

/THE EFFECTS OF COMMERCIAL INSECTICIDE PRODUCTS  
ON ACID AND DISPERSE DYES ON NYLON CARPET FIBER/

BY

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## INTRODUCTION

A wide variety of insecticide products are used in homes, recreation areas, public buildings, and work establishments to control insect pests. Our society benefits from their availability, but insecticidal chemicals may have detrimental effects to man and his environment. In addition to the health risks associated with these products, insecticides may adversely affect textiles and other materials. In periodic indoor insecticide applications, furniture and carpeting often are exposed to insecticidal chemicals. If extensively damaged by insecticidal chemicals, interior furnishing textiles may require replacement which represents a considerable consumer expenditure. Since 1980 more than \$1 million in claims have been filed against pesticide applicators and manufacturers as a result of insecticide discoloration of carpeting.

One of the largest home expenditures for consumers is carpeting. Today, most homes have carpeting in one or more rooms. Carpet manufacturers judiciously select fibers, dyes, and finishes for carpeting that are both aesthetically pleasing as well as functional and durable. Dyes, for example, are selected on the basis of application class, hue, and suitability for a particular substrate. Other considerations include price,

dyeing properties, and colorfastness to light, ozone, crocking, steam cleaning, etc.

Even though extensive testing is involved in the selection of dyes for carpeting, manufacturers are unable to evaluate the fastness properties of a dye to all agents (i.e., environmental factors, cleaning methods, or consumer products) that could possibly come into contact with the dyed textiles. Various cleaning products also have been responsible for carpet discoloration and staining.

It has been recognized for many years that certain insecticide products may adversely affect the dyes used in carpeting. This issue is certainly not a new problem, but only recently has it been discussed openly by pesticide formulators, carpet manufacturers, and certified pest control operators (39). A few years ago, complaints on insecticide discoloration of carpeting began with a few occasional calls to the National Pest Control Association (NPCA) (30). In the early 1980's, however, the number of complaints increased (15, 30, 39). The majority of the complaints have focused on selected organophosphate insecticides (30). In September 1981, the Ad Hoc Committee on Pesticides was formed by the Carpet and Rug Institute, the National Pest Control Association, the United Pesticide Formulators and Distributors Association, and a number of dyestuff and fiber manufacturers to investigate the problem of insecticide carpet discoloration (6, 13, 29). The purpose of the Committee was to investigate the

problem and to develop screening tests for evaluating insecticides and dyes. Eighteen dyestuffs and twelve insecticide products were evaluated by the Committee (6, 13).

The AATCC Midwest Section's ITPC (Intersectional Technical Paper Competition) study (12), which will be referred to as the AATCC study, expanded upon the work of the CRI Ad Hoc Pesticide Committee. They evaluated the deleterious effects of 20 insecticide chemicals on 47 selected acid and disperse dyes applied to nylon and polyester carpet yarns. Unlike the CRI study, the AATCC Committee evaluated the technical grade of the insecticide rather than commercial formulations, since other additives in insecticide products may confound the effects of insecticidal chemicals.

This study builds upon the research conducted by the AATCC Committee. Its purpose was to evaluate the susceptibility of the 28 selected acid and disperse dyes on nylon carpet fiber to discoloration by products representing 15 different commercial insecticidal chemicals. Dyed and undyed specimens were treated with insecticide products, exposed to standard temperature, high temperature and high humidity, xenon light, and ozone and instrumentally evaluated for the degree of color change or fading.

The results of this study were compared with data from the AATCC study to determine the extent to which the commercial formulations of the insecticides accelerated color change. Commercial products representing "typical" formulations of the 15

insecticidal chemicals were selected for evaluation. The majority of the products evaluated in this study were EPA-certified products for use in and about the home to control common household pests and fleas. The results of this study will aid carpet manufacturers in selecting dyes which are the least sensitive to various insecticide products. It also will enable pesticide formulators to assess the combined effects of insecticidal chemicals and formulation additives on carpet discoloration.

## REVIEW OF LITERATURE

### Carpeting

For many years, carpet was used in the home as a floor covering because of its functionality (i.e., it provided a durable wearing surface). With improved standards of living, more emphasis was placed upon the aesthetic and comfort appeal of carpeting (21). The comfort factor of a carpet is attributed to its insulative properties, sound absorption, ability to absorb energy, ease of care, and comfortable feeling underfoot. The aesthetic appeal of carpeting, being a subjective judgment, varies greatly from person to person since it takes into consideration color, pattern, surface texture, as well as numerous other qualities. Carpet is one of the principle means for introducing color into interiors (21, 27). Other important factors influencing carpet selection and serviceability include wear (abrasion) and crush resistance (resiliency); soil resistance and cleanability; and colorfastness to light, ozone, and other agents.

Traditionally, carpets were made of wool and woven on looms which limited the design possibilities. In the past 25 years, however, a revolution has taken place in the carpet industry which was caused by the development of tufting machines and man-made fibers (7). Today, man-made fibers comprise the majority of carpet face yarns. Over three-quarters of the yarns are made

from nylon fibers. Polyester, acrylic, and olefin (polypropylene), and wool, respectively, account for the remaining portion (11, 32).

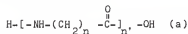
### Nylon

Nylon is used extensively in carpet fiber yarn because of its desirable characteristics. Such as its easy dyeability, high abrasion resistance (durability), good crush resistance, compressional resiliency, easy-care properties, and low cost when compared to wool. Some undesirable characteristics of nylon are that it soils easily because it is oleophilic, it is discolored by UV light and by certain chemicals, and it does not easily dissipate electrostatic charges (11).

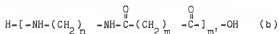
Chemical Properties, Poly (hexamethylene adipamide) or nylon 66, and polycaproamide, or nylon 6 are the two most prominent synthetic polyamide fibers. Polyamides have an amide linkage in their chemical structure as follows:



The structural unit for polymerization products of aliphatic polyamides are generally as follow:

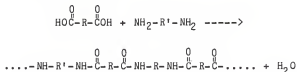


and for diamines and dicarboxylicacids is:

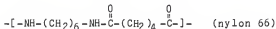
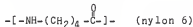


Polymers with the structural unit of (a) are known as poly ( $\omega$ -amino acids (or lactams)), or as nylon-n, such as nylon 6. Polymers with the structural unit of (b) are known as nylon-nm, such as nylon 66.

The polymerization of polyamides are of two types: 1) those derived from polymerizable monoaminomonocarboxylic acids (e.g. 6-aminocaproic acid,  $\text{NH}_2(\text{CH}_2)_5\text{COOH}$  or their amide-forming derivatives, and 2) those derived from the reaction of diamines with dicarboxylic acids (36, 40).



where R and R' are hydrocarbon groups.



Nylon 6 is a type of polyamide where the repeat units contain six carbon atoms. It is obtained by the polymerization of caprolactam. In nylon 66, there are six carbon atoms in between each amide unit in the polymer chain. The number of the  $-\text{CH}_2$  units in the structure could be as minimal as one which is called nylon 2 or polyglycine (40).

Physical Properties, Nylon 6 and 66 are melt-spun fibers. The molten polymer is forced through a spinneret (extruded as a ribbon) and allowed to solidify by cooling. The ribbon is then cut into small chips, which permits a convenient form for storage, handling, and blending. The nylon chips are then melted and extruded into a cooling chamber in which a current of air is swept across the filaments. Subsequent to spinning, the filament are cold drawn to increase tenacity. Nylon fibers are manufactured with a range of properties, depending on end-use. Industrial applications, for example, usually require fiber with higher tenacities and lower extensibilities, compared to nylon fibers used in apparel textiles.

Nylon because of its low density (1.12-1.15 g/cc), is lighter than many other common fibers. For example, if nylon and cotton were to be made into two identical fabric constructions, the nylon fabric would be considerably lighter than the cotton fiber. One of the major advantages of nylon fibers is their strength which is higher than most natural fibers. Nylon will lose some of its strength when it is wet. Nylon 66 has a dry tenacity of 4.5 to 5.8 grams per denier and will lose up to 20% of its strength when wet. Nylon 6 is stronger than nylon 66. It has a dry strength of 5.6 to 7.0 gram per denier. When wet, nylon 6 retains 85 to 90 percent of its strength. The extension at break of nylon 66 is 22 to 25 percent with a very powerful force of recovery, while the breaking elongation of nylon 6 is only 15



percent (36). Nylon is a highly elastic fiber with good elongation properties. Its elongation increases as the relative humidity rises. The degree of moisture regain for nylon at any given relative humidity is considerably less than that for some textile fiber such as silk, cotton, wool or rayon, but it is higher than that of polyester and the olefins (19). Nylon 6 has a greater affinity for dyes and moisture than nylon 66 (36). The melting point of nylon 6 is around 213-225° C, compared with nylon 66 which is around 256-265° C (1, 40).

Nylon has a high resistance to abrasion which is due to its toughness, natural pliability, and ability to under go a high degree of flexing without breaking down. The abrasion resistance of nylon probably is the most significant factor contributing to its use as the number one carpet fiber.

Nylon is inert to many organic acids, carbon disulfide, halogenated hydrocarbons, alkalies, soap, gasoline, benzene, aldehydes, ketones, and alcohols, but formic and carbolic acid are solvents for nylon. Other solvents which dissolve nylon include meta-cresol, xylenol at 77° F (25° C), oxidizing agents, hot glacial acetic acid, and mineral acids, such as concentrated hydrochloric and sulfuric acids. Cold concentrated nitric acid also will rapidly decompose nylon (19).

Nylon is highly resistant to attack by most insects and bacteria compared to natural fibers. Carpet beetles and clothes moth larvae do not eat nylon as a food source as they do in the

case of wool. However, they may cut their way out of nylon, if imprisoned. Undyed, unfinished nylon yarns and fabrics have been found to be highly resistant to molds and microorganisms, however, antibacterial finishes are used on nylon carpet for certain applications (i.e., hospital use) (19).

Nylon exhibits similar light resistance as cotton, but if it is left in direct sunlight for several weeks, it may actually decompose. Dyestuffs applied to nylon may either accelerate or retard the rate of photodegradation in the fiber during light exposure (19).

#### Chemistry of Dyestuffs

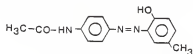
Historically, researchers investigated the molecular structure of dyes in an attempt to understand chemical properties responsible for the color of dyestuffs. It has been suggested by Witt (36) that certain functional groups such as nitro, nitroso, azo, and carbonyl give substances the potentiality of becoming colored. He called these groups "chromophores". Later he found that in addition to the chromophores, other functional groups called "auxochromes", which included amino, substituted amino hydroxyl, sulphonic or carboxyl groups, assisted chromophores in becoming a useful dyes (36). Organic compounds that are observed as having color are those whose absorption bands fall within the visible radiation range (sensitive to the human eye) (36).

Dyestuffs may be classified according to their application. Acid and disperse dyes are two examples of this classification.

They also may be classified according to their chemical constitution. A specific chemical class (i.e., azo -N=N-) can be found amongst several of the application classes (5). The chemical classes of the acid and disperse dyes used in this study will be reviewed.

#### Azo Dyes

The characteristic chromophore of the azo chemical class of dyes is the azo group -N=N-. Azo dyes usually contain hydroxyl (-OH) or amino (-NHR, -NR) functional groups as auxochromes. This class is the largest single class of synthetic dyes and has the widest range of applications. Azo dyes are divided according to the number of azo groups present in the dye structure. The processes of diazotization or coupling is applicable to a great number of compounds, which enables the synthesis of "disazo" and "polyazo" dyes of various types. Certain azo compounds themselves are capable of being diazotized or coupled (5, 37). An example of an azo class dye is C.I. Disperse Yellow 3.

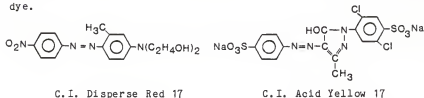


C.I. Disperse Yellow 3

#### Monoazo Dyes

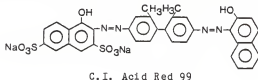
Monoazo dyes have only one azo group (R-N=N-R') in their structure. In Colour Index (5), monoazo dyes are subdivided into

1) dyes without water solublizing groups, and 2) water-soluble dyes containing  $-COOH$ ,  $-SO_3H$ , or other water solublizing groups. C.I. Disperse Red 17, and C.I. Acid Red 17 are respective examples of water-insoluble and water-soluble classes of monoazo dye.



#### Disazo Dyes

This class of dyes has two azo groups ( $R-N=N-R'-N=N-R''$ ) in their structure. They are more complex dyes which often contain other constituents such as phenol, naphthol, aminonaphthol, sulfonic acid, or/and water solublizing groups. The majority of disazo dyes are acid mordant dyes (i.e., C.I. Acid Red 99). Only a few of them belong to the water-insoluble class of dyes.



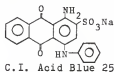
#### Anthraquinone Dyes

The characteristic feature of the anthraquinone dyes is the carbonyl group as the chromophore which may be present once or more times in the structure.

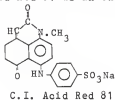


The carbonyl group is frequently associated with auxochromic hydroxy or amino groups and their substituted forms such as -NHR, -NR, -NHCOR, -OR.

Anthraquinone dyes are subdivided into two groups: 1) dyes without a heterocyclic nucleus fused to a central vating system, and 2) dyes with a heterocyclic nucleus fused to a central vating system. Dyes in the first group contain the simplest quinones and their derivatives, such as C.I. Acid Blue 25:



Dyes in the second group contain at least one heterocyclic nucleus fused to a carbocyclic nucleus, such as anthraquinone or benzanthrone. C.I. Acid Red 81 is an example for this group:



#### Application Classes of Carpet Dyes

Acid and disperse dyes are commonly used for dyeing nylon

fibers, although basic dyes can be used on cationic dyeable carpet yarns for styling purposes, such as bidyes and tridyes, and to achieve differential dyeing effects (5, 10).

The acid dyestuffs are water-soluble anionic compounds that are characterized by the presence of one or more sulphonic acid ( $-SO_3H$ ) or other acidic groups in their molecules, but a few contain carboxylic acid groups. Most acid dyes are sodium salts of organic acid, and their active coloured components are anions. They usually are applied in a bath containing mineral or organic acid such as sulphuric acid or ammonium sulphate. Acid dyes have affinity for fibers that have amine groups on their molecules, such as wool, silk, nylon, and modified acrylic fibers. Chemically, acid dyes consist of azo, anthraquinone, triphenylmethane, azine, xanthene, ketonimine, nitro, and nitroso compounds. A complete range of hues can be obtained with acid dyes. Many of them are very bright and have fastness properties from poor to very good (5, 36, 37).

There are three main application classes of acid dyes, based on the acidity of the dye bath and concentration of the electrolyte. The first type is usually called Leveling Acid Dyes. The type of acid used in this method is sulphuric acid, which is a strong acid used to maintain the pH of dye bath less than 3.5. Glauber's salt is employed in the dye bath as a retarding agent to control the rate of dye exhaustion. The second type is called Milling or Less Leveling Acid Dyes (5, 35). Acetic acid was

traditionally used in this method because it is a weaker acid than sulphuric acid. The pH value of the dyebath is between 3.5-5.5. The retarding agent also should be used in this method to slow down the rate of exhaustion. The last type is Super Milling Dyes or Neutral Dyeing Acid Dyes. Ammonium acetate or ammonium sulphate is used in this method and pH is between 5.5 - 7.00. Glauber's salt is not used in this method because it accelerates rather than retards the rate of dyeing. The washfastness and lightfastness of Super Milling Dyes usually are greater than dyes within the two other types (5, 36, 37).

Disperse dyes were previously known as acetate dyes, dispersal dyes, or dispersion dyes. They are currently defined by the Society of Dyers and Colourists as "substantially water-insoluble dyes" having substantivity for one or more hydrophilic fibers, and usually are applied from a fine aqueous dispersion (5). The importance of water insoluble disperse dyes has increased even more with the development of man-made fibers, such as polyester, nylon, triacetate, and acrylics, all of which are more hydrophobic than cellulose acetate (5, 36, 37).

Disperse dyes usually are primary, secondary, or tertiary amines of one of the following three types: 1) aminoazobenzene, 2) aminoanthraquinones, and 3) nitrodiarylamines. Nearly all disperse dyes are azo (mostly monoazo) dyes or anthraquinone, substituted by  $\text{NH}_2$  or  $\text{NRR}'$ , in which R and/or R' are  $-\text{CH}_2-\text{CH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CN}$ , or similar groups designed to balance hydrophobic and

hydrophilic properties. The fastness properties of disperse dyes have increased greatly since 1953 (5, 36).

Disperse dyes must be brought into a state of fine suspension in the dyebath by adding a sufficient amount of water and synthetic dispersing agent (36). Table I shows the different dyeing methods suitable for applying disperse dyes as suggested by Colour Index (5).

#### Colorfastness of Dyes

Colorfastness properties are among the most important criteria used in assessing the commercial use of a dye. Colorfastness is affected by light exposure, ozone, other atmospheric conditions, or the presence of certain chemicals (i.e., acne medicine) which may degrade the chemical structure of the dye. The important categories of fastness of dyes are color fastness to light, gas fumes, ozone fading, sublimation, and washing (26).

When dyes are degraded, two changes may occur. First is a change in the shade (hue) and/or depth of shade, and second is physical degradation of the dye (26, 35). The change of the shade or discoloration of the dye is an important concern for textile and carpet industries. The colorfastness of a dyed fiber is dependent upon the chemical structure of the dye chromophore, the functional groups present; and the molecular weight, size, and shape of the dye (45). For example, dye structures with hydroxyl groups are, in general, sensitive to alkaline conditions



TABLE I

Summary of Typical Methods of Applying  
Disperse Dyes to Nylon Fiber

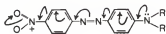
Dyeing Method	Nylon
N (Normal Temperature)	80-100°C, 45-90 minutes
Ne (Normal Temperature + Carrier)	
HT (High Temperature, i.e., in pressurized Systems)	110-130°C, 30 minutes (Coverage of physical variations improved over method N)
DD (Diazotise and Develop; a Three Bath Process)	(i) Dyes Base Dye = Method N (ii) Diazotise = 20°C, 30 minutes (iii) Develop Commence Cold, Raise Temperature to 60°C, Maintain for 30 minutes
3A (3 Bath Azoic)	Not Applicable
2A (2 Bath Azoic), Includes also Methods 2Az.c and 2Az	(i) Apply Ase Dye = Developer or Azoic Combination (ii) Diazotise = 10 minutes Cold Raise to 60°C; Maintain 30 minutes
T (Pad/ Thermofix)	Pad, dry and fix for 60 seconds at 185-190°C (nylon 6), or 200-210°C (nylon 6-6)
Pad/Roll	Batch, 2-4 hours at 90-95°C, drybulb and 85-90°C wet bulb
Pad/Steam	Fix as for prints

which can cause color shifts (i.e., red dyes shift to bluer or duller shades) (47).

The effect of light on the chemical constitution of the dyestuffs is a complicated subject which still is not clearly understood. When the dye molecule absorbs light, electrical transitions occur in the structure of the dye molecule which convert it into an excited state within the single or/and triplet state. Such an excited molecule can even react with atmospheric gases (i.e., ozone, moisture) or the fiber substrate. Some dye types undergo oxidation and others reduction (9, 26, 35).

The photostability of anthraquinone dyes in man-made polymers has been studied (26). Anthraquinone type disperse dyes are used on synthetic fibers. Different derivatives of anthraquinone dyes have different properties based on their functional groups. Hydrogen anthraquinone derivative dyes are commercially important because of their high light resistance properties as disperse dyes on polyester fibers or as vat dyes on cellulosic fibers. Alizarin dye or 1,2-dihydroxyanthraquinone with the chemical structure of  $(C_{14}H_6O_4) Fe_2$ .  $FeO$  is another derivative with high light stability. Alizarin has been used for centuries in coloring furnishings such as the world famous Persian carpets. However, 2-hydroxyanthraquinone dyes have poor lightfastness properties. These studies show that the reason 1-hydroxy-substituted anthraquinone has high lightfastness is because it deactivates the photoexcited dye within the singlet

and/or triplet state by reversible exchange of protons across the strong intermolecular hydrogen bond. In the case of 2-hydroxy derivatives, the high polarity of the dye weakens the intermolecular hydrogen bonds which results in poor lightfastness (26). In general, the fastness of dyestuffs to light depends on the  $\pi$ -electron delocalization or electron mobility. For example, the predominant contributing structure of nitrodimethylaminoazobenzene increases the electron mobility of the molecule, thereby decreasing lightfastness.

