b = Yellow (+) to blue (-) component

ΔE = Total color difference from standard; Standard = nonirradiated

K/S = Color strength

Preliminary results indicated that only ammonia gas plasma was successful in improving the dyeability of Nomex filament yarn with the acid dye. Ammonia plasma is believed to have incorporated reactive functional groups on the Nomex filament surface to bind the acid dye. The nitrogen and oxygen plasmas were not able to enhance the dyeability of Nomex filament yarn with respect to irradiation time. Therefore the investigation of dyeability of only ammonia plasma irradiated Nomex filament yarn with acid dyes was pursued.

Effect of Ammonia Plasma Irradiation on Surface Chemical Composition

The nature of changes in elemental surface atomic composition of Nomex filament yarn was investigated by x-ray photoelectron spectroscopy (XPS). Nomex filament yarn specimens were analyzed by XPS immediately upon removal from the plasma reactor.

After ammonia plasma irradiation, XPS analysis indicated a substantially higher oxygen and nitrogen content at the Nomex filament yarn surface. The elemental surface atomic composition of the Nomex filament yarn surface before and after ammonia plasma irradiation is presented in Table 3. The increased surface nitrogen content of irradiated yarn indicated that amination at the Nomex yarn surface may have occurred to some degree. There was a linear trend of increasing nitrogen concentration with respect to the irradiation time, while oxygen content decreased to some extent after 120 s irradiation time. However, the oxygen content of all the irradiated specimens remained above the nonirradiated specimens. The surface carbon composition of the irradiated Nomex filament yarn was somewhat lower than for the

Table 3

XPS Results: Elemental Surface Atomic Composition and Ratio of Oxygen and Nitrogen Atoms to Carbon Atoms

	<u>% Composition</u>			<u>Ratio*</u>
	<u>% Carbon</u>	<u>% Oxygen</u>	<u>% Nitrogen</u>	$\frac{O + N}{C}$
Nonirradiated	80.00	13.00	6.90	0.4640
Irradiated, 60 s	78.60	14.26	7.13	0.6378
Irradiated, 120 s	78.53	14.26	7.21	0.6427
Irradiated, 180 s	77.60	13.90	8.42	0.5387

* Ratio of the number of oxygen and nitrogen atoms to carbon atoms, as measured by O_{1s} , N_{1s} , and C_{1s} peak areas.

nonirradiated, and declined a bit with increased irradiation time. The N_{1s} spectra of ammonia plasma irradiated and nonirradiated Nomex filament yarns exhibited some differences (Figure 8). The N_{1s} peak of irradiated Nomex filament yarn was broader and was shifted to a position of slightly lower binding energy (.1-.2 ev). XPS is a sensitive technique for surface analysis, and for shifting of binding energy within .1-.2 ev, it can detect differences in surface elemental composition. A decrease in electron density (or a more electropositive character) of the atoms results in a higher binding energy (B.E). Therefore, the shifting of the N_{1s} peak to a lower B.E indicated an increase in electron density of nitrogen atoms. The higher atomic oxygen concentration after plasma irradiation may have been due to the partial oxidation at the surface of Nomex filament yarn as indicated by shifting of the O_{1s} peak to lower B.E (Figure 9). A plasma irradiation effect that has been established is the formation of free radicals at the yarn surface through abstraction of hydrogen atoms from the fiber polymer chain. Atmospheric oxygen atoms readily combine with free radicals upon exposure to air, so some oxidation at the Nomex filament yarn surface may have occurred.

The ratio of numbers of oxygen and nitrogen atoms to carbon atoms was 16.1 to 38.5% higher after plasma irradiation (Table 3). These data indicate some oxidation of carbon (C_{1s} peak shifted to higher B.E, Figure 10), some reduction of nitrogen and oxygen atoms, and simultaneously the possible addition of oxygen and nitrogen atoms at the

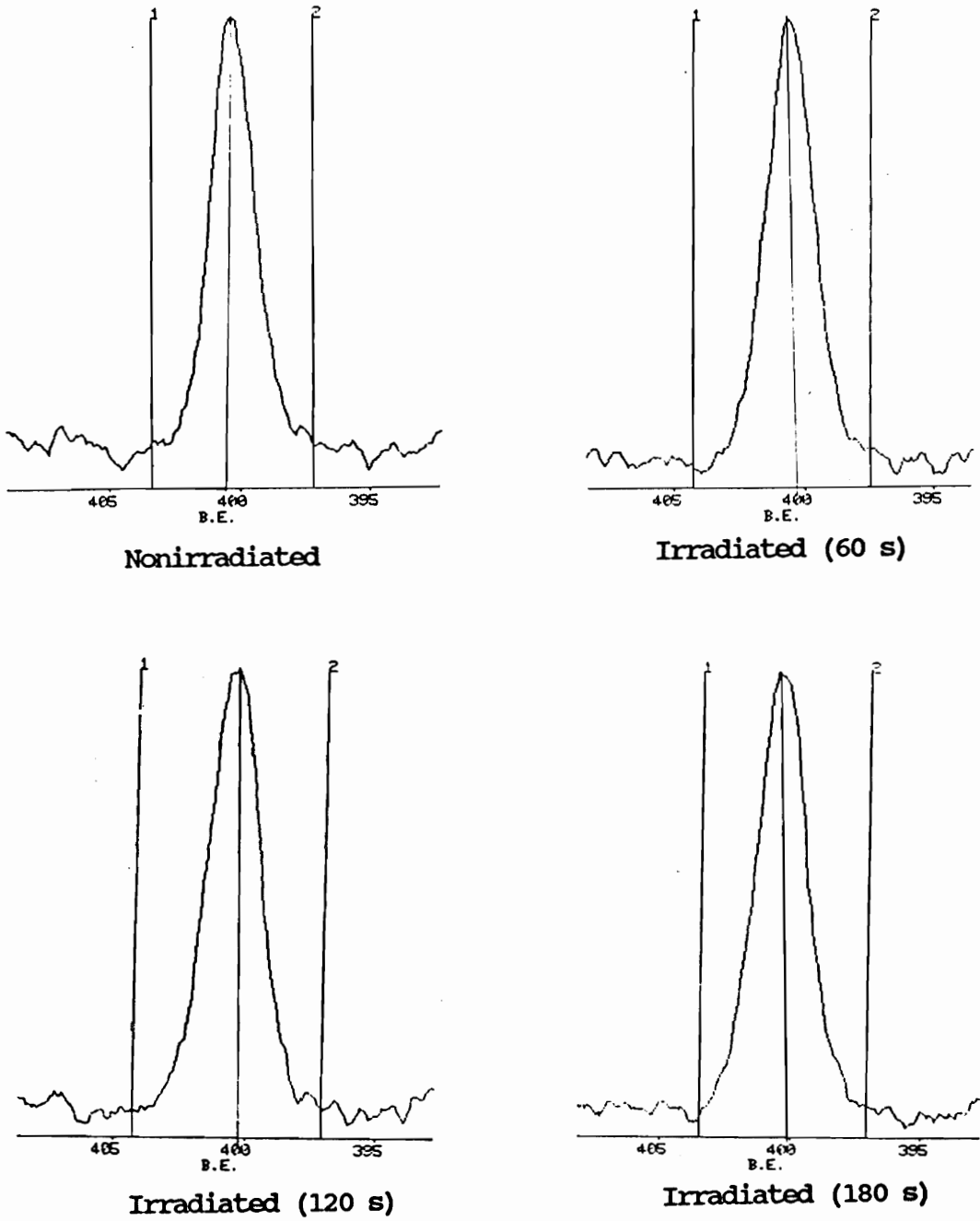


Figure 8. N_{1s} Photopeaks of nonirradiated and irradiated (60 s, 120 s, and 180s) Nomex filament yarns.