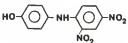
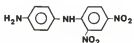

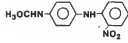
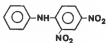



The introduction of different substituted functional groups, such as amino, aminohydroxy, aminochloro, or aminocarboxy groups, often results in a decrease in lightfastness properties (45, 46). On the other hand, electron withdrawing groups inserted in the ortho position often improves lightfastness. For example 2-fluoroalkyl groups seems to be very effective on lightfastness, while having fluorine atoms on the C<sub>3</sub> or C<sub>4</sub> positions have no additional effect on lightfastness properties. Dye structures with nitro group in the ortho position also are more resistant to light, whereas, nitro groups in the para positions often reduce the lightfastness of the dye (see Table II) (26, 35).

Gas fading is caused by nitrogen dioxide ( $\text{-NO}_2$ ), sulfur

Table II

## Light Fastness Properties Of Dyestuffs With Nitro Groups

Structure	Light Fastness
	Moderate
	Moderate
	Excellent
	Excellent
	Moderate
	Excellent

Sunthakar, S.V., "Chemical Constitution and Fastness of Disperse Dyes".

dioxide ( $-SO_2$ ), and other gases present in the atmosphere. The fastness of dyes to  $NO_2$  gas is dependent upon the nucleophilicity of the amino or alkylamino groups present in the dye structure. The gas is first absorbed by the fiber, then it reacts with dye molecules, starting with diazotization of the primary amino groups, then nitroization of the secondary amino groups and at last oxidation of the dye. Azo dyes ( $-N=N-$ ) are more sensitive to gas fading than are many other chemical classes of dyes (see Table III) (26, 35).





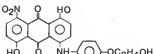
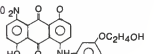
Atmospheric ozone ( $O_3$ ) also causes fading in dyed fabrics. Since ozone is a more powerful oxidizing agent than nitrogen dioxide, it can easily react with nucleophilic groups such as those that react with nitrogen dioxide (26).

The fastness of a dye to washing is dependent upon the size of the dye structure and method of dye/fiber association. Dye molecules with a larger chemical structure are more resistant to washing (26). Covalent and ionic bonding imparts greater substantivity and resistance to washing than hydrogen bonding or other secondary valence forces.

No published research studies are available on the mechanisms involved in the discoloration of dyestuffs with insecticide products. In the case of organophosphate insecticides, however, some theories suggest that the organophosphate insecticides are converted to phosphoric acid which reacts with the dyes causing dye discoloration.

Table III

## Gas Fastness Of Dyestuffs With Amine Groups

Structure	Gas Fastness	AATCC Gray Scale Units
	Very Good	2
	Good	4
	Poor	5
	Poor	4-5
	Very Good	2
	Very Good	2

Sunthakar, S. V., "Chemical Constitution and Fastness of Disperse Dyes".

### Pesticides

The National Household Pesticide Usage Study (15) showed that from every ten households in the United States, nine are using some type of pesticide in the house, garden, yard, or on family pets. Such wide-spread use of pesticides in and about the home is considered a significant source of pesticide exposure to the general population. This study also showed that the proportion of pesticides used in households differed among the various geographic regions of the United States. Households in the Southeastern region were using pesticides more frequently than those in Northern and mountainous areas. The number of different pesticide formulations used by the 8,254 householders in this study was over 500. Among the pesticide products listed, 15 pesticide formulations accounted for 65.5 percent of the total volume of pesticides. As shown in Table IV, among the 14 pesticides listed, 12 were insecticides, one was a herbicide (2-4-D and Silvex), and one was a rodenticide (Warfarin) (15).

The most efficient means of controlling pests is to select insecticides which are effective on specific target insects. There are different kinds of pests which can be found in homes. Some of the common household pests are cockroaches, (Oriental, American, German, and Brown-banded), house flies, black carpet beetles, webbing clothes moth, silverfish, fleas, ticks, ants, termites, and boxelder bugs (3).

TABLE IV

Most Prevalent Pesticides in U.S. Households\* :  
National Pesticide Usage Study

Pesticide Formulations	Estimated Number of U.S. Households With Compounds
Dichlorvos	9,868,937
Resmethrin	7,080,779
Pyrethrin	6,434,842
Chlordane	5,510,906
Sevin	5,053,027
2-4-D and Silvex	3,998,269
Diazinon	3,671,212
Baygon and DDVP	3,286,920
Malathion	3,123,392
Metaldehyde	3,000,746
Warfarin	2,779,982
Arprocarb	2,771,806
Captan, Methoxychlor, Rotenone and Rotenoids	2,240,339
Ovex, Lindane, Rotenone and Folpet	2,150,398

\*The total number of households in United States at the time of the study was 73,297,000.



Each of the above pests tend to have a different inhabitation and life cycle. For example, brown-banded cockroaches prefer living rooms of dwellings and apartments where they hide in cracks, woodwork, or furniture. German cockroaches tend to appear in kitchens and bathrooms and are very difficult to control. Fleas and brown-dog ticks attack the host animal or the bedding of the infested host animal (3). Table V shows insecticides recommended for killing various household pests (3).

#### Commercial Pesticide Formulations

Pesticides are substance used to control pests. There are various categories of pesticides, depending on the type of pest for which they are intended to control (i.e., insecticides, fungicides, herbicides, rodenticides, bactericides, etc.). Most pesticidal chemicals are not used in their pure form, but are formulated into commercial products. Formulations of the pesticidal compounds usually improve ease of application, effectiveness, handling, storage, and safety to the applicator and environment. The formulation can be done either by the pesticide manufacturer or formulator. The formulation, concentration, and additive chemicals vary in commercially formulated products, depending on the properties of the active pesticidal chemical and the intended end-use. Common formulations of pesticides include sprays; dusts with carrier such as talc and clay; aerosols; granulars; fumigants; and baits such as sugar, starches, or meat scraps. Each of these forms have their

TABLE V  
Recommended Insecticides for Different Insects

Recommended Insecticides											
Insects and Related Pests	Baygon Residual Spray (c)	DDVP	Diazinon Residual Spray (c)	Dursban Residual Spray (c)	Ficam W (d)	Multicide Residu- al Spray (c)	Pyrethrins Spray (a)	Pyrethrins Contact (a)	Resmethrin Contact (b)	Sevin Dust (c)	Sevin Residual Spray (b)
Ant	1	2	1	1	1	1	2	2	2	2	2
Boxelder Bug			2		2	2	1				
Carpet Beetle	2	2	1	1	1	2	2	2	2		
Clothes Moth		2				2	1	1	2		
Cockroach	1	2	1	1	1	2	1	1	1		2
Fleas, Cat/Dog	2	2	2	2	1	2	2	2	2	2	
Silverfish/Firebrat	1	1	1	1	1	2	1	2			
Flies	2	1	1	1	2	1	1				
Tick	1	2	1	1	1	2	2	2	2	2	2

Key to Comments

- (a) Short Residual (less than one day) for quick knockdowns.
- (b) Moderate Residual (1-15 days), gentle spray.
- (c) Long Residual (more than 15 days), limited to crack and crevice, spot treatment or baits.
- (d) Long Residual (more than 15 days), general treatment.

Insecticidal Groups

- (1) Material of choice of proven value to PCO's in controlling this pest.
- (2) Alternative material useful in some situations.

own subdivisions. For example, spray forms are available as emulsified concentrates, wettable powders, oil solutions, soluble pellets, sprayable suspensions, and fogging agents (38).

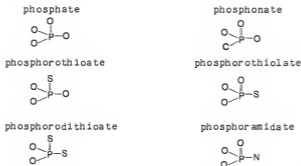
#### Chemistry of Insecticides

Raw materials for insecticides include arsenicals, petroleum oils, nicotine, pyrethrum, rotenone, sulfur, hydrogen cyanide gas, and cryolite. Insecticides are divided into different classes based on their chemical content (38). Organochlorines, organophosphates, organochlorines, organosulfurs, botanicals, carbamates, formamidines, thiocyanates, dinitrophenols, organotins, and synergists (or activators) are examples of major insecticide classes. The insecticides selected for this research are members of following classes:

Organophosphates (OP) are commonly used around the home and garden. Other common names for this class are organic phosphates, phosphorus insecticides, nerve gas relatives, phosphoric acid esters or phosphorus esters, phosphates, and phosphate insecticides. Normally, organophosphate is used as a generic term, and all the insecticides within this class are derived from phosphoric acid. They are generally the most toxic chemical class of insecticides. Because of the chemical structure and mode of action of OP's, they are related to the "nerve gases". They impose their toxic action by inhibiting certain important enzymes in the nervous system. Compared to organochlorines the OP's are more chemically unstable or nonpersistent. Because of

this characteristic, they often are used as a substitute for the more persistent organochlorines (20, 38).

Various combinations of oxygen, carbon, sulfur, and nitrogen can be attached to the phosphorus moiety to make different types of OP insecticides. The six subclasses of OP's are (38):



The OP's are further divided into three classes: the aliphatic, phenyl, and heteracyclic derivatives. The aliphatics have a linear structure containing short carbon chains. Malathion, trichlorfon (Dylox), and dichlorvos (Vapona) are three examples of this class. Malathion is commonly used in and around the home with little or no hazard either to humans or their pets. It is more sensitive to alkaline than acidic conditions. Trichlorfon is a chlorinated OP which has been useful for insect control on crops, in barns, and around the home. Another OP's insecticide, dichlorvos, has a high vapor pressure feature which makes it useful in fumigant applications. It has been incorporated into

plastic pet collars and pest strips, from which it is released slowly. It is colorless and has a mild fruity odor. It is slightly soluble in water, is miscible in most solvents, and it lasts several months. It is useful for insect control in the home and in other closed areas (20, 38).

The phenyl organophosphate insecticides contain a benzene ring. Frequently, one of the hydrogens in the ring is displaced by a phosphorus moiety, and the other hydrogens are replaced by Cl, NO<sub>2</sub>, CH<sub>3</sub>, CN, or S. Parathion and Ronnel (Korlan) are two insecticides belonging to this class (38).

Heterocyclic organophosphate insecticides are characterized by ring structure having different or unlike atoms. For example, the carbon atoms in the ring are displaced by oxygen, nitrogen, or sulfur. One of the first insecticides within this class was diazinon which contains two nitrogen atoms that are substituted for two carbon atoms in the heterocyclic ring. Diazinon is frequently used in home, on lawns and gardens, on ornamentals, around pets, and for fly control in stable and pet quarters. Chlorpyrifos, another example in this class, has become the most frequently used insecticide in homes and restaurants for controlling cockroaches and other household insects (20, 38).

Carbamates are derivatives of carbamic acid HOOC-NH<sub>2</sub>-R. Carbaryl (Sevin) was the first successful carbamate insecticide, partly because of its two distinct qualities: low dermal toxicity and effectiveness in controlling a broad spectrum of insects. It

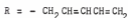
is widely used as a lawn and garden insecticide and in the home. Propoxur (Baygon) is a carbamate that can be used for controlling those insects that have resistance to the organophosphates or organochlorines. Because it is a very effective insecticide against cockroaches, it used by structural pest control operators for controlling cockroaches and other insects in restaurants and homes (38).

Thiocyanates insecticides are characterized by a thiocyanate group (-SCH) in their structural formulas. They have a distinct odors which often is objectionable, but they are relatively safe to use around humans and animals. They have the quality of quick knockdown of flying insects. Lethane 384 and Lethane 60 are two examples of this class (38).

Botanicals are naturally occurring insecticides that come from the flowers, leaves, and roots of certain plants. The plant material is either used alone or mixed with other chemicals. Nicotine, pyrethrin, and rotenone are examples of insecticides within the botanical class. The insecticides containing pyrethrin are ideal for home use because they have a rapid "knockdown" quality. They are among the safest insecticides for use around humans and domestic animals. However, because of their relatively low toxicity, insects "downed" by pyrethrin insecticides may recover and return to life again. Thus, a synergists often is added to commercial formulations to increase the effectiveness of the pyrethrin-containing insecticides.

Pyrethrins usually are a mixture of four compounds: Pyrethrin I and II, and cinerin I and II. They differ in two functional groups and the structural formula of each component is attached to the main ester structure as shown below (38):

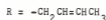
PYRETHRIN I



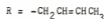
PYRETHRIN II



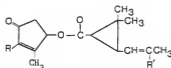
CINERIN I



CINERIN II



For examples:



Effect of Chemicals on Carpet

The carpet industry has become increasingly concerned with the discoloration of carpets caused by different chemicals. These chemicals either destroy the dyestuffs, alter it, or stain the carpet by leaving a topical residue which changes the perceived color. Chemicals such as laundry bleaches, cleaners for kitchen counters, and institutional cleaners containing bleaches may cause dye discoloration on carpeting. The chlorine-based chemicals leave light yellow spots, while oxygen bleaches fade all dyes to an off-white color. It has been reported that

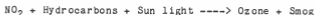
even 2-3 hours of high humidity may initiate their attack on dyes. Pool chemicals used for cleaning and controlling bacteria growth may cause discoloration in carpet dyes; and disinfectants such as air deodorizers and household sprays that contain phenolic chemicals are solvents for some fibers and dyes. Face creams that are used for removal of freckles, birthmarks, and other darkened areas in human skin can fade dyes appreciably. Also, products such as plant foods and fertilizers which usually contain organophosphates for growth, dandruff shampoos containing sulfur compounds, tile cleaners with strong detergents, mildew fighters with chlorine compounds, and pesticides may cause dye discoloration in carpets (6). In the last few years, many products such as acne medicines and pet care medicines for mange have entered the market containing benzoyl peroxide as the active ingredient. Benzoyl peroxide is a very strong oxidizing agent which is water-insoluble and cannot be easily washed off of skin or out of fabrics. An extremely low concentration of this chemical (<0.02%) is capable of destroying most dyestuffs used in carpet. Since benzoyl peroxide was approved by the Food and Drug Administration for over-the-counter sale, products containing spots. The reaction between benzoyl peroxide and a dye results in a bright yellow spot with an orange border or halo on polyamide or a bone yellow stain on polyester, cellulosic, or polyolefin fibers. On blue carpet, the spots usually appear slightly pink. Other textiles such as pillow cases, sheets,



towels, upholstery fabrics, and clothing also can be discolored by products containing benzyl peroxide. Humidity accelerates the discoloration, thus making these spots more apparent (4, 6). Acne medicines containing benzoyl peroxide are considered as "latent intruders". This refers to the products which spill on the carpet, but cannot be seen immediately. It can sit on the carpet for months, until conditions (high humidity and temperature) initiate its attack on dyes, thus making these spots more apparent (4, 6).

#### Effect of Ozone on Carpet

In nature ozone (O<sub>3</sub>) is generated from oxygen by ultraviolet radiation in the stratosphere. The concentration of the ozone in the upper atmosphere can reach 500 parts per hundred million (pphm), depending on the season and the latitude. The concentrations of ozone at ground level is usually around 1-5 pphm at sea level, 2-5 pphm during the day, and in the lower range during the night. Another source for ozone is electric charges of lightening during thunderstorms (16, 31). Ozone also exists in smog in large cities. It is produced when atmospheric pollutants such as hydrocarbons and nitrogen dioxide are irradiated with ultraviolet light in the presence of air. Various aldehydes and acids also may cause the formation of ozone. The photochemistry of ozone formation is shown below:



Ozone fading was first discovered during a field test that evaluated the effects of nitrogen oxides ( $-\text{NO}_2$ ) on blue anthraquinone dyed acetate fabrics. The result of this test showed that nitrogen oxides were not responsible for faded samples of blue anthraquinone acetate, but some other agent caused the fading. Further studies by Salvin and Walker (22) showed that all blue and some red anthraquinone dyes were sensitive to ozone (22, 23, 31).

Haylock and Rush (17) examined the effects of fiber properties, exposure conditions (temperature, humidity and ozone concentration), and dye structure on the rate of ozone fading on nylon carpet yarn. Fiber properties evaluated included cross-section, steam heat setting, and fiber draw ratio. Results showed that fibers with round cross-sectional shapes with a low surface area were more resistant to ozone fading than a Y-shaped fibers with a higher surface area. Heat setting was another important factor that affected ozone fading. A dramatic increase in the rate of ozone fading occurred as the heat setting temperature was increased. Ozone fading was reduced in nylon by increasing the draw ratio. Generally, increases in drawing ratio leads to the higher orientation which imparts greater resistance to ozone (16, 18).

Haylock and Rush (17) also found that by increasing both temperature, humidity, and ozone concentration, the rate of ozone fading was increased. Under high humidity conditions, the

structure of nylon fiber becomes more open, therefore, ozone can easily diffuse into the fiber and destroy the dye (16, 17, 24). Selvin (31) also reported that high humidity conditions accelerated ozone fading of disperse dyes on nylon 6 and 66. (22, 31). Since most of the carpet fading complaints attributed to ozone came from coastal areas of Texas and Florida, this type of fading was labeled "Gulf Cost Fading". Both of these places have hot and humid climates which accelerate ozone fading (16, 22, 24).

Since the molecular size of the dye influences dye migration to the fiber surface where ozone fading is more likely to occur, smaller dye molecules have a greater potential for ozone fading (17, 24). Similarly, disperse dye desorb from nylon at a much higher rate than basic dyes or acid dyes. Basic dyes are less resistant to ozone fading than acid dyes (16, 17, 23).

For better ozone fastness on nylon carpets, Lewis (39) suggested that "since it is only the disperse blue component causing an ozone fastness problem, there is an alternative to completely reformulating with acid dyes. Substitution of a level dyeing acid blue dye for the disperse blue used along with a disperse yellow and red is the easiest change to make." Almost no ozone fading was observed on disperse azo red and yellow dyes or diphenylamine yellow dyes (23). Ozone fading also may be improved by manipulating fiber morphology by mechanical and/or thermal means to give a more fiber compact structure which

decreases dye mobility; or by using high molecular weight dyestuffs which diffuses more slowly (24).

#### Effect of Insecticides on Carpet

Certain insecticides have been found to cause color changes on carpet. This issue is certainly not a new problem, but only recently has it been discussed openly by pesticide formulators, carpet manufacturers, and certified pest control operators. In 1979, the Carpet and Rug Institute (CRI), National Pest Control Association (NPCA), as well as individual insecticide manufacturers and formulators, began receiving occasional complaints pertaining to insecticide discoloration of carpeting. The majority of the complaints focused on selected red dyes on nylon carpets which reacted with certain organophosphate insecticides. Many red dyes are acid-base sensitive; thus, acidic or alkaline conditions may alter the color of a carpeting containing a red dye to green (30, 39). This can happen either around the baseboard areas if a localized application method had been used, or to the entire carpet surface if the pesticide had been applied in the form of a mist (25).

Color change or fading caused by insecticides is accelerated by high temperature and high humidity and may be made more drastic by direct exposure to sunlight or strong ultraviolet sources, such as "plant lights" (29). In some cases, insecticidal chemicals that were no longer active on pests at a

latter time, changed the color of the carpeting. In such cases, usually moisture and humidity or light exposure were responsible for discoloration (33).

Also there have been several reports of stained carpets that have resulted from the application of insecticides on carpeting to control fleas (2). These reports showed that direct contact of certain insecticidal chemicals on carpets have resulted in dye discoloration of selected dyestuff. The need for indoor flea control has increased enormously in the last decade because the dry summers in many regions of the country which is favorable for development of flea larvae. For successful flea control treatment, indoor certified pest control operators suggested that residual insecticides should be applied to carpets, floors, furniture, and pet resting areas (2, 34). Two methods that usually are suggested by industry for flea control are fan spraying around the baseboard or edges of carpets, and pin steam applications (30).

Insecticide products which are widely used for indoor flea control are Precore, Knox Out, Tetramethrin, Resmethrin, Ronnal, Pyrethrin, Malathion, Ficam, Dursban, Baygon, Safrofin, DDVP, and Sevin (2). Recent research indicates that several of the above insecticides such as Diazinon, Vaponite (DDVP), and Malathion can cause color changes in carpeting by chemically reacting with the dyes (4, 25, 30). Research by Reagan et al (12), has shown that, in addition to the above insecticides, resmethrin, tetramethrin,

permethrin, and carbaryl can cause appreciable color change, especially with high temperature and humidity and light exposure.

Because of the increase in the number of consumers complaints in recent years and the severity of the carpet discoloration, the CRI Ad Hoc Committee on pesticides was established in September 1981. The purpose of this committee was to investigate the reasons for discoloration of the carpet by pesticides, to develop screening tests for evaluating insecticides and dyes, and to disseminate the results of the study to the carpet and pesticides industries (6, 13). The Committee evaluated eighteen dyestuffs and twelve different pesticides. The dyestuffs included: C.I. Disperse Red 17, 55, 340, and 309; Telon Acid Red RLL, Eastman Acid Red KSC, 2BDR, and; C.I. Acid Red 299, 337, 360, 361, 394, and 396. The pesticides tested were: Malathion, DDVP, Diazinon, Dursban, Knox Out, Dursban L.O., Safrotin, Orthene, Sumithion, Ficam W, and Baygon (6, 13). The result of this study showed that the following pesticides create an unacceptable color change in the above carpet dyes: DDVP, Malathion, orthene, and Sumithion (6, 13).

One carpet manufacturer on the Ad Hoc Committee reported that fenitrothion, sold by Samitomo Chemical American Inc. under the trade name of Sumithion was not even recommended for use on carpets in the U.S. The finding of CRI investigation, in addition to many carpet discoloration reports resulted in the inclusion of warnings on insecticide products by manufacturers. For example,

Chevron has added warning statements to the labels of suspected rug-discoloring chemicals (29). Perntiss Company also has included warnings on their Prentox products; and since June of 1982, Shell Chemical Company has placed a more cryptic, but equally effective, notice on their Vaponite labels which reads: "Do Not Use On Carpet" (39).

The AATCC study investigated the effects of 20 insecticidal chemicals (technical grade) on the colorfastness of 21 acid dyes and 9 disperse dyes applied to nylon, and 17 disperse dyes applied to polyester carpet yarn. The insecticides evaluated in this study were representative of different chemical classes of pesticides such as, botanicals, carbamates, carboximides, chlorinated hydrocarbons, organophosphates, pyrethroids, and thiocyanates. Specimens were treated with 5% (w,w) insecticide/acetone solutions and exposed to following tests. 1) standard condition, 2) high temperature and humidity, and 3) xenon light. The treated/exposed specimens were evaluated instrumentally for color change (12).

The result of this study showed that some of the insecticidal chemicals caused an appreciable color change in standard temperature conditions. The greatest amount of discoloration in this test was caused by fenitrothion, dichlorvos, pyrethrum, carbaryl, and acephate, respectively. The least amount of color change among all the specimens were observed for the untreated samples. The result of the high temperature and humidity test

showed that among the insecticides evaluated acephate, allethrin, carbaryl, dichlorvos, fenitrothion, malathion, pyrethrum and trichlorfon caused the greatest discoloration on the dyed carpet samples. The least amount of color change in this test was exhibited by lindane, methoxychlor, carboximide, and lethane 384. Diazinon, propetamphos, and chlorpyrifos caused less color change on than did the other organophosphates. Among the pyrethroids, allethrin was responsible for the greatest color change in this test.

In xenon exposure test, many of the insecticides decreased the lightfastness of the dyed samples. Fenitrothion, carbaryl, and trichlorfon were responsible for the greatest color change during light exposures. The pyrethroids also caused decreases in lightfastness. Minimal discolorations were obtained by the chlorinated hydrocarbon insecticides, dicarboximide which was the only a synergist, and Lethane 384 (12).

The AATCC study was the most comprehensive investigations on the influence of insecticides on dyed carpet. The CRI Committee only evaluated red acid and disperse dyestuffs, and a limited number of insecticidal chemicals (5). In the above studies, no attempt was made to identify the chemical mechanism responsible for discoloration, such as functional groups susceptible to deterioration by insecticides and the resulting chemical change.



The purpose of this study was to 1) investigate the effects of selected commercial insecticidal products (rather than pure form) on the colorfastness of acid and disperse dyes, 2) to evaluate the effects of inactive ingredients in the formulation on the same samples by comparing the data of this study with the AATCC study. This research is needed because emulsifiers, dilutents, and other product additives may influence the deleterious effects of insecticidal chemicals. This study included products representative of the insecticidal chemicals previously evaluated in AATCC study.

The commercial insecticides selected for evaluation were EPA-approved for home use. A few of the insecticides (fenitrothion, thrichlorfon, methoxychlor) were not represented in this study because they are no longer used in and about the home to control insect pests. The results of this study will be of benefit to carpet manufacturers in selecting dyes which are the least sensitive to various insecticides. It also will enable pesticide formulators to assess the combined effects of insecticidal chemicals and formulation additives on carpet discoloration.

## EXPERIMENTAL PROCEDURE

This study investigated the effects of 15 commercial insecticide products on the colorfastness of 21 acid dyes and 9 disperse dyes applied to nylon 6 carpet yarn. The carpet samples were treated with 5% (w/w) concentration of the insecticide products. The parameters examined were the influence of 1) standard temperature, 2) high temperature and humidity, 3) xenon light and 4) ozone exposure on the color of dyed and treated samples.

### Fabric

To facilitate insecticide application, subsequent exposure of the yarn to the four parameters of the study, and instrumental color evaluation, the ANSO 80-IV nylon 6 (Allied Fiber and Plastics Company) staple carpet yarns were constructed into 7.5 cm diameter single bar, circular filling knit test sleeves. They were cut into 8-meter lengths and then randomly assigned to the acid and disperse dyes. Fiber, yarn, and fabric properties as well as construction characteristics are specified in Table VI. Both the fiber type and yarn characteristics are typical of those used in the manufacturing of tufted residential carpeting.

TABLE VI  
Characteristics of Nylon 6 Fabric

---

Commercial name	ANSO 80-IV
Fiber type	T-880
Staple length	20 cm
Fiber denier	15
Cross-section	Trilobal
Luster	Bright
Yarn count	3's/2 ply
Twist	4.9z/4.2S
Heat set (yarn)	126°C
Fabric count:	
Wales/cm	2.7
Courses/cm	3.2
Fabric weight	599 g/m

---

## Dyestuffs

The acid and disperse dyes evaluated in this study were selected on the basis of hue, application class, and accepted usage on nylon carpet fibers. The C.I. Generic Names, C.I. Constitution Number, and chemical class for each dye are listed in Table VII.

The dyeing conditions used by Allied Fibers and Plastics in applying the acid and disperse dyes to the nylon fabric are specified below. All dyes were applied at a 0.5% owf depth of shade.

### Dyeing procedure for nylon 6 in Saucier sample back dyeing machine:

1. Liquid-to-goods ratio: 30:1
2. Set bath at 25°C, add 1.0% owf Triton X-100 wetting agent (for disperse dyebaths) or 1.0% owf Dowfax 2 Al leveling agent (for acid dyebaths), and run for 5 minutes.
3. Add dye (premix concentrate), adjust pH to  $7.0 \pm 0.2$  with monosodium phosphate, and run for 5 minutes.
4. Raise bath temperature 3°C/minute to the dyeing temperature of 96-98°C and run for 45 minutes.
5. Cool bath, dump, and rinse twice at 25°C for 10 minutes.
6. Centrifugal extract.
7. Dry at 120°C in Grieve oven for 30 minutes.

### Sample Preparation

The nylon knitted test sleeves (7.5 cm diameter, 18 cm circumference) were cut into samples measuring 12.7 x 17.8 cm and randomly assigned to the 15 pesticide treatments. Two random samples were used as the untreated controls. A total of 17

TABLE VII

## Rejected Acid and Disperse Dyes

Dye	Constitution Number	Constitution Class	Chemical Structure
Disperse Yellow 3	11825	Azo *	
Disperse Red 17	11218	Monazo *	
Disperse Red 369	---	Azo *	
Disperse Red 348	---	Monazo *	
Disperse Blue 3	61583	Anthraquinone *	
Disperse Blue 7	62288	Anthraquinone *	
Disperse Blue 26	63389	Anthraquinone *	
Disperse Violet 29	61162	Anthraquinone *	
Acid Red 37	---	Monazo *	
Acid Red 99	23283	Diazo *	

TABLE VII (continued)

Dye	Constitution Number	Constitution Class	Chemical Structure
Acid Red 114	23633	Diazso	
Acid Red 266	-----	azo *	
Acid Red 277	-----	Diazso *	
Acid Red 317	-----	Monazo *	
Acid Red 320	-----	azo *	
Acid Red 360	-----	Monazo *	
Acid Red 361	-----	-----	
Eastern Acid Red HSC	-----	-----	
Eastern Acid Red 2850R	-----	-----	
Acid Yellow 49	-----	azo *	
Acid Yellow 151	-----	Diazso *	
Acid Yellow 219	-----	-----	
Acid Blue 25	63805	Anthraquinone *	
Acid Blue 48	63125	Anthraquinone *	
Acid Blue 68	61385	Anthraquinone *	
Acid Blue 277	-----	Anthraquinone *	
Acid Blue 364	-----	Anthraquinone *	
Acid Orange 182	-----	-----	
Acid Orange 156	-----	Diazso *	

\* Dyes that have been suggested by Colloc Indes for dyeing nylon fiber.

samples were prepared from each dye type. The samples were then labeled with the appropriate insecticide/dyestuff codes.

#### Insecticide Treatment

The 15 commercial insecticide products selected for this study represented the major classes of insecticides that are frequently used in pesticide products EPA approved for home use. The major chemical classes of insecticides evaluated in this study were: organophosphate, pyrethroid, carbamate, and thiocyanate. The commercial name of each insecticide along with the class, common name, chemical name, and structural formula are given in Table VIII (28).

The insecticide solutions were prepared prior to each treatment to prevent degradation. The water-soluable insecticides were diluted to 5% (w/w) solutions with the proper amount of water, based on percentage of active ingredient in each commercial insecticide. The petroleum-soluble insecticides with less than 5% of the active ingredients were used in the concentrated form as packaged by the manufacturer. Table IX shows the percentage of active ingredient and recommended diluent for each of the insecticide products.

An immersion technique was selected for treating the carpet specimens with the insecticide solutions. The buret technique was not suitable for this project because the aqueous solutions of insecticides were not adsorbed readily by the nylon as were

TABLE VIII

## Selected Commercial Insecticide Products

Commercial Name	Common Name	Chemical Class	Chemical Name	Chemical Structure
Bonide House Hold Flea Killer	Lethane 364	Thiocyanate	Beta-butoxy beta-thiocyanodiethyl ether	$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{S}-\text{CN} \\   \\ \text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$
Baygon	Propoxur	Carbamate	2-Isopropoxyphenyl methylcarbamate	
Diazinon 4E	Diazinon	Organophosphate	O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyridinyl) phosphorothioate	$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \\   \\ \text{C}_2\text{H}_5\text{O}-\text{P}(=\text{S})-\text{O}-\text{N} \\   \quad   \quad   \\ \text{CH}_3 \quad \text{HC} \quad \text{CH}_3 \\ \quad \quad \quad   \\ \quad \quad \quad \text{C}_5\text{H}_4\text{N} \end{array}$
Dureban LO	Chlorpyrifos	Organophosphate	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate	
Dylox	Trichlorfon	Organophosphate	dimethyl(1-hydroxy-2,2,2-trichloroethyl)phosphonate	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\   \quad // \\ \text{CH}_3-\text{O}-\text{P}-\text{O}-\text{CH}_2-\text{C}(\text{OH})(\text{Cl})_2 \end{array}$
Everoid Cocoon-treats 2362	Fenvalerate	Pyrethroid	Cyano(3-phenoxypheyl)-methyl 4-chloro-alpha-(1-methylsilyl) benzeneacetate	
Flocsa W	Bendiocarb	Carbamate	2,2-dimethylbenzo-1,3-dioxolan-4-yl methylcarbamate	
Orthene	Acetate	Organophosphate	O,O-dimethyl N-acetylphosphorothioate	$\begin{array}{c} \text{CH}_3-\text{O} \\   \\ \text{CH}_3-\text{O}-\text{P}(=\text{S})-\text{NH}-\text{CO}-\text{CH}_3 \end{array}$



TABLE VIII (Continued)

Commercial Name	Common Name	Chemical Class	Chemical Name	Chemical Structure
Multicide Concentrate 215N	Phenothrin	Pyrethroid	3-phenoxybenzyl-4-cis & trans chrysanthemate	
Procox Malathion	Malathion	Organophosphate	O,O-dimethyl S-(1,2-di(ethoxy-carbonyl)ethyl) phosphorodithioate	$\text{CH}_3\text{O}-\text{P}(\text{S})_2-\text{CH}(\text{CO}-\text{O}-\text{CH}_2-\text{CH}_3)-\text{CH}_2-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_3$
Pyrocid Fogging Concentrate 7192	Pyrethrins	Pyrethroid	a series of ketonic alcohols and acids obtained from the flower of <i>Achysanthes almarianifolium</i>	
Safrotin	Propetaphos	Organophosphate	0,2-isopropoxyoxaronyl-1-methylvinyl 0-methyl ethylphosphor-salothioate	$\text{CH}_3\text{O}-\text{P}(\text{S})(\text{O}-\text{C}(\text{CH}_3)_2-\text{CH}(\text{O}-\text{CH}_2-\text{CH}_3)-\text{C}(\text{O}-\text{CH}_3)=\text{CH}_2)$
Sevio SL	Carbaryl	Carbamate	1-naphthyl methylcarbamate	
Syntax	Resmethrin	Pyrethroid	(5-benzyl-3-furyl)methyl-2,2-dimethyl-3-(2-methylpropenyl) cyclopropenyl cyclopropane	
Tapnite 2	Dichlorvos	Organophosphate	2,2-dichlorovinyl dimethyl phosphate	$\text{H}_3\text{CO}-\text{P}(\text{O})(\text{OCH}_3)-\text{O}-\text{CH}=\text{CCl}_2$

TABLE IX

## Percentage of Active Ingredient In Commercial Insecticide Products

Trade Name	Chemical Name	Rec. Conc.	% A.I.	5% Concentration	
				Actual Amount (gr)	H2O (ml)
Bonid House Hold Flea Killer	Lethane 384		3.1	1000.0	0.0
Baygon 70%	Propoxur	1.0%	76.0	71.4	928.6
Diazinon 4E	Diazinon	0.5-1.0%	47.0	105.3	894.7
Dursban L0	Chlorpyrifos	0.2-0.5%	42.0	119.0	881.0
Dylox Liquid Solution	Trichlorfon		40.5	123.5	876.5
Evercide Conc. 2362	Fenvalerate		7.1	280.9	719.1
Ficam W	Bendiocarb	0.1-0.5%	76.0	65.8	934.2
Multicide Conc. 2154	Phenothrin		25.0	200.0	800.0
Orthene PC0	Acephate	0.8-1.0%	97.0	51.6	948.4
Prentox Malathion 50% conc.	Malathion		50.0	100.0	900.0
Pyroicide Fogging Conc.	Pyrethrum		5.0	1000.0	0.0
Safrotin	Propetamphos	0.5-1.0%	50.0	100.0	900.0
Sevin SL	Carbaryl		43.0	116.3	883.7
Syntox	Resmethrin		2.5	1000.0	0.0
Vaponite 2	Dichlorvos	0.5%	24.7	202.4	797.6

the insecticide/acetone solutions (AATCC Study) (12). The droplets of insecticide solution maintained their spherical shape and ran off the surface of the substrate. Therefore, the amount of insecticide applied to the sample could not be controlled.

Because the buret application technique was not suitable, an immersion method was chosen for insecticide application. Immersion methods have been used in laundering studies on removing insecticide residues from contaminated textiles. The disadvantage of this method is that the add-on cannot be precisely controlled. Several preliminary tests were conducted to determine the most effective immersion time and concentration. The amount of insecticide solution applied to the sample was approximately equivalent to two times the weight of the sample's dry weight. The dry weight of untreated samples was recorded, samples were treated with the insecticide solution, and after allowing the samples to drip for two minutes, the samples were reweighed to determine the percent wet pickup.

Because insecticide discoloration of dyes usually occurs after repeated application, a 5% concentration was selected for insecticides treatment which is equivalent to approximately ten times the recommended concentration for the application of commercial insecticide products.

Pyrex dishes were used for specimen treatment. The specimens for each insecticide treatment were divided into two groups. The bottom of the Pyrex dish was covered with a sheet of fiber

glass screen. After filling the dish with the insecticide solution, the specimens were immersed in the solution for 5 minutes and subsequently removed by raising the fiber glass screen. After the samples were allowed to drip-dry for 2 minutes, they were placed in another Pyrex dish that was covered with two layers of paper towels to absorb excess solution. The specimens were placed individually on racks covered with aluminum foil and allowed to air dry in the fume hood.

After each series of insecticide applications, the Pyrex dishes and glassware were rinsed with acetone, washed with detergent solution, treated with a standard sulfuric acid and potassium dichromate solution for 30 minutes, washed, rinsed twice with acetone and distilled water, and air dried. Pesticide respirators and other protective clothing were used during treatment to minimize exposure of the researcher to the insecticides.

The same procedure was repeated for all insecticides used in this research. A total of 496 nylon samples were treated (includes controls). After treatment the samples were cut into four specimens and exposed to : 1) standard temperature, 2) high temperature and high humidity, 3) xenon light, and 4) ozone.

#### Standard Conditions

Individual pesticide-treated specimens (5.1 x 6.4 cm) were separated by Fisherband glass fiber filter circles (24 cm diameter), wrapped in Saran, and packed in zip-lock plastic bags. The bags were stored at standard temperature ( $21 \pm 3^{\circ}\text{C}$ ) for 1,000

hours, then instrumentally evaluated for color change.

#### High Temperature/ High Humidity Exposure

The purpose of this test was to determine whether or not the high temperature and high humidity would accelerate the color change of the insecticide-treated samples. A modification of the test developed by the Collins and Aikman Corporation (8), and specified in the AATCC study was used for this test. The specimens were inserted into one-pint mason jars containing 2.5 cm of water so that the bottom of the specimen was 5-8 cm above the top of the surface of the water. Figure 1 illustrates how the specimens were positioned in the jars. Subsequent to sealing, the jars were placed in an oven heated to 100<sup>0</sup>C for 8 hours, after which the samples were removed, air dried for 24 hours, and evaluated for color change.

#### Xenon Light Exposure

Two specimens each (10.0 x 6.5 cm) were mounted in Fade Ometer Test Mask No. 801-8A and stapled in place as shown in Figure 2. Covers A, B, C, and D then were removed from the masks prior to mounting them in the metal sample holders (Type SL).

The procedures in the AATCC Test Method 16E, Colorfastness to Light: Water Cooled Xenon-Arc Lamp, Continuous Light (1) were followed for the Xenon light exposure tests. Specimens were exposed for 80 AATCC Fading Units (AFU'S), based on the L6 Blue

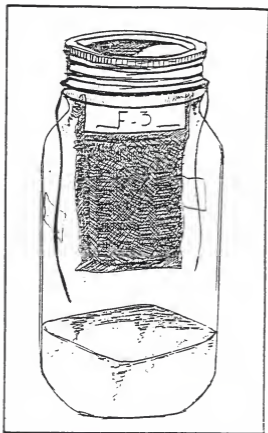
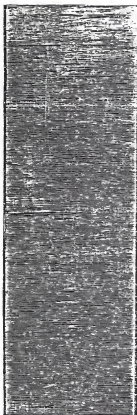


Figure 1. The inserting of the Specimen in the Jar for High Temperature/  
High Humidity Exposure.



(a)

SAMPLE IDENTIFICATION	
DATE	
485. 024	
070. 000	
A	
485. 024	
070. 000	
B	
FOB-1400	CONTROL
485. 024	
070. 000	
C	
485. 024	
070. 000	
D	
A	
B	
C	
D	
<small>APLUS ELECTRIC DEVICE CO. CHICAGO, ILL. 60613          FOG-METER TEST MASK NO. 25, 26          REVISED APRIL, 1962      PART NO. 1712-01</small>	

(b)

Figure 2. Placement of Specimens in Fade-Meter Test Mask (a) and Closed Test Mask with Covers A, B, C, and D, removed (b).