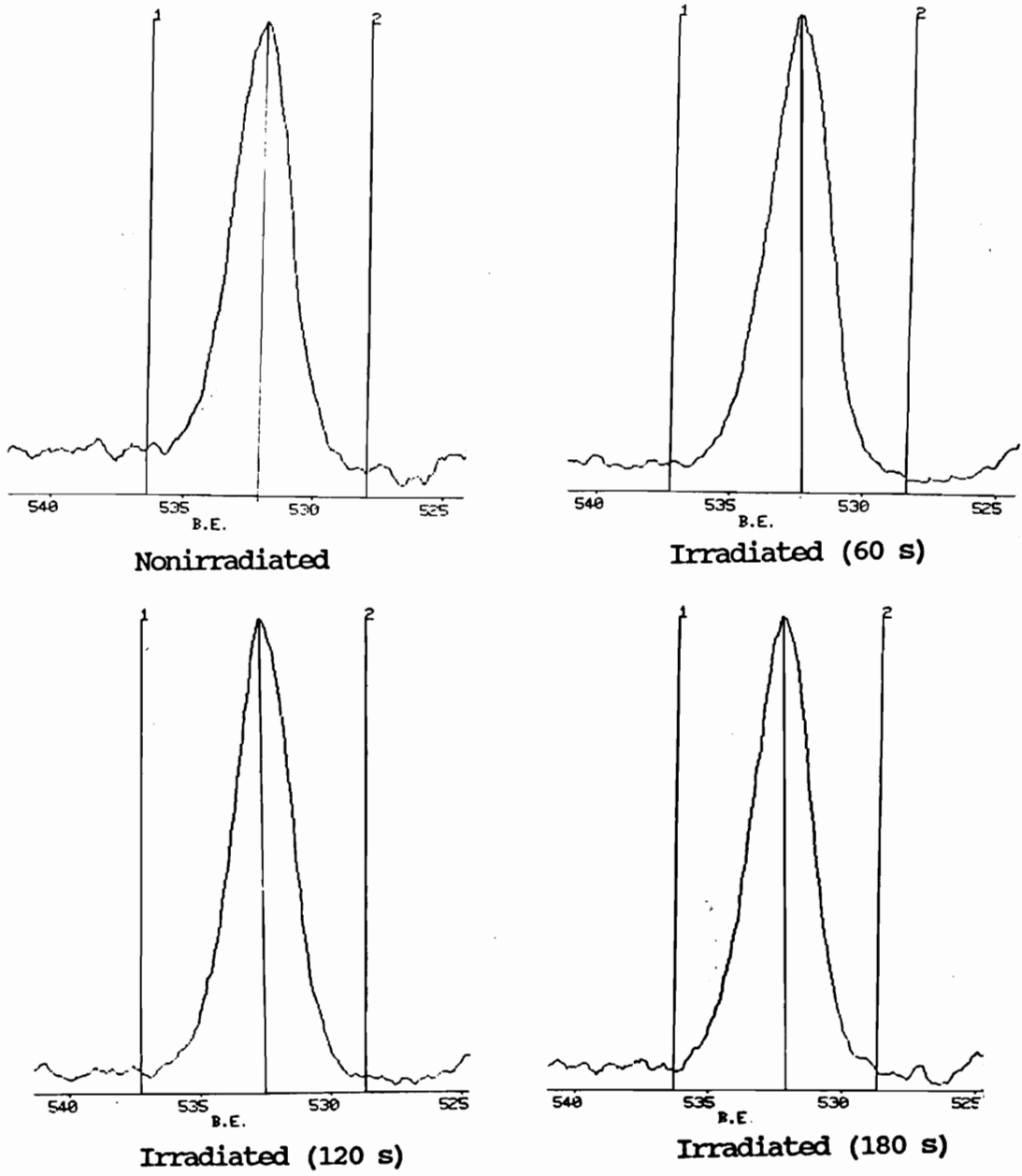


Figure 9. O_{1s} photopeaks of nonirradiated and irradiated (60 s, 120 s, and 180 s) Nomex filament yarn.

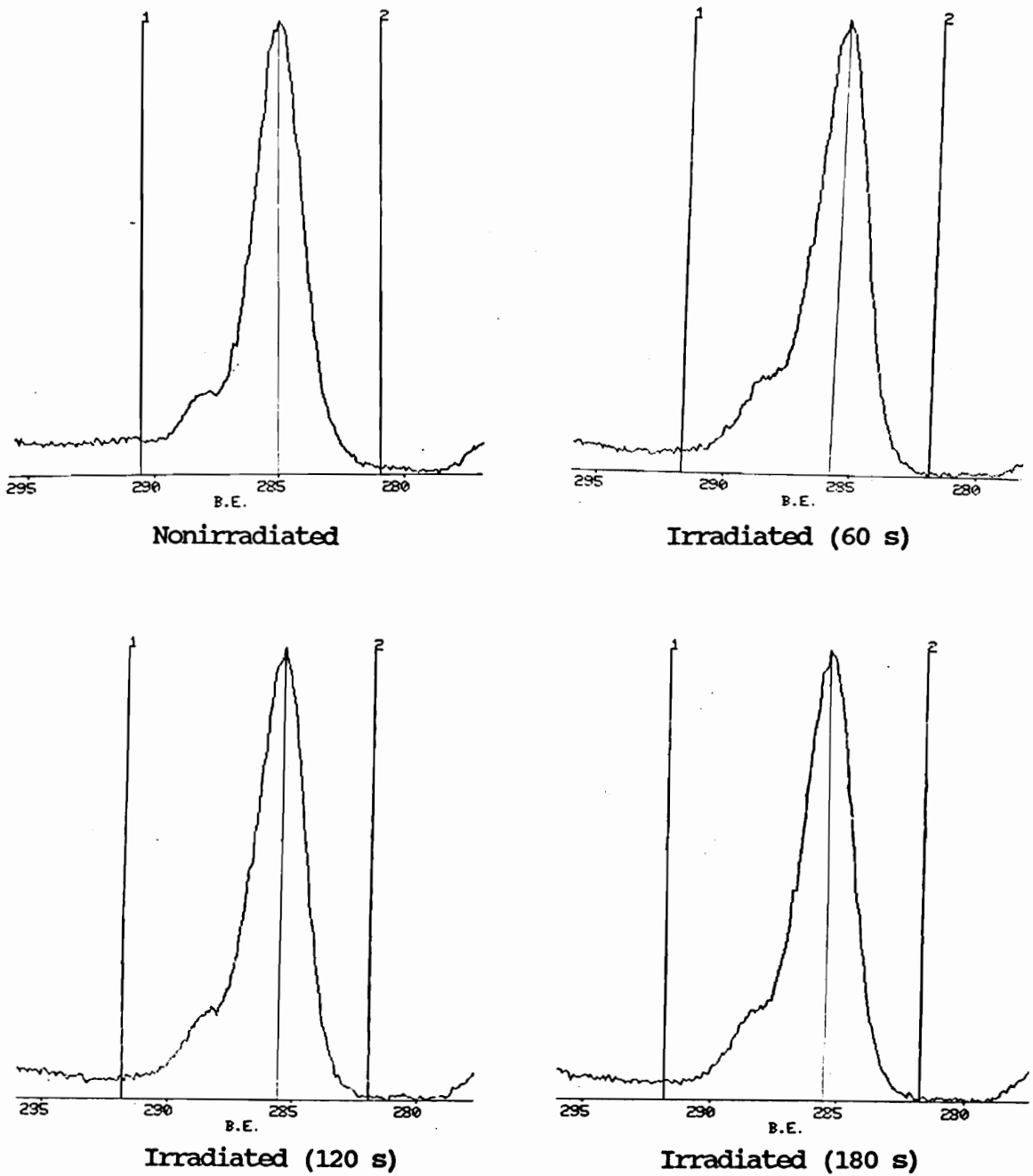


Figure 10. C_{1s} photopeaks of nonirradiated and irradiated (60 s, 120 s, and 180 s) Nomex filament yarn.

surface. The increased surface oxygen and nitrogen content may have also resulted in a greater number of reactive atoms on the Nomex yarn surface and in increased access to its polar compounds.

Plasma Amination Kinetics

XPS results indicated the higher concentration of nitrogen atoms at the Nomex fiber surface after ammonia plasma irradiation. Higher nitrogen content was hypothesized due to possible addition of amino (-NH_2) groups at the fiber surface. Therefore, the surface amine concentrations of both nonirradiated and irradiated Nomex filament specimens were determined by amination kinetics by dyeing Nomex filament yarn with Ponceau 3R. It has been established that sulfonic acid groups of Ponceau 3R bind with the protonated amino groups on the fiber surface through ion-exchange reactions (Bernashid & Tesoro, 1990).