Wool lightfastness Standard, conditioned for 24 hours in a standard atmosphere ( $21 \pm 3^{\circ}\text{C}$ ,  $65 \pm 2\%$  RH), and then instrumentally evaluated for color change.

Test specimens was exposed simultaneously with a specimen (10.0 x 6.5 cm) of the L6 Blue Wool Lightfastness Standard until the latter showed "just appreciable fading" equal to a Step 4 on the AATCC Gray Color change which is equivalent to 80 AFU's of exposure.

Light exposures were continuous, except for stoppages necessary for routine maintenance (i.e., cleaning filters after 100 hours, changing inner filters after 300 hours or changing outer filters after 1,500 hours). The black panel thermometer temperature and relative humidity during lamp operation were  $63 \pm 1^{\circ}\text{C}$  and  $30 \pm 5\%$ , respectively.

An Atlas Xenon Arc Weather-Ometer was used for the tests. The Xenon burner tube (preaged) was fitted with borosilicate inner and outer glass filters which are used to simulate spectral radiation of average or typical sunlight. The Xenon burner tube was cleaned after every 100 hours and replaced or after 1,500 hours of use.

#### Ozone Exposure

Test were conducted to determine if the insecticides accelerated color change in selected acid and disperse dyes when exposed to ozone atmospheres at elevated temperatures and high humidities. Procedures in the AATCC Test Method 129,



Colorfastness to Ozone in the Atmosphere under High Humidity (1), were followed. The insecticide-treated specimens (13.0 x 6.5 cm) were exposed to two cycles of fade as determined by the Standard of Fading No. 129 for high humidities. For each cycle of fade, a swatch of Control Sample No. 129 was simultaneously exposed to ozone in an Atlas Ozone Chamber until the control samples showed a color change corresponding to the standard of fade. The exposure chamber was maintained at  $85 \pm 5\%$  relative humidity and  $40 \pm 5^{\circ}\text{C}$ . At the end of the exposure cycle, the test specimens were removed from the chamber and instrumentally evaluated for color change.

#### Color measurement

The degree of color change in the insecticide treated samples was evaluated instrumentally by the Hunterlab D25-M colorimeter and expressed in  $\Delta E$  (CIELAB) units for total color difference.  $\Delta E$  units are the root-mean-square difference between the  $L^*$ ,  $a^*$ ,  $b^*$  values for the exposed and unexposed samples as described by the following equation:

$$\Delta E_{\text{CIELAB}} = [ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 ]^{1/2}$$

The  $L^*$  value is a measure of the lightness and varies from 100 (white) to 0 (black). The  $a^*$  value represents redness when plus, gray when zero, and green when minus. The  $b^*$  value represents yellowness when plus, gray when zero, and blueness

when minus. The above equation only defines the magnitude of the color change, but not the direction. Therefore, it is possible that two samples may have the same  $\Delta E$  values but a different hue or visual appearance. The limits of visual detection are about 2-3 Hunter units of color change, depending on the color of the dye and the response of the observer (1).

#### Statistical Analysis

The color difference values ( $\Delta E$ ) of the undyed and dyed nylon specimens after insecticide treatment and exposure to standard temperature, high temperature and humidity, xenon light, and ozone were analyzed for significant differences using the analysis of variance procedure and the Duncan's Multiple Range Test for variance.

## RESULT AND DISCUSSION

This study investigated the effects of 15 commercial insecticide products on the colorfastness of 20 acid dyes and eight disperse dyes applied to nylon 6 carpet fibers. In addition, the color difference values attributed to insecticide treatment and exposure were compared with those obtained in the 1983 AATCC Study (12), which used 5% insecticide/acetone solutions, so that the effects of the inactive ingredients in formulated insecticides also could be evaluated.

Specimens were treated with 5% (w/w, active ingredient) solutions of each of the insecticide products, and exposed to standard temperature ( $21 \pm 3^{\circ}\text{C}$ ) for 1,000 hours, high temperature ( $100 \pm 5^{\circ}\text{C}$ ) and humidity for eight hours, xenon light for 80 AFU's, or ozone for two cycles of fade. The treated and exposed specimens were instrumentally evaluated for color change to determine the effects of the commercial insecticide products on the acid and disperse dyes.

The 15 commercial products evaluated in this study contained insecticidal chemicals that are members of the following major chemical classes of insecticides: carbamate, organophosphate, thiocyanate, and pyrethroid. The tradenames, chemical names, chemical classes, and chemical structures of the insecticide products are given in Table VIII.

A total of 1856 observations, representing 484 dye/insecticide combinations exposed to four test conditions, were analyzed statistically using the ANOVA Test and a Duncan's Multiple Range Test.

#### Standard Temperature

The color difference ( $\Delta E$ 's) values and descriptors for the type of color change that occurred in the undyed and the dyed nylon 6 specimens treated with the 15 insecticide products and exposed to standard temperature ( $21 \pm 3^{\circ}\text{C}$ ) for 1,000 hours are presented in Table X and XI, respectively. The rank order of the mean  $\Delta E$  values for the 16 insecticide treatments (15 insecticide products plus untreated), based on the Duncan's Multiple Range Test are listed in Table XII. A bar chart of the mean color difference values also was constructed to facilitate comparisons among insecticide products (see Figure 3).

As was expected, the insecticide products caused the least amount of color change in the undyed and dyed nylon in the standard temperature test, compared to the results obtain after exposure to high temperature and humidity, xenon light, and ozone. In general, Sevin SL was responsible for the greatest color change (mean = 14.8  $\Delta E$ ), and untreated samples had the least amount of color change (mean = 0.4  $\Delta E$ ) in the standard temperature test (see Figure 3). In addition to Sevin SL, the insecticide products that exhibited mean  $\Delta E$  values greater than 3.5 units were: Vaponite 2 (13.4  $\Delta E$ ), Ficam W (12.8  $\Delta E$ ), Baygon



TABLE XI

Discolorations For Color Change in the Dyes Treated  
With Insecticides and Exposed to Standard Temperature Test

Dyes Applied to Nylon	Baygon	Diazinon 4E	Datban 10	Dylox	Fyreside Concentrate 2362	Fyreside Concentrate 2154	Orthene	Fyreside Concentrate 7192	Saryston	Sylox SL	Sylox	Vadonite 20
Disperse Yellow 3	DCK											
Disperse Red 17	DCK											
Disperse Red 389	DCK											
Disperse Red 348	DCK											
Disperse Red 3	DCK											
Disperse Blue 7	DCK											
Disperse Blue 26	DCK											
Disperse Violet 28	DCK											
Acid Red 37	DCK											
Acid Red 92	DCK											
Acid Red 114	DCK											
Acid Red 124	DCK											
Acid Red 239	DCK											
Acid Red 337	DCK											
Acid Red 368	DCK											
Acid Red 368	DCK											
Eastman Acid Red NSC	DCK											
Acid Yellow 43	DCK											
Acid Yellow 43	DCK											
Acid Yellow 151	DCK											
Acid Yellow 151	DCK											
Acid Yellow 213	DCK											
Acid Blue 25	Gr-B											
Acid Blue 48	DCK											
Acid Blue 68	DCK											
Acid Blue 277	DCK											
Acid Blue 328	DCK											
Acid Orange 122	DCK											
Acid Orange 122	DCK											
Acid Orange 136	DCK											
Un dyed	Dckh Dk R											

5(E)3

Examples

Bleached = B  
 Blue = B1  
 Blue-Green = Br  
 Chalky = Ch  
 Creamy = C  
 Barter = Dk  
 Duller = D  
 Grayer = D  
 Greenish = Gr  
 Lighter = L  
 Purplish = P  
 Redder = R  
 Weaker = M  
 Whiter = Wh  
 Yellow = Y  
 Soots (stains) = S  
 Orange = O  
 Greenish-Blue = GrBl  
 Greenish-Purple = GP  
 Purplish-Red, Dull = PRD  
 Black Spots = BS  
 White Chalky Residue = MCh

Table XII

Duncan's Multiple Range Test on Mean Color Difference Values ( $\Delta E$ 's) for Insecticide in the Standard Temperature Test

Insecticide	Mean $\Delta E$	Groupings *
Sevin SL	14.8	A
Veponite 2	13.4	A B
Ficam W	12.8	A B
Baygon	10.4	A B
Dylox	9.9	C B
Pyrocid Fogging		C B
Concentrat 7192	9.8	C B
Prentox Malathion	8.7	C B
Orthene	5.8	C E
Diazinon 4E	4.6	F E
Safrotin	3.9	F E
Syntox	3.9	F E
Dursban LO	3.4	F E
Multicide Concen- trate 2154		F E
Evercide Concen- trate 2362	3.3	F E
Bonide Flea Killer	1.7	F E
Untreated	0.4	F

\*Means with the same letter are not significantly different.



Figure 3. Bar Chart of Mean Color Difference Values ( $\Delta E$ 's) for Insecticides in the Standard Temperature Test.



(10.4  $\Delta E$ ), Dylox (9.9  $\Delta E$ ), Pyrocidate Fogging Concentration (9.8  $\Delta E$ ), Prentox Malathion (8.7  $\Delta E$ ), Orthene (5.8  $\Delta E$ ), Diazinon 4E (4.6  $\Delta E$ ), Safrotin (3.9  $\Delta E$ ), and Syntox (3.9  $\Delta E$ ). [Note: Based on AATCC Gray Scale for Color Change, a "noticeable change" is Step 3 rating, which is equal to  $3.5 \pm 0.4 \Delta E$  CIELAB units]. Conversely, the least amount of color change occurred in the specimens treated with the following insecticides types: untreated (0.4  $\Delta E$ ), Bonide House Hold Flea Killer (1.7  $\Delta E$ ), Evercide Concentrate 2362 (3.0  $\Delta E$ ), Multicide Concentrate 2154 (3.3  $\Delta E$ ), Dursban LO (3.4  $\Delta E$ ). The mean  $\Delta E$  values for these insecticide products was less than 3.5 units (see Table XII and Figure 3). However, generalizations concerning the overall deleterious effects of these insecticide products must be stated judiciously since, in many instances, a high mean color difference values was attributed to a selected number of dyes, rather than to discoloration of many dyes. For example, many of the dyes treated with Vaponite 2, Dylox, Prentox Malathion, Orthene, Diazinon 4E, Safrotin, and Syntox showed no appreciable color change; and the high mean color difference values were attributed a few select dyes that exhibited considerable color change. Conversely, some of the insecticide products such as Sevin SL, Ficam W, and Baygon caused appreciable color change in the majority of dyes.

As shown in Table X, the distribution of the  $\Delta E$  values for the 29 dyes for certain insecticides was very wide; hence, the

amount of color change among dye types varied greatly and depended on dye/insecticide combination. In addition, the dye/insecticide combinations that exhibited the greatest amount of color change also was influenced by exposure condition. In the standard temperature test, Vaponite 2, Dylox, Orthene, and Prentox Malathion exhibited the greatest range between the highest and lowest color difference values for specific dye types. For example, Vaponite 2 (dichlorvos) with the mean  $\Delta E$  value of 13.4, had values that ranged from of 1.2 (C.I. Acid Red 299) to 77.4 (Eastman Acid Red KSC) for individual dye types. Dylox (trichlorfon) had values that ranged from 0.9 (C.I. Acid Blue 40) to 58.9 (Eastman Acid Red KSC), Orthene (acephate) had  $\Delta E$  values that ranged from 0.4 (undyed) to 55.3 (Eastman Acid Red KSC), Prentox Malathion had  $\Delta E$  values that ranged from 1.1 (C.I. Acid Red 99) to 48.2 (C.I. Acid Red 360) units, and Diazinon 4E had  $\Delta E$  values that ranged from 1.0 (C.I. Acid Red 114) to 22.0 (C.I. Acid Red 360). All five of the above insecticides belong to the organophosphate chemical class of insecticides. These insecticide products caused a dramatic color change from red to purple or dark blue on the following red dyes, as evidenced by the extremely high  $\Delta E$  values: Eastman Acid Red KSC, C.I. Acid Red 360, Eastman Acid Red 2BDR, and C.I. Disperse Red 17 (see Tables X and XI). These results support the premise that selected acid and disperse red dyes are sensitive to some organophosphates insecticides. Two of the products containing

organophosphate insecticides, Dursban (chlorpyrifos) and Safrotin (proprtamphos), did not cause the dramatic hue shift in the above acid and disperse red dyes. In general, the organophosphate insecticides caused the greatest color change on selected acid and disperse red dyes. Many of the acid and disperse blue dyes and some of the acid and disperse red dyes were not appreciably affected by the organophosphate insecticide products (see Table X).

The Bonide House Hold Flea Killer containing Lethane 384, a thiocyanates insecticide, had the lowest mean  $\Delta E$  value (1.7) of all of insecticides products evaluated with color difference values for individual dyes ranging from 0.1 to 4.7  $\Delta E$  units. Except for C.I. Acid Yellow 151, C.I. Acid Blue 40, and C.I. Disperse Violet 28, the  $\Delta E$  values were less than 3.0 for all of the dyes treated with this insecticide product.

Sevin SL which contained carbaryl, a carbamates insecticide, caused appreciable color change in all of the dyes in the standard temperature test with values ranging from 7.4 to 21.6  $\Delta E$  units. It also exhibited the highest mean color difference value (14.8  $\Delta E$ ) among all of the products evaluated in this study. The color change appeared to be attributed to a "chalky" surface coating deposited on the surface of the samples which modified the apparent color of the dyes, rather than an actual color change in the dyes themselves. Similar effects were observed in the specimens treated with the other carbamate insecticide

products [Baygon (propoxur) and Ficam W (bendiocarb)]. Baygon and Ficam W, both powder-soluable insecticides, left a beige residue on the fabric which imparted a duller or dirtier appearance to the actual color of the samples. This effect was even more obvious in the undyed white nylon samples.

As mentioned previously, the rank order of the mean color difference values for the insecticide treatments in the standard temperature test are presented in Table XII. The mean  $\Delta E$  value for undyed (white) nylon samples was the fourth highest value in this test, indicating that the insecticide formulations were responsible for color changes in the undyed nylon. Insecticide products that caused appreciable color change in the undyed nylon samples were Baygon, Ficam W, and Sevin SL all of which are carbamate insecticides. The insecticide products that had a petroleum base (Pyrocide Fogging Concentration and Syntox) also caused appreciable color change in the undyed nylon samples. These oil based insecticides left a heavy yellowish residue on the dyed and undyed samples. Pyrocide Fogging Concentration caused the highest color difference value on undyed samples (mean  $\Delta E = 38.5$  units). Among the organophosphate insecticides applied to the undyed samples, Safrotin caused the greatest amount of color change in the undyed nylon. Diazinon 4E, Dursban LC, and Prentox Malathion also caused considered color change on the undyed nylon with  $\Delta E$  values of 5.0 to 6.0. Dylox, Orthene, and Vaponite 2 (organophosphate insecticides) caused minimal color

change on the undyed nylon with  $\Delta E$  values less than 1.2 units.

The results of the Duncan's Multiple Range Test performed on the means for the 29 dye types are presented in Table XIII. Eastman Acid Red KSC, C.I. Acid Red 360, and Eastman Acid Red 2BDR, respectively, exhibited the highest  $\Delta E$  values, compared to the other dye types in standard temperature test. The lowest mean color difference value in this test was obtained for C.I. Acid Red 361 (3.5  $\Delta E$ ), however, it was still considered as noticeable change (Step 3 rating of AATCC Gray Scale).

C.I. Acid Red 360 and C.I. Disperse Red 17 are azo dyes that contain the -N=N- chromophore in their structures. There were no chemical classes, constitution numbers or structural formulas available in Colour Index for Eastman Acid Red KSC and Eastman Acid Red 2BDR. As mentioned previously, selected organophosphate insecticide products (Diazinon 4E, Dylox, Orthene, Prentox Malathion, and Vaponite 2) caused a dramatic hue shift from red to purple or dark blue in these dyes, resulting in high individual as well as mean color difference values.

#### High Temperature and Humidity

The color difference values ( $\Delta E$ 's) and color change descriptors for the dyed and undyed specimens treated with the insecticide products and exposed to eight hours of high temperature ( $100 \pm 5^\circ\text{C}$ ) and humidity are given in Tables XIV and XV. The results of the Duncan's Multiple Range Test and bar chart on the mean color difference values for the insecticide products are

Table XIII

Duncan's Multiple Range Test on Mean Color Difference Values ( $\Delta E$ 's) for Dye Types in the Standard Temperature Test

Dye Applied to Nylon	Mean $\Delta E$	Groupings *
Eastman Acid Red KSC	18.7	A
C.I. Acid Red 360	17.6	A
Eastman Acid Red 2BDR	17.0	A
Undyed	9.4	B
C.I. Disperse Red 17	9.2	B
C.I. Disperse Violet 28	7.6	B
C.I. Acid Blue 277	6.8	B
C.I. Disperse Blue 3	6.8	B
C.I. Acid Blue 25	6.5	B
C.I. Acid Blue 324	6.3	B
C.I. Acid Blue 80	6.3	B
C.I. Disperse Red 340	6.3	B
C.I. Acid Orange 152	6.2	B
C.I. Acid Yellow 49	6.1	B
C.I. Disperse Blue 26	6.1	B
C.I. Acid Yellow 219	5.6	B
C.I. Acid Blue 40	5.1	B
C.I. Acid Yellow 151	5.1	B
C.I. Acid Orange 156	4.9	B
C.I. Disperse Yellow 3	4.8	B
C.I. Disperse Blue 7	4.7	B
C.I. Acid Red 57	4.6	B
C.I. Acid Red 337	4.5	B
C.I. Acid Red 299	4.3	B
C.I. Acid Red 99	4.1	B
C.I. Disperse Red 309	3.9	B
C.I. Acid Red 266	3.8	B
C.I. Acid Red 114	3.7	B
C.I. Acid Red 361	3.5	B

\* Means with the same letter are not significantly different.

TABLE XIV  
Colorfastness of Dye Treated with Insecticides and Exposed to High Temperature and Humidity  
Color Difference,  $\Delta E$  (CIELAB) Units

Dyes Applied to Nylon	Positive Dyeing Hold	Purple Killer	Baygon	Diazinon 4F	Butron LD	Dylon	Evercide Concentr	Floran K	Mallinckrodt	Terz 2154	Orthene	Terzox Methylate	Tyrocide Fasting Concentrate 7192	Safocin	Devlo SL	Synon	Spanite 2	Overcast
Disperse Yellow 3	4.7	6.3	5.1	3.8	38.0	2.0	18.9	4.4	8.6	12.2	18.8	4.7	8.2	2.6	16.2	1.7		
Disperse Red 17	3.7	7.0	5.9	2.2	38.8	4.1	12.2	3.4	11.8	17.4	9.4	4.1	12.3	3.2	36.0	1.8		
Disperse Red 348	1.6	4.4	2.7	7.2	58.6	2.3	13.0	3.0	7.3	21.9	8.3	18.2	17.8	2.9	8.0	8.4		
Disperse Blue 3	1.5	15.2	4.2	3.7	18.0	6.3	23.0	2.1	8.6	8.5	24.7	6.2	11.5	3.1	9.2	0.8		
Disperse Blue 7	1.3	18.0	2.1	3.7	3.7	4.2	15.0	2.0	8.6	2.4	17.7	2.6	9.4	5.8	3.8	1.8		
Disperse Blue 26	4.0	17.4	2.4	2.3	7.0	3.1	25.1	3.6	1.9	2.7	25.2	2.6	11.6	7.6	4.3	2.0		
Disperse Violet 28	4.0	11.4	7.4	6.3	7.5	3.9	22.8	7.1	2.1	6.4	33.8	6.8	13.2	18.1	7.2	8.0		
Acid Red 59	2.1	7.7	2.7	2.7	25.7	1.9	11.2	2.7	8.3	4.2	18.6	1.6	4.8	4.2	11.8	8.6		
Acid Red 114	2.2	7.2	1.2	1.4	3.9	3.7	8.9	2.6	1.1	8.6	3.8	2.9	6.3	2.3	2.9	8.7		
Acid Red 255	2.0	6.3	1.9	8.3	16.4	2.6	17.0	3.0	1.7	6.1	6.8	2.1	5.3	2.4	2.4	8.4		
Acid Red 259	2.4	18.4	2.4	4.8	2.7	2.3	9.9	3.2	3.3	6.7	18.7	1.8	3.7	3.6	5.3	8.3		
Acid Red 277	2.1	6.0	2.1	2.3	34.7	2.9	12.8	3.1	1.6	4.2	6.7	18.7	8.9	4.3	1.5	1.9		
Acid Red 368	2.8	7.2	6.9	15.8	58.5	2.5	12.8	4.4	14.5	62.2	7.7	14.0	9.4	2.7	48.1	2.4		
Acid Red 361	1.7	7.3	1.2	2.3	19.1	2.5	7.8	1.8	8.3	3.8	3.8	7.9	1.7	2.6	3.9	9.5	1.3	
Eastern Acid Red HSC	8.0	6.4	3.2	15.7	63.2	2.9	18.5	3.2	62.3	63.0	7.1	11.7	5.8	2.1	73.7	1.2		
Eastern Acid Red 280R	1.1	7.8	7.6	21.4	62.7	2.4	18.4	2.9	41.4	68.4	6.2	13.3	3.2	2.3	66.1	1.8		
Acid Yellow 151	2.8	18.2	2.9	2.4	4.9	2.4	28.3	7.8	8.8	3.6	23.1	2.6	17.1	1.9	4.4	8.6		
Acid Yellow 219	1.6	12.6	3.4	7.9	18.3	3.7	22.9	3.8	8.9	3.4	9.6	2.5	7.5	5.7	1.2	8.6		
Acid Blue 23	1.7	12.1	3.3	3.1	8.8	2.6	25.3	2.9	5.8	24.4	22.3	2.8	18.2	4.2	3.2	1.5		
Acid Blue 48	3.4	9.1	4.4	4.2	18.1	3.2	18.6	2.9	1.6	3.2	15.7	4.9	18.1	2.8	7.6	1.7		
Acid Blue 88	2.4	17.3	2.2	3.3	2.3	2.8	18.0	2.8	8.8	1.1	23.3	2.1	12.5	2.3	2.8	8.6		
Acid Blue 277	1.7	17.1	2.8	2.6	5.3	2.2	23.0	2.5	1.8	3.7	23.6	1.4	11.3	4.3	3.9	8.6		
Acid Blue 304	2.2	14.6	3.6	3.1	36.3	4.8	17.0	2.5	1.8	9.2	17.3	2.9	14.1	4.2	16.7	1.3		
Acid Orange 152	1.9	9.6	7.8	9.9	1.8	3.8	22.4	4.8	1.2	38.2	18.7	8.1	15.5	3.2	4.8	1.2		
Acid Orange 156	1.8	3.9	7.2	7.6	2.6	2.3	19.4	2.0	9.9	59.6	9.8	3.2	12.4	2.9	2.7	1.4		
Un dyed	6.0	28.5	6.8	5.2	3.8	2.9	26.5	5.1	1.2	2.9	31.2	9.6	13.9	17.8	3.0	2.2		

TABLE XV

Disclosures for Color Change in the Dyes Treated with Insecticides and Exposed to High Temperature and Humidity Test

Dyes Applied to Nylon	Spindle House No.	Flare Killer	Region	Distortion	Durability	Dye	Acidic Content	Temp 25±2	Temp 5	Melted Concentr.	Orthox	Preox. Malathion	Preox. Forging Concentr. 1:1	Preox. 1	Sp. 15	Sp. 10	Sp. 5
Disperse Yellow 3	MCH					DND						M	VD	D			
Disperse Red 17	MCH					DND						LPHB	VD	D	DCK		
Disperse Red 309	MCH					DND						LPHB	VD	DH	DCK		
Disperse Red 348	MCH					PhH						LPHB	VD	D	DCK		
Disperse Blue 7	MCH					D							VD	D	DCK		
Disperse Blue 26	MCH					D							VD	D	DCK		
Disperse Violet 20	MCH					D							VD	D	DCK		
Acid Red 95	MCH					LPH						M	VD	D	DCK		
Acid Red 114	MCH					LPH						DND	VD	D	DCK		
Acid Red 266	MCH					LPH						DND	VD	D	DCK		
Acid Red 299	MCH					LPH						B	VD	D-P	DCK		
Acid Red 777	MCH					LPH						M	VD	D	DCK		
Acid Red 349	MCH					PhH						PhH	VD	DPR	DCK		
Acid Red 361	MCH					DND						PhH	VD	DPR	DCK		
Eastern Acid Red 85C	MCH					DND						PhH	VD	DPR	DCK		
Eastern Acid Red 20DR	MCH					DND						PhH	VD	DPR	DCK		
Acid Yellow 49	MCH					Dk						M	VD	D	DCK		
Acid Yellow 151	MCH					Dk						M	VD	D	DCK		
Acid Yellow 219	MCH					Dk						Lp	VD	D	DCK		
Acid Blue 23	MCH					Dk						D	VD	D	DCK		
Acid Blue 48	MCH					D						D	VD	D	DCK		
Acid Blue 277	MCH					DH						D	VD	D	DCK		
Acid Blue 277	MCH					DH						D	VD	D	DCK		
Acid Blue 354	MCH					DH						DND	VD	D	DCK		
Acid Blue 354	MCH					Gr-B1						DND	VD	D	DCK		
Acid Orange 152	MCH					DND						LPH	VD	D	DCK		
Acid Orange 152	MCH					DND						LPH	VD	D	DCK		
Acid Orange 152	MCH					DND						LPH	VD	D	DCK		
Unyad	MCH					C						LPH	VD	D	DCK		
Unyad	MCH					YMH						LPH	VD	D	DCK		

KEYS:

- Bleached = B
- Black = Bl
- Brownish = Br
- Chalky = Ch
- Creasy = C
- Darker = Dk
- Dull = D
- Grayed = G
- Light = L
- Lighter = Lr
- Chalky = Ch
- Creasy = C
- Darker = Dk
- Dull = D
- Washed = W
- Yellowed = Y
- Spots (beetles) = S
- Water = W
- Miter = M
- Spots (beetles) = S
- Greenish-Blue = Gr-B1
- Brown-Purple = Br
- Purple-Red, Dull = Pr-D
- Light Blue = LB
- White Chalky Residue = WCh



presented in Table XVI and Figure 4. The untreated dyed and undyed samples exhibited a mean color difference value of 1.1, and individual  $\Delta E$  values ranged from 0.3 to 2.2. Hence, the high temperature and humidity condition itself did not cause appreciable color change in the untreated nylon samples.

Because these conditions often accelerate reaction rates, it was expected that the result of the high temperature and humidity test would be similar to standard temperature test in terms of insecticide/dye combinations with the greatest amount of color change, but with higher  $\Delta E$  values. However, unlike the standard temperature test, Prentox Malathion caused the greatest amount of color change among the 15 insecticide products evaluated. The mean  $\Delta E$  value of this insecticide was 22.6, compared with the lowest mean  $\Delta E$  value of 1.1 for untreated samples. Minimal color change occurred in the dyed specimens treated with the following insecticide products (mean  $\Delta E$ 's): untreated (1.1  $\Delta E$ ), Bonide (2.0  $\Delta E$ ), Evercide Concentrate 2362 (3.0  $\Delta E$ ), Diazinon 4E (3.6  $\Delta E$ ), and Multicide Concentrate 2154 (3.8  $\Delta E$ ). These insecticides had mean  $\Delta E$  values less than 4.0 units. Insecticide products causing mean color difference values above 4.0 in this test were as follows: Prentox Malathion (22.5  $\Delta E$ ), Dylox (18.7  $\Delta E$ ), Ficam W (16.8  $\Delta E$ ), Vaponite 2 (15.1  $\Delta E$ ), Pyroicide Fogging Concentrate 7192 (14.7  $\Delta E$ ), Baygon (10.4  $\Delta E$ ), Sevin SL (9.3  $\Delta E$ ), Dursban LO (5.9  $\Delta E$ ), Orthene (5.6  $\Delta E$ ), Safrotin (5.5  $\Delta E$ ), and Syntox (4.5  $\Delta E$ ) (see Figure 4).

Table XVI

Duncan's Multiple Range Test on Mean Color Difference Values ( $\Delta E$ 's) for Insecticides in the High Temperature and Humidity Test

Insecticide	Mean $\Delta E$	Groupings *
Prentox Malathion	22.5	A
Dylox	18.7	A B
Fican W	16.7	B
Vaponite 2	15.2	C B
Pyrocide Fogging		C B
Concentrate 7192	14.8	C B
Baygon	10.4	C D
Sevin SL	9.3	C D E
Dursban LO	5.9	F D E
Orthene	5.6	F D E
Safrotin	5.5	F D E
Syntox	4.5	F E
Multicide		F E
Concentrate 2154	3.8	F E
Diazinon 4E	3.6	F E
Evercide		F
Concentrate 2362	3.0	F
Bonide Flea Killer	2.0	F
Untreated	1.1	F

\*Mean with the same letter are not significantly different.



Figure 4. Bar Chart of Mean Color Difference Values ( $\Delta E$ 's) for Insecticides in the High Temperature and High Humidity Test.

Individual color difference values for the dyed specimens treated with Prentox Malathion, which caused the greatest color change among all of insecticides, ranged from 1.1 (C.I. Acid Blue 80) to 69.4 (C.I. Acid Yellow 219)  $\Delta E$  units (see Table XIV). Prentox Malathion caused the greatest amount of color change on the following dyes in the high temperature and humidity test: C.I. Acid Yellow 219, C.I. Acid Red 299, Eastman Acid Red KSC, C.I. Acid Red 360, Eastman Acid Red 2BDR, C.I. Acid Orange 156, C.I. Disperse Red 309, C.I. Acid Orange 152, C.I. Disperse Red 17, and C.I. Disperse Red 340. In some instance, the types of color changes that occurred in this test differed from those that were observed in the dyed specimens after exposure to standard temperature (see Table X). For example, some of the dyes treated with Prentox Malathion and exposed to high temperature and humidity exhibited a substantial color loss (bleached or lightened appearance) or a combination of a hue shift with substantial whitening (i.e., C.I. Disperse Red 17, 309, and 340; C.I. Acid Red 299, and 360; Eastman Acid Red KSC and 2BDR; C.I. Acid Yellow 219; and C.I. Acid Orange 152, and 156). Dylox (trichlorfon) also caused some of these acid and disperse dyes to become appreciably lighter (see Table XV). The other organophosphate insecticide products [Dursban (chlorpyrifos), Dylox (trichlorfon), Vaponite 2 (dichlorvos), Orthene (acephate), Safrotin (propetamphos), and Diazinon 4E] did not exhibit this pronounced bleaching effect. Vaponite 2 caused the greatest

amount of color change among all of the products tested on the following dyes: C.I. Acid Red 360, Eastman Acid Red KSC and 2BDR. These red dyes had a hue shift to dark blue color. In addition, other acid and disperse red dyes exhibited appreciable color change when treated with this insecticide. Only eight of the 29 dye types had  $\Delta E$  values of less than 3.5 when treated with Vaponite 2. Minimal color change occurred in the dyed specimens treated with Diazinon 4E, Orthene, and Safrotin, except for a few acid and disperse red dyes that become darker, or duller.

Sevin SL (carbaryl), Ficam W (bendiocarb), and Baygon (propoxur), the carbamate insecticide products, appreciably discolored the majority of the dye types. The majority of the dyed specimens treated with Baygon and Ficam W exhibited color difference values above 4.0  $\Delta E$  units (see Table XIV) in the high temperature and humidity conditions. Except for C.I. Acid Red 361, all dye types discolored appreciably when treated with Sevin SL.

The pyrethroid insecticide products, Evercide Concentrate 2362 (fenvalerate), Multicide Concentrate 2154 (phenothrin), and Syntox (resmethrin), also varied in the amount and type of color change they induced. In general, however, the pyrethroids caused less color change in the acid and disperse dyes than did the organophosphate and carbamate insecticide products. Among the pyrethroid products evaluated, Syntox exhibited the highest mean color difference value, followed by Multicide Concentrate 2154

and Evercide Concentrate 2362 which had a significantly lower mean  $\Delta E$  values (see Table XVI). Pyroicide Fogging Concentrate 7192, with a mean  $\Delta E$  value of 14.7, had individual  $\Delta E$  values ranging between 5.7 and 33.0. Pyroicide Fogging Concentrate 7192 appreciably discolored all of the dyed and undyed samples in high temperature and humidity test.

Similar to the result of the standard temperature test, Bonide House Hold Flea Killer (lethane 384) had the lowest mean  $\Delta E$  value among all of the insecticide products evaluated in this test (see Table XVI and Figure 4). Except for undyed sample (6.8  $\Delta E$ ) and C.I. Disperse Violet 28 (4.8  $\Delta E$ ), the dyed samples treated with this insecticide exhibited  $\Delta E$  values less than 3.3 which was not considered noticeable change (see Table XIV).

The undyed samples obtained the sixth highest mean color difference value (10.4  $\Delta E$ ) among the 16 insecticide treatments (see Table XVI). The undyed samples also exhibited similar mean  $\Delta E$  value in standard temperature test. The insecticide treatments that caused the greatest amount of discoloration (i.e.,  $\Delta E$  values greater than 10.0) in the undyed nylon were Pyroicide Fogging Concentrate 7192 (pyrethrum), Ficam W (bendiocarb), Baygon (propoxur), Syntox (resmethrin), and Sevin SL (carbaryl). All of the carbamate insecticides caused a great amount of color change on undyed samples. These wettable-powder insecticides left brownish residues on both the white and dyed samples. Oil base insecticides (Pyroicide Fogging Concentrate and Syntox) also left

a yellowish oil residue on the surface of the samples which changed the actual color of the dye and undyed samples.

The results of the Duncan's Multiple Range Tests performed on the means for the 29 dye types are presented in Table XVII. Among the 29 dyes evaluated, Eastman Acid Red KSC, C.I. Acid Red 360, Eastman Acid Red 2BDR exhibited the highest mean color difference values among the dyes evaluated. Conversely, C.I. Acid Red 114, C.I. Acid Red 266, and C.I. Acid Red 99 had the lowest mean color difference values in high temperature and humidity test, which is similar to the result observed in standard temperature test.

Comparing the results of high temperature test to the standard temperature test, it can be concluded that with the exception of Sevin SL, color change ( $\Delta E$  values) on the insecticide treated specimens increased with high temperature and humidity. In both tests, the color difference values of the samples treated with Sevin SL were noticeable, except for two dyes in high temperature and humidity test which had  $\Delta E$  values less than 4.0.

All dyed specimens treated with Prentox Malathion and exposed to high temperature and humidity exhibited appreciably higher  $\Delta E$  values, compared to the results of the standard temperature test. For example, C.I. Acid Orange 152, C.I. Acid Orange 156, and C.I. Acid Red 299 were the only three dye types with  $\Delta E$  values less than 4.0 units in standard temperature test;

Table XVII

Duncan's Multiple Range Test on Mean Color Difference Values ( $\Delta E$ 's) for Dyes Types in the High Temperature And Humidity Test

Dyes	Mean $\Delta E$	Groupings *
Eastman Acid Red KSC	21.3	A
Eastman Acid Red 2BDR	19.5	B A
C.I. Acid Red 360	18.2	B A
C.I. Disperse Red 340	12.0	B D C
C.I. Disperse Red 17	11.2	B D C
Undyed	10.5	D C
C.I. Acid Yellow 219	10.3	D C
C.I. Acid Orange 152	9.5	D
C.I. Acid Blue 324	9.5	D
C.I. Disperse Violet 28	9.4	D
C.I. Disperse Red 309	9.1	D
C.I. Acid Orange 156	9.1	D
C.I. Acid Red 299	9.0	D
C.I. Disperse Blue 3	8.8	D
C.I. Disperse Yellow 3	8.6	D
C.I. Acid Yellow 49	8.0	D
C.I. Disperse Blue 26	7.8	D
C.I. Acid Blue 25	7.5	D
C.I. Acid Blue 277	7.0	D
C.I. Acid Red 337	6.7	D
C.I. Acid Blue 80	6.5	D
C.I. Acid Red 57	5.9	D
C.I. Disperse Blue 7	5.6	D
C.I. Acid Blue 40	5.6	D
C.I. Acid Yellow 151	5.2	D
C.I. Acid Red 361	4.7	D
C.I. Acid Red 99	4.2	D
C.I. Acid Red 266	4.1	D
C.I. Acid Red 114	3.8	D

\*Means with the same letter are not significantly different.



whereas, the  $\Delta E$  values of these dyes increased to greater than 50.0 in the high temperature and humidity test. Therefore, it can be concluded that the combination of malathion and high temperature and humidity has a great effect on the discoloration of the dyed samples.

#### Xenon Light

The color difference values and color change descriptors for the undyed and dyed samples treated with the commercial insecticide products and exposed to 80 AFU's of xenon light are given in Tables XVIII and XIX. The corresponding mean  $\Delta E$  values and bar chart based on insecticide type are presented in Table XX and Figure 5.

The untreated samples exhibited the least amount of fading during xenon light exposure (mean  $\Delta E = 3.2$ ). Among the untreated samples, C.I. Acid Red 360 (15.6  $\Delta E$ ) had the greatest amount of fading during xenon light exposure, followed by C.I. Disperse Blue 3 (6.8  $\Delta E$ ), C.I. Disperse Red 17 (5.4  $\Delta E$ ), C.I. Acid 299 (4.9  $\Delta E$ ), C.I. Acid Blue 324 (4.8  $\Delta E$ ), and C.I. Acid Red 361 (4.2  $\Delta E$ ). Many of the dyes without insecticide treatment exhibited good lightfastness properties which was expected since carpet dyes are often selected on the bases of lightfastness. In particular, 23 of the 29 evaluated dyes had  $\Delta E$  values less than 4.0, and in many instances there was no appreciable fading after 80 AFU's of light exposure.