Amination kinetics studies with Ponceau Red 3R are more sensitive than XPS analysis, as indicated by the significant difference in surface amine concentration between the irradiated and nonirradiated Nomex specimens. The results do support the XPS analysis. Plasma amination kinetics data indicate that ammonia plasma irradiated, as compared to nonirradiated, Nomex filament yarns bind the Ponceau 3R dye in substantially higher amounts, even for the treatment time as short as 60 seconds (Table 4). The amine concentration ($\text{NH}_2/100\text{A}^2$), number of amino groups per square nanometer, nm, of Nomex yarn) increased steadily with longer irradiation times. The separate one-way ANOVAs on amino group concentration between untreated and irradiated Nomex filament

Table 4

Results of Plasma Amination Kinetics*

	<u>Amine Concentration (NH₂/100 A²)</u>
Nonirradiated	0.0432
Irradiated, 60 s	0.1013
Irradiated, 120 s	0.1264
Irradiated, 180 s	0.1475
Standard Error	7.86 x 10 ⁻⁵

* Each value is the average of six measurements.

yarns (60 s, 120 s, 180 s) indicated a significant difference (Table 5). The orthogonal polynomial contrasts among the irradiation times indicated that both linear and quadratic curves provide the best fit (Table 5). The linear contrast identified the steady increase in amine concentration with respect to irradiation time, and the quadratic contrast suggested the stabilization of amine concentration to some extent over the irradiation time intervals. The post hoc Newman-Keuls test showed that the individual means of the nonirradiated and the 60-s irradiated yarns were statistically different from each other (Table 5).

The increase in amino group concentration shown by plasma amination kinetics further substantiates the results obtained from the XPS analysis which indicated an increase in nitrogen atom concentration with respect to irradiation time. As shown in Table 4, the difference in concentration of amino groups was large between nonirradiated and 60 seconds of irradiation time. The increase in amine group concentration with short plasma irradiation time is typical of many plasma reactions. It has been established that plasma irradiation effects on surface chemical composition usually stabilize between 60-90 seconds.

Both the XPS and plasma amination kinetics data support hypothesis 1. After the ammonia plasma irradiation the surface chemical composition was substantially altered. Both nitrogen and oxygen content at the filament surface was higher. The increase in nitrogen content may be interpreted as the possible addition of primary amino groups at the yarn surface. The increase in oxygen content is perhaps due to partial oxidation during and after the plasma irradiation.

Table 5

Statistical Analysis on Amine Group Concentration

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time	3	0.0122*
Linear	1	6.422×10^{-3} *
Quadratic	1	1.521×10^{-5} *
Residual Error	20	3.708×10^{-8}

Newman-Keuls Test

Nonirradiated vs 60 s Significant

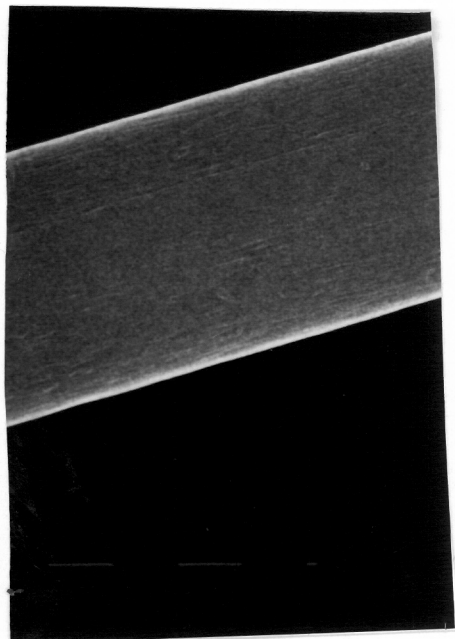
* Significant (p < 0.05)

Effect of Ammonia Plasma Irradiation on Surface Texture

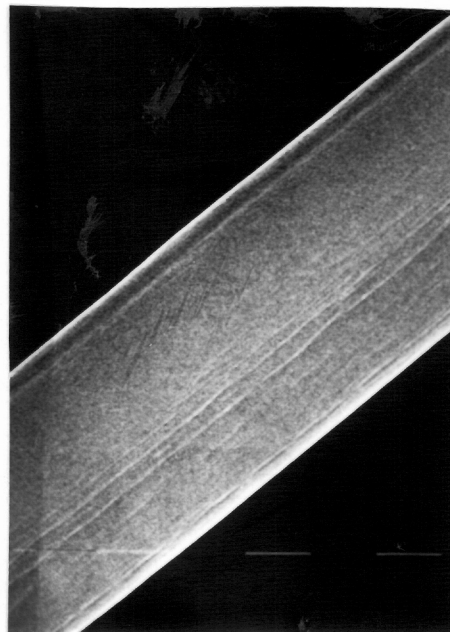
The surface texture of both irradiated and nonirradiated Nomex filament yarns was analyzed visually by comparing the photomicrographs obtained from the high resolution scanning electron microscopy (SEM). Examination at both lower (1,600 X) and higher (25,000 X) magnification indicated that individual nonirradiated filaments were quite smooth in surface texture (Figures 11 and 12). Ammonia plasma irradiated filaments revealed roughness at the surface under both low and high magnification. The irradiated specimens show slight etching at low magnification (1,600 X), but highly developed cracks and severe surface pitting are visible under high magnification (25,000 X). The pitting of the filament surface increased with the time of irradiation, the most pitting occurring at 180 s ammonia plasma irradiation. The etching and cracks at the fiber surface indicated randomly oriented striations. Plasma-induced etching and the surface oxidation may have caused the roughening of the filament surface. Hypothesis 2 was supported, because ammonia plasma irradiated specimens exhibited rougher surface compared to the nonirradiated specimens.

Effect of Ammonia Plasma Irradiation on Wettability

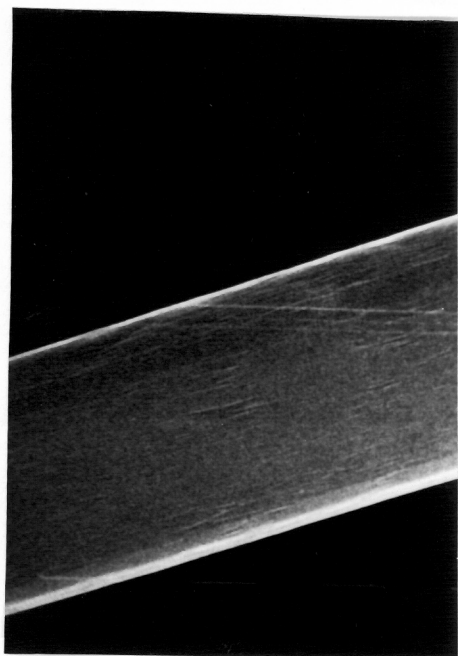
The wettability of both nonirradiated and irradiated Nomex filament yarns with de-ionized water was evaluated in terms of grams of water absorbed per gram of fiber for three immersion time periods (15 s, 30 s, 60 s). Ammonia plasma irradiation appears to enhance the wettability of Nomex filament yarn with de-ionized water (Table 6). The mean amount of water absorption was statistically analyzed by two-way



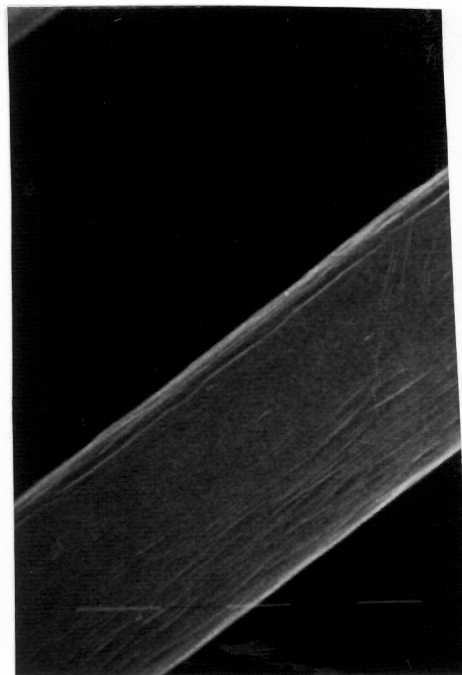
Nonirradiated



Irradiated (60 s)

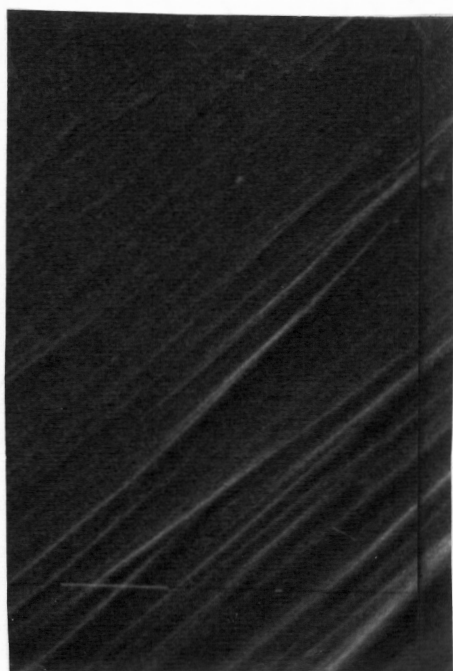


Irradiated (120 s)

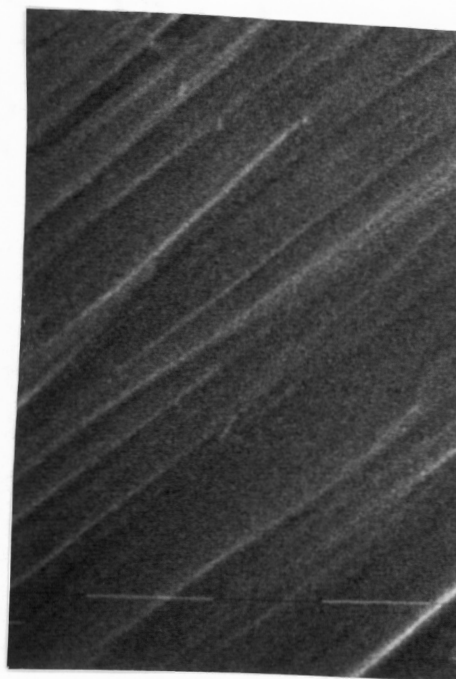


Irradiated (180 s)

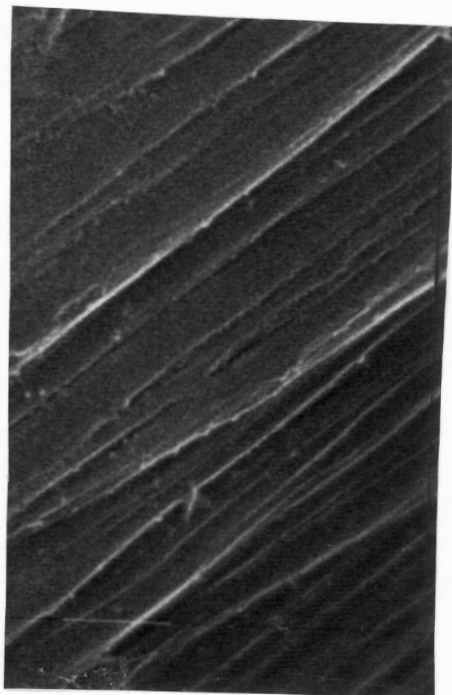
Figure 11. SEM photomicrographs of nonirradiated and irradiated (60 s, 120 s, and 180 s) Nomex filament yarn at 1,600 X.



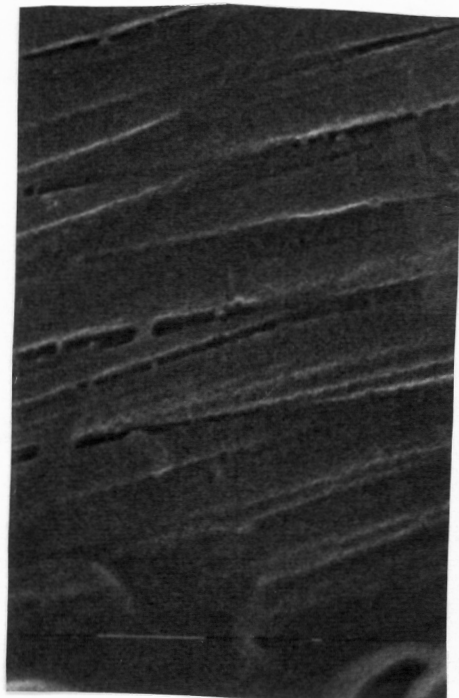
Nonirradiated



Irradiated (60 s)



Irradiated (120 s)



Irradiated (180 s)

Figure 12. SEM photomicrographs of nonirradiated and irradiated (60 s, 120 s, and 180 s) Nomex filament yarn at 25,000 X.

Table 6

Water Absorption Capacity of Nomex Filament Yarn*

Immersion Time (s)	Irradiation Time (s)				Avg
	0	60	120	180	
Relative Weight of Water Absorbed (g water/g yarn)					
15	2.58	2.94	3.58	3.57	3.17
30	2.73	3.66	3.83	4.07	3.57
60	2.78	3.65	4.17	4.13	3.68
Avg	2.70	3.42	3.86	3.92	3.48

Standard Error 0.068

* Each value is the average of 15 measurements.

ANOVA with independent variables of irradiation time and immersion time (Table 7).

The two-way analysis of variance indicated that both the irradiation time and immersion time had significant effects on the wettability of Nomex filament yarn with de-ionized water (Table 7). Nomex filament yarn was capable of absorbing more water with increased irradiation time and immersion period (Table 6). Both the linear and quadratic contrasts are significant for water absorption capacity of Nomex filament yarn with respect to irradiation time. The increase in water absorption between the irradiation times was not very great and stabilized to some extent as indicated by the significant quadratic contrast (Table 7). Post hoc Newman-Keuls analysis indicated that the amounts of water absorbed between the nonirradiated and 60-s irradiated yarns are statistically different (Table 7).

Newman-Keuls post hoc analysis also indicated the existence of a statistical difference between the means associated with the amount of water absorbed during the 15 s, 30 s, and 60 s immersion periods (Table 7). The amount of water absorbed during the 60-s immersion time was highest followed by the 30-s and 15-s immersion times (Table 6). The amount of water absorbed was greater until the 30 s immersion period and thereafter stabilized to a large extent. The results indicated that ammonia plasma treatment significantly enhanced the wettability of Nomex filament yarn with de-ionized water. The amount of water absorbed was 27 to 46% higher for irradiated yarns compared to the nonirradiated Nomex yarn specimens. Therefore hypothesis 3 was supported.

Table 7

Statistical Analysis on Relative Water Absorption

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time (RT)	3	14.4336*
Linear Contrast	1	38.3959*
Quadratic Contrast	1	4.8835*
Immersion Period (IP)	2	4.3866*
Linear Contrast	1	6.6892*
Quadratic Contrast	1	2.0838*
RT X IP	6	0.3497
Residual Error	168	0.0694

Newman-Keuls Test : Nonirradiated vs 60 s

Significant

* Significant ($p < 0.05$)

The improvement in wettability of irradiated specimens may be explained as follows. Unmodified Nomex fiber has a high degree of crystallinity and absence of polar groups on the fiber surface, making it a hydrophobic fiber. Based on the XPS results and plasma amination kinetics, ammonia plasma irradiation incorporated some reactive amine functional groups at the Nomex filament yarn surface. Atomic oxygen content was also increased, perhaps due to surface oxidation during and after plasma irradiation of Nomex filament yarns. Incorporation of electronegative atoms like nitrogen and oxygen at the fiber surface should contribute to increased polymer surface energy and result in higher wettability with water. Increase in surface nitrogen and oxygen atoms on the fiber induces more polarity, thereby increasing the water absorbing capacity of the Nomex filament yarns. Plasma irradiation was also responsible for etching at the fiber surface and the development of surface cavitations. Fiber roughening would enhance the adherence of water molecules to the fiber surface. The cracks possibly developed the porosity to diffuse the water molecules throughout the fiber phase, thus improving the water holding capacity of irradiated Nomex filament yarn.