In general, the insecticide products that caused the

TABLE XVIII

Colorfastness of Dyes Treated with Insecticides and Exposed to Xenon Light Exposure

Dyes Applied to Nylon	Color Difference, $\Delta E$ (CIELAB) Units																	
	Peroxide Bleach Hold	Saygon	Oxartins 42	Outback LD	Nylon	Overlaid Concentr.	State 20A1	State V	Malicide Concentr.	State 2124	Others	Fronton Malathion	7-Fenothal Foliage Concentrate 1192	Ketocin	Perwin SL	Pyron	Spacite 2	Overcast
Disperse Yellow 3	1.6	7.4	2.7	4.1	6.8	7.2	2.3	2.3	3.8	1.1	1.1	3.4	13.5	5.8	28.4	3.1	26.1	1.2
Disperse Red 17	7.0	6.2	3.3	4.4	32.6	6.7	13.1	6.1	3.5	4.7	3.5	3.6	13.5	5.8	28.4	3.1	26.1	1.2
Disperse Red 389	7.0	6.4	3.1	6.4	32.6	6.2	12.6	6.1	3.5	4.7	3.5	3.6	13.5	5.8	28.4	3.1	26.1	1.2
Disperse Red 349	7.7	6.7	3.9	5.6	34.0	5.2	13.5	7.4	6.3	6.3	28.5	29.2	4.6	42.6	6.2	33.6	5.4	3.4
Disperse Blue 3	6.6	12.4	3.9	13.3	28.4	6.9	24.0	7.0	7.4	7.4	12.0	32.0	3.9	33.2	16.2	18.6	16.6	6.0
Disperse Blue 7	7.0	9.3	3.8	7.2	11.0	6.3	19.3	4.7	4.0	4.0	2.0	19.7	3.4	41.4	7.6	12.6	16.6	3.6
Disperse Blue 26	13.0	13.3	10.3	13.6	26.0	10.3	27.8	12.3	14.2	14.2	13.9	31.7	6.2	22.0	15.0	23.1	3.2	3.2
Disperse Violet 28	19.8	13.2	7.3	12.0	22.6	7.7	26.3	12.2	7.0	7.2	2.2	17.4	12.3	2.3	48.2	6.4	24.6	3.2
Acid Red 37	4.7	7.3	2.7	2.6	6.4	12.4	11.9	7.2	2.9	2.9	2.6	2.6	2.0	2.2	22.4	3.7	10.7	2.2
Acid Red 39	4.7	6.9	2.7	2.6	6.4	12.4	11.9	7.2	2.9	2.9	2.6	2.6	2.0	2.2	22.4	3.7	10.7	2.2
Acid Red 114	5.4	6.8	2.5	2.3	6.0	6.0	9.1	7.9	3.2	3.2	3.2	9.1	3.0	2.2	32.2	4.2	21.5	2.7
Acid Red 255	4.9	3.7	2.0	2.3	24.3	3.8	7.6	5.2	3.2	3.2	3.2	9.1	3.0	2.2	32.2	4.2	21.5	2.7
Acid Red 259	4.3	18.5	3.0	4.0	17.3	4.5	14.1	3.9	4.4	4.4	7.5	6.7	6.2	33.4	3.3	27.7	6.9	6.9
Acid Red 337	6.1	6.3	2.8	3.1	33.3	3.5	18.7	6.0	4.4	4.4	16.4	7.0	2.2	34.9	4.0	47.2	8.9	8.9
Acid Red 358	6.6	9.2	2.8	19.0	25.3	2.9	18.0	6.4	3.4	3.4	24.7	22.0	6.2	27.2	3.9	66.0	13.6	13.6
Acid Red 381	6.5	3.6	1.7	3.7	39.0	6.0	18.0	5.0	1.2	1.2	13.2	9.7	1.0	33.8	9.3	46.5	4.2	4.2
Acid Red 383	6.9	6.2	3.1	28.3	23.0	6.7	10.3	7.7	38.2	35.4	22.0	26.0	24.3	7.6	64.0	1.6	1.6	1.6
Acid Red 384	6.9	6.2	3.1	28.3	23.0	6.7	10.3	7.7	38.2	35.4	22.0	26.0	24.3	7.6	64.0	1.6	1.6	1.6
Eastman Acid Red 209R	13.4	12.3	4.2	3.6	4.3	11.0	12.3	12.4	2.2	2.2	17.6	19.9	2.0	59.5	13.3	44.7	1.6	1.6
Acid Yellow 49	3.6	7.0	4.1	3.6	4.3	11.0	12.3	12.4	2.2	2.2	17.6	19.9	2.0	59.5	13.3	44.7	1.6	1.6
Acid Yellow 121	3.6	11.3	4.4	3.6	4.3	11.0	12.3	12.4	2.2	2.2	17.6	19.9	2.0	59.5	13.3	44.7	1.6	1.6
Acid Yellow 219	3.6	11.3	4.4	3.6	4.3	11.0	12.3	12.4	2.2	2.2	17.6	19.9	2.0	59.5	13.3	44.7	1.6	1.6
Acid Blue 25	9.1	18.2	4.9	9.3	24.4	9.9	31.4	7.0	6.5	6.5	28.3	6.1	52.1	3.4	3.4	2.8	2.8	2.8
Acid Blue 48	2.7	3.2	3.3	3.6	23.4	6.9	15.4	3.6	4.0	4.0	9.7	28.0	4.1	48.0	11.9	33.6	1.0	1.0
Acid Blue 88	18.7	13.5	2.5	11.0	21.3	7.3	24.9	7.3	10.8	10.8	7.0	32.7	3.0	49.0	22.6	15.7	3.2	3.2
Acid Blue 277	18.9	14.0	2.9	9.3	19.4	9.3	26.9	9.0	9.7	12.5	29.5	3.7	53.0	21.5	24.0	2.0	2.0	2.0
Acid Blue 359	6.8	4.8	3.7	6.2	19.6	6.4	24.0	6.9	2.0	18.0	23.9	3.2	47.3	16.6	22.8	4.0	4.0	4.0
Acid Orange 152	2.7	7.3	7.0	6.1	13.1	3.9	15.0	8.0	1.9	1.9	9.6	5.4	23.6	4.9	36.7	6.9	6.9	6.9
Acid Orange 156	2.7	7.3	7.0	6.1	13.1	3.9	15.0	8.0	1.9	1.9	9.6	5.4	23.6	4.9	36.7	6.9	6.9	6.9
Undyed	2.5	14.3	4.3	15.9	17.7	7.2	26.4	6.3	6.3	6.3	3.5	3.5	38.9	2.1	22.4	21.1	18.7	2.6

TABLE III

Discoloration For Color Change in the Dyes Treated with Insecticides and Exposed to Xenon Light

Dye Applied to Nylon	Boyd's Mouse Hold Type KLMR	Rayon	Dialan 4E	Durban 10	Dylox	Twix 2262	Flan V	Multicid Concentr	Orthane	Pyron Malalton	Pyridox Polysta	Concentr 712	Safecto	Spin II	Pyrox	Vapox 2
Disperse Yellow 3	MCK	MCK	MCK	MCK	LP	LP	DKN	DKN	DKN	LP	LP	D	D	B-Pk	OR	Cr
Disperse Red 17	MCK	MCK	MCK	MCK	LO	LO	DKN	DKN	DKN	O	O	O	O	B-Pk	OR	Cr
Disperse Red 389	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	LPk	LPk	D	D	B-Pk	OR	Cr
Disperse Red 349	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	LPk	LPk	D	D	B-Pk	OR	Cr
Disperse Blue 3	MCK	MCK	MCK	MCK	GBI	GBI	DKN	DKN	DKN	BIBr	BIBr	D	D	B-Pk	OR	Cr
Disperse Blue 7	MCK	MCK	MCK	MCK	O	O	DKN	DKN	DKN	M	M	D	D	B-Pk	OR	Cr
Disperse Blue 24	MCK	MCK	MCK	MCK	DLB1	DLB1	DKN	DKN	DKN	M	M	D	D	B-Pk	OR	Cr
Disperse Violet 28	MCK	MCK	MCK	MCK	LP	LP	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 77	MCK	MCK	MCK	MCK	C	C	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 97	MCK	MCK	MCK	MCK	D	D	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 114	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 266	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 299	MCK	MCK	MCK	MCK	PKC	PKC	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 337	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 369	MCK	MCK	MCK	MCK	PKC	PKC	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 361	MCK	MCK	MCK	MCK	PKC	PKC	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Between Acid Red HSC	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Between Acid Red EBR	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Red 49	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Yellow 45	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Yellow 151	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Yellow 219	MCK	MCK	MCK	MCK	O	O	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Blue 23	MCK	MCK	MCK	MCK	O	O	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Blue 49	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Blue 89	MCK	MCK	MCK	MCK	LPk	LPk	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Blue 277	MCK	MCK	MCK	MCK	O	O	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Blue 324	MCK	MCK	MCK	MCK	O	O	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Orange 152	MCK	MCK	MCK	MCK	DM	DM	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Acid Orange 155	MCK	MCK	MCK	MCK	DM	DM	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr
Dyed	MCK	MCK	MCK	MCK	LC	LC	DKN	DKN	DKN	DM	DM	D	D	B-Pk	OR	Cr

Legend

- Bleached = 0
- Blue = B1
- Brownish = Br
- Lighter = L
- Pink = Pk
- Orange = O
- White = W
- Black = Bk
- Dark = Dk
- Soil = S
- Wester (in brightness) = W

Example

- Greenish-Blue = G-B1
- Drain-Purple = DP
- Purple-Red, Dull = PRD
- Bluish-Grey = BG
- White Chalky Residue = WCR

Table XX

Duncan's Multiple Rang Test on Mean Color Difference Values ( $\Delta E$ 's) for Insecticide in the Xenon Light Test

Insecticide	Mean $\Delta E$	Groupings *
Sevin SL	36.8	A
Veponite 2	33.6	A
Dylox	24.9	B
Pyroicide Fogging		
Concentrate 7192	18.8	C
Ficam W	17.0	C
Prentox Malathion	15.4	C
Syntox	9.6	D
Baygon	9.4	D
Dursban LO	8.4	D E F
Evercide		D E F G
Concentrate 2362	7.3	D E F G
Orthene	7.3	D E F G
Bonide Flea Killer	7.1	D E F G
Multicide		D E F G
Concentrate 2154	6.7	D E F G
Safrotin	4.7	E F G
Diazinon 4E	4.3	F G
Untrated	3.2	G

\*Means with the same letter are not significantly different.

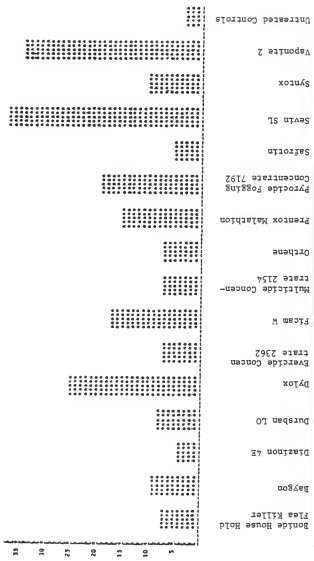


Figure 5. Bar Chart of Mean Color Difference Values ( $\Delta E^*$ ) for Insecticides in Xenon Light Test.

greatest amount of color change during light exposure, based on mean color difference values, were Sevin (36.3  $\Delta E$ ), Vaponite 2 (33.6  $\Delta E$ ), Dylox (24.4  $\Delta E$ ), Pyroicide Fogging Concentrate 7192 (18.8  $\Delta E$ ), Ficam W (17.0  $\Delta E$ ), and Prentox Malathion (15.4  $\Delta E$ ) (see Table XX and Figure 5). The above rank order of the insecticide products, based on mean  $\Delta E$  values, differed from that observed in the standard temperature and high temperature and humidity tests, thus indicating that certain dyes are more susceptible to color change when treated with insecticides and exposed to light.

In addition to causing the greatest amount of color change during light exposure, Sevin SL caused appreciable color change in all of the dyes evaluated (see Table XVIII). The individual color difference values for specific dye types ranged between 22.4 to 59.5  $\Delta E$  units. Hence, the lightfastness of all of the dyes was appreciably reduced by Sevin SL. Specifically, Sevin SL caused all of the dyes to fade and turn brown (see Table XIX). Baygon, on the other hand, had a significantly lower mean color difference value (9.4  $\Delta E$ ), and it caused an increase in fading rate. The color change caused by Ficam W varied somewhat during light exposure, depending on hue type. Many of the red dyes became lighter and several of the blue dyes had a hue shift to blue-green or yellow-green. In addition to the fading and hue shifts, part of the color change caused by the carbamate insecticide products was attributed to the powdered white coating

deposited on the surface of the specimens after treatment. C.I. Disperse Blue 3, 26, and C.I. Disperse Violet 28; C.I. Acid Blue 25, 80, 277, and 324; and C.I. Acid Yellow 49, and 219, exhibited the greatest amount of color change when treated with the carbamate insecticide products. In addition, Baygon, Ficam W, and Sevin SL, caused appreciable discoloration in the undyed nylon.

Among the organophosphate insecticide products, Vaponite 2, Dyllox, and Prentox Malathion caused the greatest color change during light exposure. The color difference values of individual dyes treated with Vaponite 2 ranged from 4.4 to 66.0  $\Delta E$  units (see Table XVIII). Many of the dyes became appreciably lighter with and without hue shifts. Orthene, Safrotin, and Diazinon caused significantly less fading during light exposure, compared to the other organophosphate insecticides. In addition, Safrotin and Diazinon had the lowest mean color difference values among all of the insecticide products evaluated. C.I. Acid Yellow 151 ( $\Delta E = 4.4$ ) had the lowest  $\Delta E$  value for this insecticide and exhibited approximately the same amount of color change when treated and exposed to the three other test conditions. The second lowest value ( $\Delta E = 10.7$ ) was obtained for the undyed sample.

The pyrethroid products, Syntox (resmethrin), Multicide Concentrate 2154 (phenothrin), and Evercide Concentrate 2362 (fenvalerate) discolored the majority of the dye types in xenon

light test (see Table XVIII). All dyed samples treated with Multicide Concentrate 2154 exhibited  $\Delta E$  value above 3.9. Evercide Concentrate 2362 caused a noticeable color change on all dye types, except for C.I. Disperse Yellow 3 (2.2  $\Delta E$ ). Multicide and Evercide did not cause hue shift on any of the dyed samples however, the dyes became lighter (see Table XIX and Figure 5). All dyed samples, except for C.I. Disperse Yellow 3 (3.1  $\Delta E$ ), C.I. Acid Red 114 (3.2  $\Delta E$ ), and C.I. Acid Red 99 (3.7  $\Delta E$ ) exhibited color difference values above 4.0 when treated with Syntox. Many red dyes treated with Syntox, an oil bases product, had hue shift to brownish-orange, and the blue dyes had hue shift to greenish-blue (see Table XIX). Part of this color change was attributed to the oil coating (yellowish color) deposited on the surface of the specimens after treatment. The same hue shift also was observed on the specimens treated with Pyrocide Fogging Concentrate 7192, also an oil-based product.

In the previous tests, Bonide House Hold Flea Killer containing Lethane 384 (a thiocyanate) caused the least amount of color change (3.0  $\Delta E$ ), however, it appreciably reduced the lightfastness of many of the dyes evaluated. Similar results were obtained with Evercide Concentrate 2362 (fenvalerate). The amount of color change attributed to these insecticides was similar in the standard temperature and high temperature and humidity tests, whereas, fading was considerably greater during light exposure. Baygon (propoxur) and Diazinon 4E, however,



exhibited similar amounts of color change in all of the tests including xenon light exposure.

The rank order of the mean color difference values for the dye types exposed to xenon light are given in Table XXI. Similar to the result of the previous test, Eastman Acid Red KSC, Eastman Acid Red 2BDR, and C.I. Acid Red 360, were among the dyes most sensitive to the insecticide products. The greatest amount of color change in these dyes was attributed to the organophosphate insecticides. The lightfastness of all C.I. Acid Red 360 specimens treated with all of the insecticides except Diazinon 4E decreased appreciably in this test, whereas all of the samples dyed with Eastman Acid Red KSC, and 2BDR and treated with insecticides appreciably faded during xenon light exposure.

C.I. Acid Yellow 151 exhibited the least amount of fading during xenon light exposure and had the lowest mean color difference value ( $\Delta E = 6.3$ ) (see Tables XVIII and XXI). None of the insecticide products, except Bonide House Hold Flea Killer, Evercide Concentrate 2362, and Prentox Malathion, caused a noticeable color change on these dyestuffs.

The undyed samples exposed to light had a mean  $\Delta E$  value of 13.4. The majority of the insecticide products caused appreciable yellowing in the undyed nylon during light exposure, except Orthene, Bonide House Hold Flea Killer, and Prentox Malathion.

In summary, the results of xenon light exposure test were almost similar to the standard temperature test based on the rank

Table XXI

Duncan's Multiple Range Test on Mean Color Difference Values ( $\Delta E$ 's) for Dye Types in the Xenon Light Test

Dyes	Mean $\Delta E$	Groupings *
Eastman Acid Red 2EDR	22.1	A
Eastman Acid Red KSC	21.6	B A
C.I. Acid Red 360	20.2	C B A
C.I. Disperse Blue 26	18.4	C B A D
C.I. Disperse Violet 26	17.6	C B A D
C.I. Acid Yellow 49	17.2	C B A D E
C.I. Disperse Blue 3	16.7	C B A D E F
C.I. Acid Blue 277	16.3	C B A D E F G
C.I. Acid Blue 25	16.0	C B A D E F G H
C.I. Disperse Red 340	15.8	C B A D E F G H
C.I. Acid Red 57	15.3	C B I D E F G H
C.I. Acid Blue 80	15.2	C B I D E F G H
C.I. Disperse Red 17	15.1	C B I D E F G H
C.I. Acid Blue 324	14.3	C J I D E F G H
Undyed	13.4	K J I D E F G H
C.I. Acid Red 361	12.7	K J I D E F G H L
C.I. Acid Red 377	12.4	K J I D E F G H L
C.I. Disperse Red 309	12.0	K J I D E F G H L
C.I. Acid Blue 40	10.8	K J I E F G H L
C.I. Disperse Blue 7	10.4	K J I E F G H L
C.I. Acid Orange 152	9.9	K J I F G H L
C.I. Acid Red 299	9.7	K J I G H L
C.I. Acid Red 266	9.5	K J I H L
C.I. Acid Yellow 219	8.7	K J I L
C.I. Acid Orange 156	8.4	K J L
C.I. Disperse Yellow 3	8.2	K J L
C.I. Acid Red 99	7.2	K L
C.I. Acid Red 114	7.0	K L
C.I. Acid Yellow 151	6.3	L

\*Means with the same letter are not significantly different.

order of the insecticides and dye types. However, the individual  $\Delta E$  values for each treated-dyed specimens were greater in xenon exposure test compared to standard temperature test.

#### Ozone

The color difference values and color change descriptors for the undyed and dyed specimens treated with the commercial insecticide products and exposed to two cycles of ozone are given in Table XXII and XXIII, and the rank orders and bar chart for the mean  $\Delta E$  values for the insecticide products are given in Table XXIV and Figure 6.

The insecticide products that caused the greatest amount of color change in the ozone test were: Dylox (21.6  $\Delta E$ ), Sevin SL (21.2  $\Delta E$ ), Ficam W (21.1  $\Delta E$ ), Vaponite 2 (19.6  $\Delta E$ ), Prentox Malathion (13.7  $\Delta E$ ), Pyroicide Fogging Concentrate 7192 (12.9  $\Delta E$ ), Baygon (12.3  $\Delta E$ ), and Orthene (9.8  $\Delta E$ ). The least amount of color change occurred in the following insecticide treatments: untreated (6.9  $\Delta E$ ), Safrotin (6.5  $\Delta E$ ), Syntox (6.4  $\Delta E$ ), Dursban LO (6.3  $\Delta E$ ), Diazinon 4E (6.2  $\Delta E$ ), Evercide Concentrate 7192 (5.2  $\Delta E$ ), Bonide House Hold Flea Killer (4.6  $\Delta E$ ), and Multicide Concentrate 2154 (3.7  $\Delta E$ ) (see Figure 6). Multicide Concentrate 2154, Bonide House Hold Flea Killer, and Evercide Concentrate 2362 also exhibited the least amount of color change in standard temperature and high temperature and humidity tests. Multicide Concentrate 2154 caused the least amount of color change value (mean = 3.7  $\Delta E$ ) in the ozone test, and 17 of the 29 dyes treated