Effect of Ammonia Plasma Irradiation on Dyeability

The effect of ammonia plasma treatment on the dyeability of Nomex filament yarn was determined by measuring the dyebath exhaustion percentage, color strength (K/S), CIE L, a, b color coordinates, and color difference (ΔE). For all three dyes, Acid Blue 45, Acid Blue 80, and Acid Green 25, the dyebath exhaustion was higher for the plasma irradiated Nomex filament yarn in comparison to nonirradiated specimens

(Table 8). For all three acid dyes, the ammonia plasma treated Nomex filament yarns showed higher color yield compared to nonirradiated specimens (Table 9). Ammonia plasma treated specimens were darker (lower "L" values) and showed a higher degree of color saturation ("-a" and "-b"). Hypothesis 4 was supported as the dyeability of plasma irradiated Nomex yarn was substantially higher than the nonirradiated yarn. The improved dyeability shown by ammonia plasma irradiated Nomex filament yarn may be explained as follows. As suggested by XPS analysis, plasma irradiated Nomex filament yarns had a higher surface composition of electronegative atoms such as oxygen and nitrogen. The presence of oxygen and nitrogen atoms on the Nomex fiber surface was apparently effective in inducing polarity which produced and enhanced the hydrophilic surface layer. The increase in the polarity of the fiber surface was evidenced by the improved wetting of irradiated specimens. The improvement in degree of polarity on the fiber surface may have been responsible for improved wetting by water, subsequently increasing the uptake of the aqueous dye solution by Nomex yarn.

According to the ammonia plasma decomposition process, $\cdot\text{NH}_2$ is the most likely species available for recombination with polymer surface radicals. The short exposure of Nomex filament yarns to activated species of ammonia may result in the loss of hydrogen atoms from the yarn surface. Subsequent reactions may lead to the formation of primary amino groups on the surface of the fiber. During ammonia plasma irradiation, the radical may be formed anywhere along the chain of the Nomex filament yarn, because the energy of the active species is

Table 8

Dyebath Exhaustion Percentages*

	<u>Acid Blue 45</u>	<u>Acid Blue 80</u>	<u>Acid Green 25</u>
Nonirradiated	17.3059	16.1242	16.4958
Irradiated, 60 s	24.1716	23.0306	23.6073
Irradiated, 120 s	24.6552	23.5903	24.2545
Irradiated, 180 s	24.2313	23.6881	22.5879

Standard Error	0.1451
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* Each value is the average of six measurements.

Table 9
Comparative Color Yield of Dyes*

	<u>L</u>	<u>a</u>	<u>b</u>	<u>ΔE</u>	<u>K/S</u>
Acid Green 25					
Nonirradiated	66.20	-6.74	-0.29	-	0.50
Irradiated (60 s)	63.36	-9.56	-1.10	4.08	0.70
Irradiated (120 s)	62.16	-10.06	-1.08	5.29	0.79
Irradiated (180 s)	55.56	-11.41	-1.07	12.08	0.92
Acid Blue 45					
Nonirradiated	80.34	-0.71	2.03	-	0.10
Irradiated (60 s)	71.39	-1.55	-0.47	9.30	0.26
Irradiated (120 s)	70.05	-1.63	-0.78	10.71	0.28
Irradiated (180 s)	69.15	-2.01	-1.86	11.92	0.32
Acid Blue 80					
Nonirradiated	79.30	-2.35	-0.66	-	0.13
Irradiated (60 s)	75.29	-4.51	-3.60	0.24	0.23
Irradiated (120 s)	75.30	-4.35	-3.56	7.60	0.26
Irradiated (180 s)	72.46	-4.52	-4.69	8.95	0.34

* Each value is the average of six measurements.

L = Lightness-darkness component: 0 = Black, 100 = White

a = Red (+) to green (-) component

b = Yellow (+) to blue (-) component

ΔE = Total color difference from standard; standard = nonirradiated

K/S = color strength

sufficient to generate indiscriminate reactions along the Nomex yarn surface.

The acidic pH of the dyeing condition was maintained (3.5-4.0), which protonated the surface amine functional groups ($-NH_2$) to $+NH_3$. In aqueous medium, the acid dye was ionized to colored anions. Since the dyes had a negative charge and the irradiated fibers carried positively charged amino groups, electrostatic attraction between the dye and the fiber was expected. The ion-exchange reaction between the dye anions and fiber cations probably resulted in the formation of ionic bonds, as indicated by significantly higher color intensity for the ammonia plasma irradiated Nomex filament yarns.

Two-way analysis of variance (Table 10) indicated significant differences between the mean percentages of the dyebath exhaustion for the nonirradiated and irradiated (60 s, 120 s, and 180 s) Nomex filament yarn specimens. The orthogonal polynomials show the insignificant linear and quadratic contrasts in dyebath exhaustion with respect to irradiation time. The post hoc Newman-Keuls showed a significant difference in dyebath exhaustion between the nonirradiated and the 60-s irradiated Nomex filament yarn. Hypothesis 5 is supported because the dyebath exhaustion did not differ significantly between the irradiation times (60 s, 120 s, and 180 s) as observed by polynomial contrasts. The change in dyebath exhaustion is significantly noticeable between the nonirradiated and irradiated yarns for the 60-s plasma irradiated specimens, but stabilized to a very large extent in the 120-s and 180-s

Table 10

Statistical Analysis on Dyebath Exhaustion Percent

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time (RT)	3	232.8828*
Linear Contrast	1	0.7723
Quadratic Contrast	1	3.0239
Dye Types (DT)	2	6.2204*
RT X DT	6	1.5083
Residual Error	60	1.5155

Newman-Keuls Test

Nonirradiated vs 60s (Irradiation Time)

Significant

Dye Types : Acid Blue 45* Acid Green 25 and Acid Blue 80 NS

* Exhaustion mean of Acid Blue 45 significantly different from Acid Blue 80 and Acid Green 25 ($p < 0.05$).

treated specimens. The stabilization in dyeability between irradiation times may be explained by the little alteration in the surface chemical composition of irradiated Nomex filament yarn after 60 s of plasma treatment as indicated by the XPS and plasma amination kinetics.

Two-way ANOVA (Table 10) indicated significant statistical differences between the dyes regarding their exhaustion percentages as well as significant interactions between the irradiation times and the dye types. The post hoc Newman-Keuls analysis indicated statistical equivalence between exhaustion means of Acid Blue 80 and Acid Green 25 (Table 10). Exhaustion for Acid Blue 45 was statistically higher than for both Acid Blue 80 and Acid Green 25. Higher exhaustion for C.I. Acid Blue 45 may be explained as follows. All three acid dyes used in the research for measuring the dyeability were based on anthraquinone and two sulfonic acid groups in the dye molecule. The dye structures differed in their molecular weight by virtue of a difference in side groups. Acid Blue 45 had the lowest molecular weight (474), followed by Acid Green 25 (621) and Acid Blue 80 (678). The lower the molecular weight of a dye, the higher is its capability to diffuse across the fiber phase resulting in higher exhaustion of the dye. Since Acid Blue 45 has the lowest molecular weight, greater migration of the dye molecules across the fiber phase was probably responsible for greater dyebath exhaustion. Acid Green 25 and Acid Blue 80 have almost identical molecular weights, which would be consistent with the similarity in their dyebath exhaustion percents.

The very low K/S value for the Acid Blue 45 and Acid Blue 80 dyes

for nonirradiated Nomex filament yarns indicated very poor color yield (Table 9). Post hoc Newman-Keuls analysis indicated the statistical difference in color strength between the three dyes examined (Table 11). The mean value of K/S for Acid Green 25 was very high in comparison to Acid Blue 45 and Acid Blue 80. The relatively higher color yield of Acid Green 25 may be explained by its high coloring or tinctorial power as indicated by its higher absorbance observed in the absorbance vs concentration curves (Figures 5, 6, 7). Hypothesis 6 is rejected because the three dyes showed significant difference in dyebath exhaustion percent and color strength.

Although ammonia plasma irradiation improved the dyeability of Nomex filament yarn with acid dyes significantly, the dyebath exhaustion is not very high compared to the commercial dyeing process of polyamide fibers with anionic dyes. The low dyebath exhaustion for Nomex irradiated yarn may be explained in terms of the adsorption isotherms of polyamide fibers with acid dyes. Plasma irradiation is only effective at the surface and does not alter the bulk properties of the irradiated fiber. The dyeing of polyamide fibers with ionic dyes occurs in the three following steps: (1) migration of the dye from the solution to the interface, accompanied by adsorption on the surface of the fiber; (2) dye diffusion from the fiber surface towards the center; and (3) fixation of the dye molecules within the fibers by covalent or hydrogen bonds, or by other forces of a physical nature.

Since plasma irradiation is restricted to the fiber surface and has no effect on chain mobility beneath the surface, the diffusion of

Table 11

Statistical Analysis on Color Strength

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time (RT)	3	0.2633*
Linear Contrast	1	0.2321*
Quadratic Contrast	1	0.0017
Dye Types (DT)	2	0.0398*
RT X DT	6	0.01683*
Residual Error	60	4.216x10 ⁻⁴

Newman-Keuls Test

Nonirradiated vs 60s (Irradiation Time)	Significant
Dye Types	Significant

* Significant (p < 0.05)

dyes into the Nomex fiber phase probably was not altered. The modification in surface chemical composition and surface texture was responsible for binding the dyes only on the filament yarn surface. Diffusion of dyes inside the fiber phase increases the dyebath exhaustion percent by transferring the dyes into the core of the fibers from the surface. Since Nomex has a high order of crystallinity and plasma irradiation does not alter the fiber morphology, there was saturation of the dyes only on the surface and the plasma irradiated Nomex yarn did not show very high dyebath exhaustion.

Effect of Ammonia Plasma Irradiation on Tensile Properties

The effect of ammonia plasma irradiation on the tensile properties of Nomex filament yarn with respect to the exposure times was investigated. The tensile properties studied were breaking tenacity, breaking elongation and toughness. Separate one-way ANOVAs were conducted for each of the response variables (tenacity, breaking elongation, and toughness), and the Newman-Keuls post hoc test was conducted between nonirradiated and 60s to make the pairwise comparison when ANOVA showed significant differences between means. Orthogonal polynomial tests between irradiation times were made to identify the effects of irradiation increments on the selected tensile properties of Nomex filament yarn.

Effect of Ammonia Plasma Irradiation on Tenacity

Table 12 shows the tensile performance of both nonirradiated and irradiated yarn. Based on the one-way ANOVA results, the tenacity of Nomex filament yarn was significantly affected by the ammonia plasma

Table 12

Tensile Performance of Nomex Filament Yarn*

	Breaking Tenacity (<u>g/denier</u>)	Breaking Elongation (<u>percent</u>)	Toughness (<u>inch²</u>)
Nonirradiated	4.294	18.1	3.31
Irradiated, 60 s	4.462	16.7	3.22
Irradiated, 120 s	4.124	17.4	3.00
Irradiated, 180 s	3.116	16.3	2.02
Standard Error	0.0436	0.1866	0.0533

* Each value is the average of 25 measurements.

irradiation exposure times (Table 13). The tenacity of yarn irradiated for 60 s was significantly higher, by 3.9%, than the tenacity of the nonirradiated yarn but the tenacity was lower at longer irradiation times (Table 12). Newman-Keuls analysis indicated a statistical difference between the means of nonirradiated and 60-s ammonia plasma irradiated specimens (Table 13). Orthogonal polynomials indicated that both the linear and quadratic curves provide the best fit. This means that the tenacity was stabilized to some extent between 60 s and 120 s and thereafter decreased with increase of irradiation time to 180 s.

The increased tenacity of the 60-s plasma irradiated yarns may be explained by the increased cohesion between the filaments. This is supported by the result of Byrene and Brown (1972) showing that plasma exposure improved the strength of cotton yarn after plasma treatment though the tenacity was lowered as the irradiation time increased.

Nomex, as classified by the Federal Trade Commission, is a fully aromatic fiber. The benzene ring in the monomer, along with carbonyl groups (C=O), perhaps made it susceptible to light absorption. Since plasma irradiation is in the region of ultraviolet, the fiber's tensile properties were perhaps deteriorated by ultraviolet light absorption. The filament pitting and cracking near the surface could also be held responsible for a weak, plasma-modified surface layer leading to tensile failure. The mechanism of filament yarn strength degradation was most probably due to tensile stress at a multitude of imperfections on the fiber surface where there were microscopic cracks leading to rupture at much lower force.

Table 13

Statistical Analysis on Breaking Tenacity

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time	3	9.1392*
Linear Contrast	1	22.6465*
Quadratic Contrast	1	0.8704*
Residual Error	96	0.0475

Newman-Keuls Test

Nonirradiated vs 60 s	Significant
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* Significant ($p < 0.05$)

Effect of Ammonia Plasma Irradiation on Breaking Elongation

Elongation or extensibility is described by the deformation of the fiber that is produced by a given stress. Quantitatively the breaking elongation is defined by the fractional increase in specimen length with respect to the initial length when subjected to the stress that will cause the specimen to rupture. The one-way ANOVA on elongation (Table 14) indicated the existence of a significant difference between means associated with the treatments. The breaking elongation of irradiated Nomex filament yarns was below that of the nonirradiated yarns. The reductions in mean breaking elongation when compared to the nonirradiated yarns were 7.6% for 60 s exposure, 3.8% for 120 s, and 9.9% for 180 s. Orthogonal polynomials indicate that the quadratic curve provided the best fit. This means that the breaking elongation was stabilized between 60 s and 120 s to some extent and thereafter reduced when irradiation time increased to 180 s. Newman-Keuls analysis indicated a significant difference between the breaking elongation means for nonirradiated and 60-s irradiated yarns (Table 14). The decrease in breaking elongation of 60-s irradiated Nomex specimens is consistent with the improvement in the breaking tenacity for these yarns. The decrease in elongation at 180 s was most probably due to the yarn brittleness as a result of etching and surface cavitation. Table 12 showed that breaking elongation was affected most by the 180-s irradiation treatment.

Effect of Ammonia Plasma Irradiation on Toughness

Toughness is quantitatively described as the work required to

Table 14

Statistical Analysis on Breaking Elongation Percent

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time	3	15.3893*
Linear Contrast	1	0.7578
Quadratic Contrast	1	13.1276*
Residual Error	96	0.8708

Newman-Keuls Test

Nonirradiated vs 60 s	Significant
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* Significant ($p < 0.05$)

rupture the specimen, which is evaluated from the area under the stress-strain curve. The one-way ANOVA on toughness indicated significant differences between the mean areas under the curves, showing the effect of ammonia plasma irradiation on Nomex filament yarn (Table 15).

Newman-Keuls pairwise comparison showed the statistical equivalence between the mean values of nonirradiated and 60-s treated specimens (Table 15). Orthogonal polynomials indicated that both linear and quadratic curve provides the best fit. This means that toughness was stabilized to some extent between 60 s and 120 s and thereafter reduced with the increase in irradiation time to 180 s. Toughness, as measured by the area under the stress-strain curve, was much lower, by 38.7 % for 180-s plasma irradiated specimens compared to the nonirradiated specimens.

Toughness is an indicator of the degree of brittleness. The more brittle the specimen, the less will be the ability to absorb stress. Surface cavitations and pitting may have been responsible for defects between the crystallites in the surface fibrils and resulted in increased brittleness of the Nomex filament yarn. Increase in brittleness leads to less stretching capability of a yarn and simultaneously reduces the toughness. Since analysis of variance indicated significant differences between means of breaking tenacity, elongation at break, and toughness, hypothesis 7 was rejected.