TABLE XXII

Colorfastness of Dyes Treated with Insecticides and Exposed to Ozone Test

Dyes Applied to Nylon	Color Difference, ΔE (ICELAB) Unit																		
	Taas Killer	Baygon	Diazinon 4E	Pyrethrin 10	PyLax	Pericide 2352	Telam V	Multicide Concent	Pericide 2154	Orthene	Pericide Malathion	Pericide Fogging 7192	Diazinon	Baylon SL	Pyrethrin	Pericide	Pericide 2	Untreated	
Disperse Yellow 3	6.9	6.4	2.9	2.6	2.4	1.5	17.6	4.9	4.9	2.4	1.1	1.0	2.7	21.1	2.7	21.1	2.1	4.2	
Disperse Red 17	4.9	4.1	2.0	2.2	2.4	1.4	17.6	4.9	4.9	2.4	1.1	1.0	2.7	21.1	2.7	21.1	2.1	4.2	
Disperse Red 369	4.1	6.3	7.1	6.7	43.6	3.6	22.0	3.7	2.7	7.0	30.0	5.1	4.0	16.6	4.1	4.0	16.6	2.7	16.2
Disperse Red 348	6.9	6.7	4.6	3.1	13.7	2.0	14.6	1.1	2.7	14.4	16.0	6.1	4.0	15.0	6.0	32.9	6.0	32.9	2.2
Disperse Blue 3	5.0	3.9	4.3	23.6	45.0	23.3	33.0	1.9	12.3	44.9	34.0	35.2	39.3	35.2	39.3	17.9	34.6	16.3	35.3
Disperse Blue 7	9.9	21.3	17.0	9.2	28.6	6.3	23.9	2.9	19.3	14.3	28.3	12.2	22.6	6.9	13.6	16.3	16.3	13.7	16.3
Disperse Blue 26	7.7	24.6	14.7	16.1	23.2	7.4	28.4	2.3	7.6	13.5	24.0	6.9	26.6	14.7	16.6	13.7	16.6	13.7	16.6
Disperse Yellow 26	1.6	0.6	4.6	2.7	15.9	7.9	12.6	1.7	6.0	13.0	27.7	3.1	26.4	14.7	11.9	17.4	3.1	27.6	11.9
Acid Red 37	1.6	0.6	4.6	2.7	15.9	7.9	12.6	1.7	6.0	13.0	27.7	3.1	26.4	14.7	11.9	17.4	3.1	27.6	11.9
Acid Red 39	4.4	16.5	1.1	2.0	2.0	2.1	22.6	3.0	6.0	1.0	4.1	1.3	17.0	2.6	3.2	3.2	3.2	3.2	3.2
Acid Red 114	4.9	16.5	2.2	3.6	1.9	2.3	21.3	3.0	1.1	2.2	4.1	1.3	17.0	2.6	3.2	3.2	3.2	3.2	3.2
Acid Red 856	1.2	0.7	1.9	1.4	4.3	1.9	17.6	1.9	6.6	1.6	4.4	1.7	17.0	2.6	3.2	3.2	3.2	3.2	3.2
Acid Red 299	1.4	16.1	2.9	2.4	4.9	2.7	22.6	2.3	6.6	2.3	3.6	2.3	22.6	3.7	5.6	3.7	5.6	3.7	5.6
Acid Red 237	1.6	0.3	2.7	2.9	14.4	2.1	26.7	2.2	6.9	6.1	1.0	5.0	23.1	19.7	2.9	15.2	2.9	15.2	2.9
Acid Red 264	4.3	0.3	2.9	2.7	99.0	4.0	17.4	4.6	29.9	61.1	4.3	5.0	23.1	2.9	69.9	2.4	2.9	69.9	2.4
Acid Red 261	1.1	6.4	2.3	2.6	14.6	1.4	14.3	1.7	6.7	1.2	7.2	11.2	17.6	1.8	76.6	3.0	6.7	76.6	3.0
Acid Red 262	1.1	6.4	2.3	2.6	14.6	1.4	14.3	1.7	6.7	1.2	7.2	11.2	17.6	1.8	76.6	3.0	6.7	76.6	3.0
Eastern Acid Red H2C	3.6	7.9	3.2	7.1	99.9	3.9	22.0	4.3	42.3	64.6	16.0	14.1	16.6	14.1	16.6	14.1	16.6	14.1	16.6
Eastern Acid Red 230R	3.6	7.9	3.2	7.1	99.9	3.9	22.0	4.3	42.3	64.6	16.0	14.1	16.6	14.1	16.6	14.1	16.6	14.1	16.6
Acid Yellow 43	1.0	12.0	4.3	7.9	3.9	6.0	22.4	6.5	11.6	3.0	4.5	4.0	17.5	4.8	3.0	4.8	3.0	4.8	3.0
Acid Yellow 151	1.0	12.0	4.3	7.9	3.9	6.0	22.4	6.5	11.6	3.0	4.5	4.0	17.5	4.8	3.0	4.8	3.0	4.8	3.0
Acid Yellow 219	1.9	7.1	8.3	3.4	6.9	3.2	26.1	2.8	6.0	3.3	7.2	4.4	24.0	2.6	2.2	2.6	2.2	2.6	2.2
Acid Yellow 23	2.6	14.9	6.2	11.2	29.1	3.0	36.1	3.0	10.3	7.2	21.3	6.2	32.1	9.4	19.2	2.4	9.4	19.2	2.4
Acid Blue 46	2.1	9.9	3.2	10.6	22.9	3.6	17.2	2.4	6.0	4.4	17.2	4.1	17.3	7.6	13.8	2.4	7.6	13.8	2.4
Acid Blue 89	3.3	16.2	2.9	16.6	34.7	3.0	21.4	2.4	11.6	3.3	27.6	3.1	22.7	12.1	16.3	9.7	12.1	16.3	9.7
Acid Blue 277	4.6	16.4	3.2	7.3	27.4	3.7	23.3	4.3	7.9	7.7	24.6	3.6	24.7	9.4	22.2	7.6	9.4	22.2	7.6
Acid Orange 152	1.3	16.3	7.1	6.6	25.8	6.9	23.4	3.9	9.9	4.0	19.1	1.7	19.1	3.7	27.0	3.1	3.7	27.0	3.1
Acid Orange 153	1.8	15.1	6.1	4.1	1.7	4.7	22.7	3.6	5.2	4.0	7.0	4.3	26.6	3.1	2.2	4.4	3.1	2.2	4.4
Acid Orange 156	1.8	15.1	6.1	4.1	1.7	4.7	22.7	3.6	5.2	4.0	7.0	4.3	26.6	3.1	2.2	4.4	3.1	2.2	4.4
Undyed	2.0	15.3	4.5	9.1	1.4	3.1	27.3	3.7	1.7	3.9	29.2	11.6	15.3	20.1	4.2	6.9	11.6	15.3	20.1

TABLE XXIII  
 Discolorers For Color Change in the Dyestuffs Treated with Insecticides  
 and Exposed to Sun

Dye Applied to Nylon	Inside House Bold	Flon Killar	Bayton	Darshon 42	Darshon 40	Pylox	Everide Green	Everide 262	Fluon W	Multicide Green	Green 215	Orfide	Phenox Metholon	Mactol	Everide 51	Pylox	Reposite
Diapers Yellow 3	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Red 17	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Red 349	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Red 348	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Blue 3	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Blue 26	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Blue 26	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Diapers Violet 28	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 57	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 59	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 114	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 114	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 256	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 299	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 327	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 328	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 328	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Red 351	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Eastman Acid Red 82C	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Eastman Acid Red 28DR	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Yellow 49	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Yellow 151	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Yellow 219	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Blue 23	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Blue 48	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Blue 48	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Blue 277	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Blue 324	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Blue 324	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Orange 122	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Acid Orange 126	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Undyed	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F

EXEII

Bleached = B  
 Bluer = Bl  
 Brownish = Br  
 Chelly = Ch  
 Creamy = C  
 Darker = Ds  
 Dull = B  
 Greener = G  
 Greenish = Gr  
 Lighter = L  
 Pink = Pk  
 Purpler = P  
 Redder = R  
 Heavier (in brightness) = H

EXEIII

Whiter = Wh  
 Yellower = Y  
 Redder (less) = R  
 Orange = O  
 Greenish-Blue = Gr-B  
 Purple-Purple = PP  
 Purple-Red, Dull = PRD  
 Green Spots = BS  
 White Chelly Residue = MCh

TABLE XXIV

Duncan's Multiple Range Test on Mean Color Difference Values  
( $\Delta E$ 's) for Insecticide in the Ozone Test

Insecticide	Mean $\Delta E$	Groupings *
Dylox	21.6	A
Sevin SL	21.2	A
Ficam W	21.1	A
Vaponite 2	19.6	A
Prentox Malathion	13.7	B
Pyroicide Fogging		B
Concentrate 7192	12.9	B
Baygon	12.3	B
Orthene	9.8	B C
Untreated	6.9	D C
Safrotin	6.5	D C
Syntox	6.4	D C
Dursban LO	6.3	D C
Diazinon 4E	6.2	D C
Evercide		D C
Concentrate 2362	5.2	D C
Bonide House Hold		D C
Flea Killer	4.6	D C
Multicide		D
Concentrate 2154	3.7	D

\* Mean with the same letter are not significantly different.

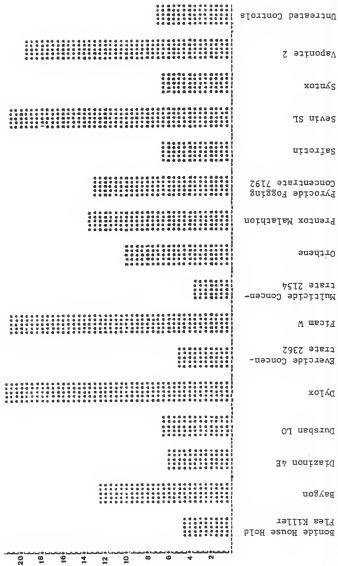


Figure 6. Bar Chart of Mean Color Difference Values ( $\Delta E^*$ 's) for Insecticides in Ozone Test.

with this insecticide had  $\Delta E$  values less than 4.0. The highest color difference value for Multicide Concentrate 2154 was obtained for C.I. Disperse Blue 3 (10.1  $\Delta E$ ) (see Table XXII).

Many of the untreated anthraquinone disperse blue dyes included in this study exhibited appreciable ozone fading which was not unexpected. Some of the red and blue acid dyes also were affected, although the fading or color change was not as extensive. The mean color difference value for the untreated samples in this test was 6.9  $\Delta E$  units. Specifically, the greatest amount of color loss or ozone fading in the untreated specimens ( $\Delta E$  values greater than 10.0) occurred in C.I. Disperse Blue 3, 7, and 26 and C.I. Disperse Violet 28 which are anthraquinones, and in C.I. Acid Red 57 which is a monoazo dye. Although the amount of color change was not as extensive as that which occurred in the above disperse dyes, many of the anthraquinone acid blue dyes (C.I. Acid Blue 80, 277, and 324) faded appreciably (see Table XXIII). In addition to the anthraquinone dyes, selected azo and disazo dyes (C.I. Disperse Yellow 3, C.I. Disperse Red 309, C.I. Acid Red 99 and 266, and C.I. Acid Orange 152 and 156) also had an appreciable color change after exposure to ozone. The highest mean color difference values in ozone test were associated with Dylox (trichlorfon), Sevin SL (carbaryl), Ficam W (bendiocarb), and Vaponite 2 (dichlorvos) (see Table XXIV).

The type of color change that occurred in the ozone test



varied, depending on the insecticide/dye combination. The anthraquinone acid and disperse blue dyes often became lighter and/or exhibited a reddish hue shift which is characteristic of ozone fading. The acid red dyes that had a dramatic hue shift from red to purple in the standard temperature and high temperature and humidity tests had similar changes in the ozone test (see Table XXIII).

Dylox for example, accelerated ozone fading in C.I. Disperse Red 309 and 340, C.I. Disperse Blue 3 and 26, C.I. Disperse Violet 28, C.I. Acid Red 337 and 361, and C.I. Acid Blue 25, 40, 80, 277, and 324. Many of the acid and disperse dyes, however, exhibited color change that was characteristic of the insecticide treatment, in general, rather than ozone fading (i.e., C.I. Acid Red 17 and 360 and Eastman Acid Red KSC and 2BDR). Dylox caused the least amount of color change (1.4  $\Delta E$ ) on the undyed sample, however, the  $\Delta E$  values of individual dyed samples treated with Dylox ranged between 0.9 to 64.7.

In the ozone test, the carbamate insecticides, Baygon (propoxur), Ficam W (bendiocarb), and Sevin SL (carbaryl) appreciably discolored all the 28 dyes and undyed samples evaluated; however, the color changes often were similar to those previously described; however, these insecticides also increased ozone fading in some of the anthraquinone dyes: C.I. Disperse Blue 3 and 26, and C.I. Disperse Violet 28. Sevin SL obtained the second highest mean color difference value among all the

insecticides, and Baygon with a mean  $\Delta E$  value of 12.3 exhibited the least amount of color change among the carbamate insecticide products evaluated.

In addition to Dylox (trichlorfon), the organophosphate insecticide products that caused the greatest increase in ozone fading in some of the anthraquinone acid and disperse blue dyes were Vaponite 2 (dichlorvos) and Prentox Malathion. Other organophosphate insecticide products (i.e., Diazinon 4E, Dursban LO (chlorpyrifos), and Safrothin (propetamphos) did not increase ozone fading appreciably; except on C.I. Disperse Blue 3.

In some insecticide/dye combinations, the insecticide had a protective effect and reduced ozone fading in some of the anthraquinone dyes such as C.I. Disperse Blue 7 and 26. The majority of the insecticide products accelerated ozone fading in C.I. Disperse Blue 3 and decreased fading in C.I. Disperse Blue 7.

The untreated/undyed sample was appreciably discolored after ozone exposure (8.9  $\Delta E$ ). Some insecticides such as Bonide Flea Killer, Diazinon 4E, Dylox, Evercide Concentrate 2362, Multicide Concentrate 2154, Orthene, Prentox Malathion, and Vaponite 2 exhibited  $\Delta E$  values smaller than that observed by untreated-undyed sample when exposed to ozone. The results of the previous tests showed that these insecticide always had the least amount of color change on the undyed samples. As discussed previously, the carbamate insecticide products and oil based

insecticide products (Pyroicide Fogging Concentrate 7192, and Syntox) caused the greatest discoloration on the undyed control samples. In ozone test, Pyroicide Fogging Concentrate 7192 (29.2  $\Delta E$ ), and Syntox (26.1  $\Delta E$ ), followed by Sevin SL (15.5  $\Delta E$ ), Baygon (15.3  $\Delta E$ ), and Ficam W (9.3  $\Delta E$ ) caused the greatest amount of color change on the undyed nylon (see Table XXII).

The rank order of the mean color difference values for the dye types exposed to ozone are given in Table XXV. As mentioned previously, C.I. Disperse Blue 3 (mean = 31.2  $\Delta E$ ) exhibited the greatest amount of ozone fading among all of the dye evaluated. The individual color difference values for this dye ranged from 10.1 to 46.0 for the various insecticide products. The least amount of color change on C.I. Disperse Blue 3 was associated with Multicide Concentrate 2154 and the untreated samples, whereas the greatest amount of color change was associated with Dylox. All untreated and insecticide treated samples of C.I. Disperse Blue 3 were appreciably discolored in the ozone test, suggesting that the chemical structure of this dye (an anthraquinone dye with the  $-NHCH$ , and  $-NH(CH_2)_2 OH$  functional groups) is very susceptible to ozone degradation. Other anthraquinone dyes such as C.I. Disperse Violet 28, C.I. Disperse Blue 7 and 26 containing  $-NH-R$  groups in their structure also appreciably discolored when exposed to ozone.

As in the previous tests, C.I. Acid Red 360, Eastman Acid Red KSC, Eastman Acid Red 2BDR exhibited the greatest amount of

TABLE XXV

Duncan's Multiple Range Test on Mean Color Difference Values ( $\Delta E$ 's) for Dye Types in the Ozone Test

Dye	Mean $\Delta E$	Groupings *
C.I. Disperse Blue 3	31.2	A
Eastman Acid Red KSC	21.8	B
Eastman Acid Red 2BDR	20.5	B C
C.I. Acid Red 360	19.4	D B C
C.I. Disperse Blue 7	16.6	D B C E
C.I. Disperse Blue 26	15.1	D B C E
C.I. Disperse Violet 26	14.8	D B C E F
C.I. Acid Blue 25	13.8	D G C E F
C.I. Acid Blue 324	13.0	D G H E F
C.I. Acid Blue 80	12.8	I D G H E F
C.I. Acid Blue 277	12.5	I D G H E F
C.I. Disperse Red 17	11.2	I G H E F
C.I. Disperse Red 309	10.3	I G H E F
C.I. Undyed	9.6	I G H E F
C.I. Acid Blue 40	9.2	I G H E F
C.I. Acid Yellow 49	8.9	I G H F
C.I. Disperse Red 340	8.8	I G H F
C.I. Acid Orange 152	7.5	I G H F
C.I. Acid Red 57	7.4	I G H F
C.I. Acid Blue 324	6.7	I G H F
C.I. Disperse Yellow 3	6.4	I G H
C.I. Acid Orange 156	6.4	I G H
C.I. Acid Yellow 151	6.0	I G H
C.I. Acid Yellow 219	5.9	I H
C.I. Acid Red 299	5.6	I H
C.I. Acid Red 99	5.4	I H
C.I. Acid Red 114	5.2	I H
C.I. Acid Red 361	5.1	I H
C.I. Acid Red 266	5.0	I

\* Mean with the same letter are not significantly different.

color change during ozone exposure, compared to the other red dyes evaluated. The highest  $\Delta E$  values for these dyes were attributed to certain organophosphate insecticides, such as Dyllox, Orthene, Prentox Malathion, Safrotin, and Vaponite 2 (see Table XXII). The color change that occurred in the organophosphate sensitive red dyes was attributed primarily to the insecticide, rather than to ozone.

All of the dyed samples treated with insecticides and exposed to ozone exhibited mean  $\Delta E$  values exceeding 4.0. Although the four lowest mean color difference values for C.I. Acid Red 266, C.I. Acid Red 114, and C.I. Acid Red 99 were greater than 4.0, the red dyes were less sensitive to ozone than the blue dyes.

The greatest amount of color change in the acid yellow dyes was caused by the carbamate insecticide products. The acid yellow dyes evaluated in this study were azo dyes, but their chemical structure were not available in Colour Index. Among all of the disperse dyes evaluated, the yellow dye (C.I. Disperse Yellow 3) was the least sensitive to ozone fading.

In summary, the majority of the acid and disperse blue dyes exhibited appreciable color change in the ozone test, especially those in the anthraquinone chemical class. In many instances, the insecticides accelerated ozone fading in these dyes. Other hue types had appreciable color change, but the type of color changes that occurred were similar to the results obtained in the

standard temperature or high temperature and humidity tests.

Effects of Commercial Insecticide  
Formulations on Acid and Disperse Dyes

To evaluate the effects of the inactive ingredients in the commercial insecticide products on the colorfastness of acid-and disperse-dyed nylon carpet fibers, the data of this study were compared with the results of AATCC study. As mentioned previously, the AATCC study investigated the effects of the technical grade (active ingredient) of the insecticidal chemicals (applied with an acetone solvent) on the dyed nylon samples. The same acid and disperse dyes were used in both studies. The relative effects of the inactive ingredients can be assessed by comparing the difference between the amount of color change for the unformulated (technical grade) insecticides and formulated (commercial insecticide) products. However, no information was available on the chemical component(s) used as the inert ingredient in each commercial insecticide product evaluated. Certain insecticides such as Bonide House Hold Flea Killer, Diazinon 4E, Dursban LO, Multicide Concentrate 2154, and Syntox contained aromatic petroleum solvents in their formulations. Pyroicide Fogging Concentrate 7192 contained piperonyl butoxide (a synergist) in addition to active ingredient (pyrethroid) and an aromatic solvent. This research contributes valuable knowledge for the future researcher investigating the effects of different inactive chemicals contained in commercial formulations.

The individual  $\Delta E$  values of each of the insecticides from both studies exposed to standard temperature, high temperature and humidity. and xenon light are given, respectively, in Tables XXVI, XXVII, and XXVIII.