Table 15

Statistical Analysis on Toughness

Analysis of Variance

<u>Sources of Variation</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Irradiation Time	3	8.7283*
Linear Contrast	1	17.9118*
Quadratic Contrast	1	2.3909*
Residual Error	96	0.8709

Newman-Keuls Test

Nonirradiated vs 60 s Not significant

* Significant ($p < 0.05$)

Chapter VI

Summary, Conclusions, and Implications

Summary

The objectives of this research were : (1) to determine the effect of ammonia plasma irradiation upon the surface chemical composition and surface topology of Nomex filament yarn (Type 430); (2) to determine the effect of ammonia plasma irradiation on the dyeability of Nomex filament yarn with three acid dyes, in relation to surface texture modification, wettability, and reactive amine concentration on the fiber surface; and (3) to determine the effect of ammonia plasma irradiation on the tensile properties of breaking tenacity, breaking elongation, and toughness of Nomex filament yarns.

Results of preliminary experiments indicated the inapplicability of oxygen and nitrogen plasma treatment for improvement of the dyeability of Nomex filament yarn with acid dyes. Ammonia plasma treatment was found to be associated with increased dyeability of the yarn with Acid Red 18. Scoured Nomex filament yarns were subjected to ammonia plasma irradiation for 60 s, 120 s, and 180 s. Since the ammonia plasma irradiation effect is restricted to 500-1000 angstroms into the polymer surface, several analytical studies were performed to establish the relationship of plasma irradiation with physical and chemical properties of Nomex filament yarn. Surface chemical composition of the irradiated (60 s, 120 s, and 180 s) and nonirradiated yarns was investigated by x-ray photoelectron spectroscopy (XPS).

Surface amine concentration was investigated by studying the plasma amination kinetics using the anionic dye Ponceau 3R. Surface texture of the irradiated (60 s, 120 s and 180 s) and nonirradiated specimens was analyzed with high resolution scanning electron microscopy (HR-SEM) at low (1,600 X) and high (25,000 X) magnification.

The effect of ammonia plasma treatment on the dyeability of Nomex filament yarn was determined by measuring the dyebath exhaustion percentage, color strength (K/S), CIE L, a, b color coordinates, and color difference (ΔE) for the three dyes Acid Blue 45, Acid Blue 80 and Acid Green 25. Dyebath exhaustion was measured in a uv-vis spectrophotometer, Spectronic 2000. Color strength (K/S), CIE L, a, b color coordinates, and color difference (K/S) were measured in the Hunter LabScan Spectrocolorimeter. Wettability of irradiated (60 s, 120 s, and 180 s) and nonirradiated Nomex filament yarn, with de-ionized water, was evaluated in terms of grams of water absorbed per grams of yarn for three immersion time periods (15 s, 30 s, and 60 s).

The effect of ammonia plasma irradiation on the breaking tenacity, breaking elongation, and toughness of Nomex filament yarn with respect to the exposure times was investigated. An Instron tensile tester was used to evaluate the tensile properties of the irradiated and nonirradiated Nomex filament yarns. Statistical analysis methods included the analysis of variance (ANOVA) between the nonirradiated and irradiated means, orthogonal polynomial contrasts between the irradiation times, and post hoc Newman-Keuls multiple comparison tests of differences between nonirradiated and 60 s plasma irradiated means.

All statistical analyses on the research data were determined at 0.05 level of significance.

XPS analysis of surface composition indicated substantially higher surface concentration of nitrogen and oxygen atoms on the irradiated Nomex filament yarn over the nonirradiated. Increased nitrogen concentration occurred with increased time of plasma irradiation exposure of Nomex filament yarn, the highest surface nitrogen concentration being observed for the 180-s exposure time. Small increases in oxygen content suggested partial surface oxidation of the irradiated specimens. Plasma amination kinetics indicated that ammonia plasma irradiated Nomex filament yarns bound the Ponceau 3R in considerable amounts even for the shortest treatment time of 60 s. The amine concentration increased steadily with increased irradiation time. The separate one-way ANOVAs on amino group concentration between untreated and irradiated (60 s, 120 s, and 180 s) indicated a significant difference. However, the amine concentration showed the greatest increase between the nonirradiated and the 60-s irradiated yarns, with small further increase and stabilization thereafter as indicated by orthogonal contrasts. SEM photomicrographs exhibited noticeable differences between the surface textures of irradiated (60 s, 120 s, and 180 s) and nonirradiated filaments. Irradiated filaments showed substantial surface pitting, cracking, and etching. The surface pitting and etching of irradiated samples were less visible under low magnification (1,600 X), but were very apparent under high magnification (25,000 X). The surface of the nonirradiated specimen showed a smooth,

regular surface. For the irradiated specimens, the most surface etching was observed for the 180-s treated specimens, indicating longer exposure to ammonia plasma irradiation having the most effect.

Ammonia plasma treatment appeared to enhance the wetting capacity of Nomex filament yarn with de-ionized water. The two-way ANOVA indicated that both the irradiation time and immersion time had significant effect on wetting of Nomex filament yarn with de-ionized water. The water absorption capacity increased with respect to irradiation time but stabilized to a great extent after the 120-s treatment as indicated by the linear and quadratic orthogonal contrasts. Post hoc Newman-Keuls analysis indicated a significant difference in water absorption capacity between nonirradiated and 60-s irradiated specimen. For the three acid dyes, Acid Blue 45, Acid Blue 80, and Acid Green 25, the dyebath exhaustion was higher for the plasma irradiated Nomex filament yarns in comparison to the nonirradiated specimens. Mean values associated with dyebath exhaustion indicated a significant difference between the nonirradiated and irradiated (60 s, 120 s, and 180 s) Nomex filament yarn specimens. Orthogonal polynomial analysis indicated no significant difference in dyebath exhaustion between the 60-s, 120-s, and 180-s irradiation times. The color strength (K/S) values for all the irradiated Nomex yarns were higher compared to the nonirradiated specimens. Ammonia plasma treatment appeared to modify the dyeability of Nomex filament yarn with acid dyes as indicated by significant color difference between the nonirradiated and irradiated specimens.

Based on the ANOVA results, the tenacity of Nomex filament yarn was significantly affected by the ammonia plasma irradiation with respect to the exposure times. The variability in tensile properties was negligible within the individual observations of the groups of nonirradiated and irradiated specimens (60s, 120s, 180s). The 60-s plasma irradiated Nomex filament yarn showed a slight increase in tenacity over the nonirradiated samples and thereafter decreased as the irradiation time was increased. The tenacity of Nomex filament yarn was stabilized to some extent between 60-s and 120-s irradiation times and thereafter reduced steadily with increased irradiation times to 180 s, as indicated by the significant linear and quadratic contrasts. Newman-Keuls analysis indicated significant differences between the means of nonirradiated and 60-s irradiated specimens. Breaking elongation of irradiated Nomex filament yarns was lowered due to the irradiation effect. Breaking elongation was most drastically affected by the longest irradiation time of 180 s. Ammonia plasma irradiation was found to affect the toughness of the irradiated samples. Newman-Keuls pairwise comparison showed the statistical equivalence between the mean values of nonirradiated and 60-s irradiated samples. It may be argued that the etching and pitting at the Nomex filament yarn surface was responsible for increasing the brittleness and thereby reducing the stretchability of yarn leading to lower toughness.

Conclusions

Seven research hypotheses were formulated based on prior empirical results and the theoretical framework. Research hypothesis 1 was that

Nomex filament yarns after irradiation with ammonia plasma would have an altered surface chemical composition as compared to nonirradiated specimens. This hypothesis was supported since the XPS analysis results indicated increased concentration of nitrogen and oxygen atoms at the plasma irradiated fiber surface compared to the nonirradiated specimens. XPS results were further supported by plasma amination kinetics data which showed increased concentration of functional amino groups at the surface of irradiated Nomex filament yarns. Ammonia plasma treatment on the Nomex filament yarns did appear to be responsible for incorporating primary amino groups and to some extent for surface oxidation, thus changing the surface chemical composition of the irradiated specimens.

Research hypothesis 2 stated that Nomex filaments would have a rougher surface after irradiation with ammonia gas plasma. This hypothesis was supported because a difference was observed between the surface texture of nonirradiated and irradiated specimens. Visual observation of SEM photomicrographs of irradiated specimens showed pitted and etched surfaces. Surface oxidation at the aromatic fiber surface could have contributed to the surface roughening.

Research hypothesis 3 stated that ammonia plasma irradiated Nomex filament yarns would have a higher degree of wettability than would the nonirradiated specimens. This hypothesis was supported because the amount of water absorbed by ammonia plasma irradiated specimens was significantly higher than that by the nonirradiated specimens. Ammonia plasma irradiation induced the incorporation of reactive amine functional groups at the surface of Nomex filament yarns. Atomic oxygen

content was also increased at the fiber surface. Increased concentration of electronegative atoms like oxygen and nitrogen enhances the hydrogen bonding with water, thus increasing the water absorbing capability of the yarn.

The research hypothesis 4 stated that Nomex filament yarns after irradiation with ammonia gas plasma would have greater dyeability with acid dyes than would the nonirradiated specimens. This hypothesis was supported because the dyebath exhaustion percentage and the color strength (K/S) for the irradiated specimens were significantly higher than for the nonirradiated specimens. After ammonia plasma irradiation, the surface amine concentration was higher. Chemically reactive amino functional groups ($-NH_2$) were protonated in acidic medium to form $+NH_3$. Since all the dyes used were based on anthraquinone sulfonic acids, in aqueous medium the dyes were ionized to colored ions. The negative charge of the dyes and the positively charged amino groups on the fiber could have formed ionic bonds by electrostatic attraction. The improved dye uptake may be attributed to the increase in the polar functional groups and the electrostatic attraction.

Research hypothesis 5 was that there would be no significant difference in dyeability of ammonia plasma treated Nomex filament yarn with respect to plasma irradiation time, 60 - 180 seconds. Although the ANOVA indicated a statistical difference in dyebath exhaustion percent with respect to the irradiation time, the orthogonal polynomial analysis indicated insignificant linear and quadratic contrasts among dyebath

exhaustions for the 60-s, 120-s, 180-s irradiation times. The dyebath exhaustion percent for all three dyes did not change appreciably after the 60-s irradiation time. Therefore research hypothesis 5 was supported.

Research hypothesis 6 was that there would be no significant differences between the dyebath exhaustion and color strength for the three acid dyes on ammonia plasma irradiated Nomex filament yarn. This hypothesis was rejected. There were five possible acceptances or rejections for dyebath exhaustion and for color strength. Four were rejected and only one was not for dyebath exhaustion due to statistical equivalence between Acid Green 25 and Acid Blue 80. For color strength (K/S), the means of three individual dyes were statistically different.

Research hypothesis 7 stated that ammonia plasma irradiated Nomex filament yarns would have breaking tenacity, elongation at break, and toughness similar to those of nonirradiated Nomex yarns. This hypothesis was rejected. Newman-Keuls analysis indicated significant differences between the means of tenacity for nonirradiated and 60-s irradiated specimens. A significant decrease in tenacity was observed for the 180-s irradiated sample. Similarly, separate one-way ANOVAs indicated the existence of significant differences between breaking elongation means. Newman-Keuls pairwise comparison for toughness showed a statistical equivalence between means associated with nonirradiated and 60-s irradiated specimens. The filament pitting and cracking near the surface could be held responsible for a weak, plasma modified surface layer leading to the tensile failure. The pitting at the

surface might be responsible for the defects between the crystallites in the surface fibrils which affect fiber strength. Surface pitting and cracking could increase the brittleness, thus reducing the toughness.

The experimental results, followed by interpretation, indicated that irradiation with cold ammonia plasma generated by radio frequency resulted in alteration of the surface layer of Nomex filament yarn. XPS spectra showed the increase in electron density of oxygen and the addition of nitrogen atoms on the surface of the irradiated Nomex filament yarn. The irradiated filament surface was etched, cracked and visibly different from the nonirradiated specimens as shown in the SEM photomicrographs. The fiber surface roughness, along with cavitations, might be responsible for adversely affecting the tensile properties of the irradiated filament yarn. The reduction in tenacity of ammonia plasma irradiated Nomex yarn may be comparable to medium tenacity nylon yarn. The irradiated filament yarn was brittle to hand and less tough compared to the nonirradiated yarn. However, the ammonia plasma irradiation was responsible for significantly higher wettability and dyeability of Nomex filament yarn. Nomex is a strong and rigid hydrophobic fiber used in the textile industry. The unmodified Nomex fiber is one of the most difficult fibers to dye in a conventional batch process. Ammonia plasma treatment showed the possible surface dyeing capability of Nomex filament yarn with acid dyes. Plasma treatment is short, inexpensive and suitable for significant surface layer modifications of Nomex fiber. Ammonia plasma irradiation may permit dyeing of Nomex filament yarn with a range of acid dyes to obtain shade

variety and depth as required for camouflage uniforms, as well as for some commercial purposes. Besides the presence of functional amino groups on the fiber, surface ammonia plasma irradiation is also responsible for increasing surface roughness through etching and cavitations. Synthetic filament yarns, such as Nomex yarns, are susceptible to poor sizing because of their smooth surfaces and roundness. Fiber surface roughening through ammonia plasma irradiation may yield better adhesion to resin and sizing materials, though this was not examined in this research. Improved fiber bonding may be employed for more efficient weaving and for manufacturing composite materials. In conclusion the plasma irradiation techniques can be optimized through further research to contribute towards dyeing of Nomex fiber with acid dyes without substantially deteriorating its tensile properties.

Implications for Research

There has been very little research on the effect of plasma irradiation on textiles for modifying dyeability. In this research, ammonia plasma irradiation has indicated some potential for improving the dyeability of Nomex filament yarn with acid dyes. The presence of functional amino groups on the Nomex yarn surface via irradiation with ammonia plasma may allow Nomex to be dyed by fiber reactive dyes. Although fiber reactive dyes do not meet the criteria related to the infra red reflectance properties, this class of dyes should be investigated for ammonia plasma irradiated Nomex filament yarn. Fiber reactive dyes are the most preferred dyes for commercial dyeing because of their excellent wet fastness properties. The amino groups on the

surface of the Nomex fiber incorporated by the ammonia plasma irradiation may react with the halogen atoms attached to heterocyclic rings of fiber reactive dyes through a nucleophilic substitution reaction. The reaction would result in the formation of a covalent bond with surface amino groups of Nomex fiber whereby the dyed fiber would acquire excellent wet fastness.

Although this research has indicated the higher dyebath exhaustion and color yield for plasma irradiated Nomex filament yarn with acid dyes, the process would have to be further modified for its acceptance in commercial dyeing operations. The plasma effect is localized on the surface and does not alter the fine structure of the fiber, which influences the dyeing behavior to a large extent. The highly crystalline rigid morphology of Nomex fiber may be modified by the use of chemical energy with highly polar solvents such as dimethyl formamide, dimethyl acetamide, and dimethyl sulfoxide prior to the plasma irradiation. The treatment of Nomex with these solvents typically results in loss of polymer chain orientation associated with increased plasticization within the fibers. Ammonia plasma irradiation would finally incorporate reactive amino functional groups along with the modification of the Nomex fiber surface texture. This two-stage process may help higher dyebath exhaustion because the open structure of Nomex fiber may result in more uniform penetration of dye liquor and ready diffusion of dyes through the core of the fiber.

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VITA

Gautam K. Mishra was born in Cuttack, India in May, 1960. After graduation from Capital High School, Bhubaneswar, India, he attended B.J.B. College for the associate degree in Physical Science. He attended the Textile Engineering Program at the College of Textile Technology, Serampore, India in 1979. Upon graduation in 1983, he worked as a color matching specialist for Indian Rayon Corporation, Rishra, India, and a production engineer in Sonepur Spinning Mills, Sonepur, India.

He came to the U.S.A. in Fall 1986 for his graduate study in Textile Chemistry at Southeastern Massachusetts University. In his Master's program, his thesis was on the hot mercerization process for evaluating changes in physical, mechanical, and dimensional properties of cotton fiber assembly. The project was supported by the Kendal Research Organization in Massachusetts.

He entered the Ph.D program in Clothing and Textiles at Virginia Polytechnic Institute and State University in Fall 1988. While in graduate school, he worked as a graduate teaching assistant in the Department of Clothing and Textiles. He served as the president of the Virginia Tech chapter of the American Association of Textile Chemists and Colorists during 1991-1992 and was a member of the Clothing and Textiles Graduate Student Assembly.

G Mishra

Gautam K. Mishra