#### Standard Temperature

In the standard temperature test, the color difference values for the carbamate insecticides (Baygon, Ficam W, and Sevin SL) were significantly greater when applied as commercial formulations (see Table XXVI). All of the nylon samples treated with propoxur (technical grade) had color difference values less than 3.0, whereas, in this study all of the dyed samples treated with Baygon exhibited  $\Delta E$  values above 4.3. Similarly, all samples treated with bendiocarb, except C.I. Acid Red 360, Eastman Acid Red KSC, and Eastman Acid Red 2BDR, had  $\Delta E$  values of less than 3.0. When treated with Ficam W, however, appreciably more color change occurred in the dyed samples, as exemplified by the lowest  $\Delta E$  value of 6.0. Among the carbamate insecticides, Sevin SL caused the greatest amount of color change in both the pure and commercial form. Among the carbaryl samples evaluated, only seven samples had  $\Delta E$  value less than 3.0. Carbaryl caused the greatest amount of color change on C.I. Acid Red 360, Eastman Acid Red KSC, and Eastman Acid Red 2BDR. All 29 dyes types were discolored significantly by Sevin SL. Therefore, the additive chemical ingredients in carbamate insecticides were responsible

TABLE XVII

Conversion of Data with Result of 2002: Revised Study Use Standard Temperature Test

Days Analyzed to Nylon	Lactane 356	Knit House Hold	Prognost	Baygon	Plastone 42	Chlorpyrifos	Quarban 10	Trichlorfon	Dylox	Dendocarb	Fluon V	Acaphase	Orthene	Kalathion	Peronox Kalathion	Pyrethrin	Concentrate Fogline 7192	Propetamphos	Selofin	Cathyl	Sevin SL	Kemathrin	Syntox	Dichlorvos	Vapontic 2		
Sturson Yellow 3	2.0	1.5	1.7	5.0	9.1	2.5	3.0	1.3	1.4	12.3	4.3	6.3	6.3	4.1	4.8	4.3	3.5	2.4	3.4	2.5	2.8	2.5	2.3	5.4	5.3		
Encosure Red 17	6.7	6.9	6.0	6.2	1.9	2.9	1.9	2.0	11.5	22.2	2.0	7.5	22.4	5.9	7.5	23.4	2.5	4.8	1.0	2.7	3.0	12.1	1.4	2.5	23.7	18.5	
Encosure Red 209	1.9	1.7	1.1	4.9	1.9	1.0	1.9	2.1	2.0	4.4	2.3	18.4	2.5	1.4	1.6	3.1	2.3	3.2	8.4	4.2	4.0	12.1	1.4	2.1	3.5	3.2	
Encosure Red 248	1.7	1.0	0.9	2.5	1.0	3.6	1.4	2.2	4.0	13.4	4.0	3.5	7.4	6.0	2.3	5.2	3.0	6.0	6.3	5.0	3.5	11.0	1.1	3.1	15.9	14.0	
Encosure Blue 3	1.0	2.0	1.4	16.3	1.0	4.4	8.0	3.9	8.6	5.1	1.2	15.1	1.7	1.0	5.3	4.3	13.9	1.8	5.0	5.7	16.9	3.0	3.6	1.4	18.4		
Encosure Blue 5	2.5	2.8	1.4	18.0	2.0	2.0	8.0	2.9	8.5	2.2	8.7	18.4	8.5	1.2	2.7	2.5	7.0	13.0	2.0	2.0	8.4	16.9	2.0	1.1	3.2		
Encosure Blue 15	1.2	1.0	1.8	18.3	1.0	2.1	1.0	1.6	6.7	3.9	1.4	12.7	1.0	1.5	2.0	1.6	10.5	10.1	2.0	2.0	5.0	15.2	5.3	6.0	4.1		
Encosure Violet 28	1.5	3.5	0.5	16.2	2.4	5.0	8.5	4.4	1.5	4.7	8.9	15.7	2.0	2.3	2.6	6.1	13.3	20.2	1.8	4.7	1.5	17.6	2.7	3.2	1.1	3.8	
Acid Red 37	6.5	1.5	1.1	9.4	1.3	3.1	1.3	2.9	1.9	1.7	1.7	9.7	1.1	1.0	2.0	2.3	3.2	7.0	6.2	2.3	2.7	11.5	2.3	3.1	6.0	4.0	
Acid Red 71	0.7	0.3	1.1	11.0	1.2	1.3	3.5	2.6	1.4	2.0	2.2	10.2	6.5	1.2	1.3	1.1	2.1	2.0	8.0	1.0	4.0	12.1	1.9	1.1	3.0	1.0	
Acid Red 114	0.3	2.1	1.2	6.2	1.2	1.0	8.9	2.0	1.2	2.0	2.0	10.1	0.9	1.2	2.0	3.1	2.1	2.6	1.2	1.9	4.0	12.5	2.0	2.1	1.5	2.7	
Acid Red 206	1.1	1.0	1.1	2.6	1.0	1.2	2.3	4.0	2.5	0.4	3.3	0.7	0.9	1.8	2.1	2.1	2.1	2.8	1.3	1.7	2.1	12.3	1.9	2.4	1.8	3.5	
Acid Red 239	0.5	1.0	2.3	8.3	2.0	1.6	3.2	8.6	1.0	1.4	11.5	1.2	1.2	1.9	2.2	2.2	6.1	1.8	2.7	4.4	17.0	2.4	4.0	8.9	1.2		
Acid Red 257	1.1	1.0	1.0	7.0	1.1	2.1	8.4	2.3	8.2	4.2	1.4	10.7	0.8	0.9	1.5	2.6	2.1	3.2	1.0	2.5	2.0	13.4	0.0	2.3	4.3	7.0	
Acid Red 268	1.1	1.2	1.4	10.3	1.9	22.0	2.3	3.7	25.5	25.7	6.4	8.2	21.3	20.3	19.6	46.2	2.0	6.3	3.4	6.1	11.0	13.0	1.3	2.4	19.1	71.3	
Acid Red 361	4.0	1.2	0.7	3.0	1.2	1.6	1.0	2.0	8.5	2.0	1.4	3.6	1.1	0.7	1.2	2.5	3.6	6.3	1.1	2.1	3.9	12.0	2.1	2.2	1.1	6.9	
Encosure Red Red 15C	0.9	0.9	1.4	3.3	1.2	1.3	2.3	4.4	42.5	26.8	2.4	3.4	23.3	20.3	24.3	47.7	2.1	3.3	3.6	3.4	8.0	11.7	1.4	2.1	64.1	77.9	
Encosure Red Red 200B	0.8	1.2	0.9	6.7	0.7	12.6	6.9	6.0	25.3	25.2	9.2	6.7	16.4	12.3	16.3	46.2	2.7	3.4	7.5	7.5	17.4	12.4	1.1	1.9	12.0	68.9	
Acid Yellow 49	6.4	1.6	1.3	10.3	1.3	3.4	8.0	3.0	1.2	2.2	2.2	1.9	1.1	1.2	2.2	4.9	3.2	3.0	3.0	3.7	20.3	8.0	2.3	1.1	7.6		
Acid Yellow 151	1.6	4.4	0.6	12.4	6.3	2.5	1.1	6.0	0.8	6.7	2.3	18.6	1.0	2.2	1.4	3.5	2.0	3.1	1.9	2.5	5.1	13.0	2.3	4.0	1.7	2.6	
Acid Yellow 219	1.9	2.0	2.4	11.2	2.0	2.9	1.2	7.4	1.1	2.0	1.3	15.7	0.9	2.2	2.2	2.0	2.4	3.1	1.9	3.5	1.1	16.6	2.4	4.6	1.7	1.7	
Acid Blue 23	0.7	2.0	1.2	12.3	1.3	2.7	0.3	2.3	0.5	3.6	1.9	15.7	0.9	0.9	1.0	2.1	3.1	3.2	16.5	1.9	4.5	6.0	19.6	6.7	4.2	2.6	6.3
Acid Blue 48	1.4	3.3	0.9	3.3	1.0	4.0	8.0	4.0	8.2	1.0	6.9	5.0	0.9	1.0	1.1	5.1	3.7	13.7	1.2	4.0	2.9	7.4	6.0	6.5	1.1	4.9	
Acid Blue 88	6.4	1.1	0.9	18.3	1.6	2.2	6.1	1.7	6.3	6.3	6.2	13.0	0.5	2.9	1.7	1.9	17.9	25.4	0.9	2.3	4.3	17.3	5.5	5.1	6.4	2.0	
Acid Blue 277	1.1	1.9	1.2	17.1	1.6	1.7	1.2	1.7	1.5	2.0	1.3	15.8	1.6	1.9	2.1	3.0	3.6	11.2	1.1	2.0	7.9	16.4	7.4	5.4	1.0	6.3	
Acid Blue 283	0.3	2.0	2.2	13.6	1.2	2.6	2.0	2.9	8.0	2.9	1.0	10.3	1.6	1.9	2.1	2.0	3.0	11.2	1.1	2.0	7.9	16.4	7.4	5.4	1.0	6.3	
Acid Orange 15C	1.3	2.0	1.1	11.1	2.0	2.4	2.0	5.4	8.7	4.5	1.0	12.7	1.1	1.0	2.4	2.6	2.9	4.9	1.9	4.0	7.0	16.9	2.0	3.2	2.0	3.2	
Acid Orange 126	0.3	0.1	2.7	8.3	2.0	2.2	1.4	1.0	6.0	2.3	2.0	12.7	0.3	0.9	1.4	2.9	2.7	5.1	1.1	3.9	6.1	16.0	1.4	2.4	1.0	3.0	
Unlabeled	2.0	1.9	0.0	20.0	3.2	4.9	1.0	5.0	8.4	1.0	2.7	18.0	1.1	0.4	1.0	5.6	32.0	30.3	3.2	11.5	13.3	16.5	28.0	15.1	2.2	1.2	

\* Color Difference Values (ΔE\*) from 2002 Study.



TABLE 19811

Comparison of Bees with the Results of RHIZ Midwest Study in the High Temperature and Humidity Test

Species Applied to Nylon	Leathman 36a	Florida Killier	Tropopur	Baygon	Dacthion	Dacthion 42	Chlorpyrifos	Dursban 10	Trichlorfon	Dylox	Bandlocarb	Picam n	Acaphase	Oethene	Methidion	Premox Methidion	Pyrethrins	Pyrethro Forming Concentrate 7192	Propetophos	Sectoin	Carbaryl	Sevin SL	Basethrin	Synlox	Dichlorvos	Vaporize 2
Quonara Yellow 3	2.0	1.8	4.8	6.3	2.8	2.1	4.4	3.8	98.5	38.8	1.1	18.5	4.5	6.2	10.2	11.7	98.1	2.8	7.7	18.3	8.7	18.3	8.7	2.4	2.3	18.2
Quonara Red 17	1.5	8.7	1.2	6.6	2.6	3.9	5.1	18.2	35.2	36.2	1.8	7.8	22.3	11.8	46.3	37.7	8.5	6.4	3.7	4.1	4.7	3.3	3.0	3.2	1.2	16.6
Quonara Red 309	6.9	1.8	1.1	7.8	5.4	2.5	5.0	4.4	4.0	2.8	12.2	10.4	10.4	10.4	6.7	21.5	8.6	5.5	17.9	18.0	15.1	15.8	1.9	2.9	1.2	6.0
Quonara Red 348	2.8	1.5	1.4	4.4	2.4	2.7	5.1	7.2	5.1	58.6	1.6	13.8	13.3	7.3	9.7	31.9	6.6	12.3	2.5	6.2	3.5	7.8	2.7	4.3	1.7	20.5
Quonara Blue 3	7.8	1.5	1.7	15.7	2.6	4.2	1.6	8.8	7.1	18.0	1.4	23.1	1.5	8.6	6.3	8.5	18.6	16.7	1.3	4.5	3.9	10.5	6.6	5.1	1.6	5.2
Quonara Blue 7	1.8	1.5	8.5	12.8	1.5	2.1	1.7	3.7	3.7	3.7	6.0	15.8	2.4	8.6	2.2	2.4	11.2	17.1	1.8	2.6	3.6	5.4	4.6	5.0	6.0	3.0
Quonara Blue 26	8.8	8.0	17.1	1.4	2.4	2.5	2.3	4.0	7.0	8.4	25.1	1.5	1.0	1.0	6.0	2.7	15.3	26.2	2.3	2.4	2.5	15.4	5.4	7.6	1.4	4.3
Quonara Violet 28	2.5	6.8	1.1	7.4	7.4	1.1	5.3	4.8	7.5	1.4	29.0	3.4	1.5	1.1	1.9	4.4	16.6	33.8	7.4	6.8	1.5	13.2	3.0	4.2	2.9	11.8
Acid Red 57	8.5	2.1	5.9	7.7	6.3	2.7	1.4	2.7	18.9	25.7	1.8	11.2	3.4	8.5	4.0	4.2	18.4	18.4	1.2	1.4	2.2	6.3	2.4	2.3	1.1	5.9
Acid Red 114	8.5	1.2	1.2	7.2	1.8	1.4	1.2	3.4	2.7	3.9	1.8	4.9	1.4	1.1	12.9	8.6	10.7	9.0	2.2	2.9	3.2	6.3	3.0	4.2	2.9	11.8
Acid Red 219	8.5	2.1	8.7	5.9	2.0	1.4	1.3	2.1	3.4	2.0	1.7	13.0	1.0	1.2	5.1	6.1	7.5	5.0	4.5	2.1	4.4	5.3	1.7	2.4	1.7	2.4
Acid Red 265	8.7	2.0	6.7	6.5	1.1	1.9	1.0	8.9	6.8	16.4	1.0	7.9	1.0	1.7	2.4	1.5	6.7	6.5	1.1	1.0	8.9	3.7	2.5	3.6	1.3	5.3
Acid Red 299	8.7	2.0	6.7	8.4	5.4	2.4	5.9	5.8	3.1	2.7	8.6	3.9	36.7	1.3	63.3	67.8	7.2	5.7	53.4	18.8	2.2	6.4	2.7	3.0	8.6	1.5
Acid Red 329	8.5	2.1	8.5	6.0	1.0	2.1	1.2	2.5	28.1	31.7	1.2	12.0	2.7	1.6	4.4	4.2	6.7	6.7	1.1	1.7	2.2	4.9	2.4	4.3	4.7	16.4
Acid Red 348	8.5	2.2	1.1	7.2	4.7	6.3	13.8	16.8	56.0	58.5	1.2	12.8	31.6	14.5	67.8	62.2	5.6	7.7	8.0	14.6	7.4	5.6	1.6	2.7	47.9	18.1
Acid Red 361	8.7	1.7	1.1	7.1	8.0	1.2	1.3	2.2	15.1	8.8	7.0	1.8	4.5	3.4	3.4	3.4	7.2	7.1	6.3	1.7	2.0	2.6	2.8	3.9	2.5	5.6
Estion Acid Red 822	1.4	1.8	8.5	6.4	5.2	5.7	12.3	15.7	42.2	15.2	6.9	18.5	34.8	17.3	48.4	43.8	7.2	7.1	11.3	11.7	7.2	5.8	1.5	2.1	26.2	33.7
Estion Acid Red 208	8.3	1.1	2.7	7.8	12.0	7.5	20.6	21.4	58.5	62.7	1.8	18.4	25.4	18.4	62.4	10.4	5.4	6.2	3.8	13.3	7.7	5.2	1.6	2.3	43.7	46.1
Acid Yellow 43	2.1	1.8	8.7	18.2	8.7	2.3	2.1	5.4	2.7	4.9	6.9	28.3	2.8	8.8	5.1	3.5	31.2	25.1	8.9	2.5	5.8	15.1	4.6	3.9	6.0	4.4
Acid Yellow 151	1.2	2.3	3.7	8.8	8.7	2.1	2.1	2.3	18.8	18.3	2.5	15.4	3.3	4.9	13.2	5.4	6.5	9.5	8.4	4.5	1.4	7.5	1.5	5.7	8.0	13.3
Acid Yellow 179	1.7	1.5	1.6	12.5	6.6	3.4	2.8	7.8	3.8	8.5	26.9	1.5	1.9	9.0	63.4	19.5	15.5	5.0	6.0	4.0	2.8	16.7	2.5	4.2	3.7	3.2
Acid Blue 25	8.7	2.4	8.5	5.1	2.8	6.4	2.8	4.1	2.3	8.0	2.8	5.8	1.6	6.9	4.4	8.4	28.9	22.8	3.2	5.6	6.5	16.2	7.2	2.0	3.0	5.4
Acid Blue 48	8.7	2.4	1.4	17.3	2.8	6.2	1.2	4.3	2.5	18.1	1.1	18.1	1.2	8.6	1.4	3.2	38.2	35.3	1.4	2.1	4.1	12.5	6.7	5.5	1.6	2.0
Acid Blue 89	8.5	1.7	1.2	17.3	1.9	2.6	6.0	2.6	4.1	7.3	1.2	23.8	1.5	1.0	3.1	3.7	25.1	19.5	1.8	2.1	6.1	11.3	5.7	4.3	1.1	5.9
Acid Blue 237	8.3	2.2	8.7	14.3	3.3	3.6	4.1	2.1	25.8	31.3	1.4	13.8	6.8	1.8	11.1	7.2	15.1	17.3	6.5	2.9	6.3	11.1	5.4	4.2	2.0	16.7
Acid Blue 284	8.4	1.9	1.6	5.6	1.1	7.0	3.1	8.9	6.6	1.4	6.4	28.4	5.3	1.2	62.5	28.2	12.4	18.7	3.3	4.1	2.0	15.5	3.8	3.2	8.2	4.8
Acid Orange 132	1.0	1.0	1.6	5.3	1.2	7.2	22.8	7.6	3.1	2.6	1.0	19.4	13.4	8.3	50.4	23.6	11.4	14.7	6.2	3.2	2.2	12.4	2.5	2.3	1.4	2.7
Acid Orange 156	4.9	6.9	4.5	23.6	4.5	6.8	3.1	5.2	4.8	3.8	3.5	26.3	4.6	1.2	1.3	2.5	27.7	31.2	4.8	3.5	12.2	13.3	25.3	13.8	1.4	1.4
Unsped																										

\* Color Difference Values (L\*) from RHIZ Study.



for further discoloration of acid and disperse dyed and undyed nylon carpet samples.

In both this study as well as the AATCC study, the dyes that exhibited the greatest amount of color change when treated with the technical grade and formulated organophosphate insecticides were C.I. Acid Red 360, Eastman Acid Red KCS, and Eastman Acid Red 2BDR samples. The  $\Delta E$  values for the commercial insecticides products were higher than the technical grade. Among the organophosphate insecticides, Diazinon (technical grade) was the only insecticide which did not cause appreciable discoloration on the above dyes, whereas, Diazinon 4E (commercial product) did cause appreciable color change on these dyes. The color difference values of the other dyes also were greater when treated with the commercially formulated organophosphate insecticides than when treated with the technical grade.

The color difference values for dyed samples treated with lethane 384 were comparable to the  $\Delta E$  values of Bonide House Hold Flea Killer. Therefore, the additive chemical ingredients in this product had less of an effect on the dyes than did the additive chemical ingredients in some of the other insecticides, such as the carbamates and organophosphates. Resmethrin also had similar color difference values to Syntox. Syntox and Bonide House Hold Flea Killer were the only commercial insecticides which were applied in concentrations less than 5% (active ingredient).

In general, the color difference values for the commercial insecticide products for the majority of dyes were greater than those values obtained with the technical grade of the insecticidal chemicals in the standard condition test. Hence, additive chemicals in certain commercial formulations may accelerate color change in dyed and undyed nylon carpets.

#### High Temperature and High Humidity

The commercially formulated insecticides also caused greater color change in the acid and disperse dyes applied to nylon when exposed to high temperature and humidity (see Table XXVII). The majority of the color difference values for the commercial insecticides were greater than those values for the technical grade of insecticides. Baygon, Ficam W, and Sevin SL produced significantly greater  $\Delta E$  values on dyed samples, compared to the pure forms of propoxur, bendiocarb, and carbaryl.

As in standard temperature test, the color difference values of Lethane 384 and Bonide House Hold Flea Killer were almost similar. Hence, the additives in these formulated products were not responsible for additional dye discoloration in the high temperature and humidity test. Among the organophosphate insecticides, Diazinon 4E produced slightly higher  $\Delta E$  values on the majority of the dye types than did diazinon. The only dye types that exhibited greater color change when treated with technical grade of diazinon, compared to the formulated product (Diazinon 4E) were C.I. Disperse Red 309, C.I. Acid Red 299, and

Eastman Acid Red 2BDR. The technical grade of malathion also produced slightly higher  $\Delta E$  values than Prentox Malathion on C.I. Disperse Red 17, 309, and 340; C.I. Acid Red 299, and 360; Eastman Acid Red KSC, and 2BDR; C.I. Acid Yellow 151, and C.I. Acid Orange 152 and 156. Color difference values for trichlorfon and Dylox were similar in the high temperature and humidity test. Chlorpyrifos and Dursban L0 also had similar  $\Delta E$  values.

Color difference values for other organophosphate insecticides such as Orthene, Safrotin and Vaponite 2, as compared to the technical grade of the insecticidal chemicals acephate, propetamphos, and dichlorvos, caused more color change on C.I. Disperse Red 17, 309, and 340; C.I. Acid Red 299 and 360; Eastman Acid Red KSC and 2BDR; and C.I. Acid Orange 152 and 156. Other dye types treated with these insecticides exhibited similar  $\Delta E$  values in the high temperature and humidity test.

#### Xenon Light Exposure

As in standard temperature and high temperature and humidity tests, Baygon, Ficam W, and Sevin SL produced greater color change compared to propoxur, bendiocarb, and carbaryl when applied to the acid-and disperse-dyed nylon carpet samples and exposed to 80 AFU's of xenon light (see Table XXVIII). For example, the individual  $\Delta E$  values for the samples treated with Ficam W were two to three times greater than those obtained for the samples treated with the technical grade of bendiocarb. In

all test conditions, the commercial formulations of the carbamate insecticides increased the amount of discoloration on the dyed and undyed nylon.

Unlike the result of standard temperature and high temperature and humidity tests, Bonide House Hold Flea Killer caused less fading on the majority of the dye types during xenon light exposure than did Lethane 384. Among the organophosphate insecticides, Prentox Malathion and Vaponite 2 caused greater color change in all dye types as compared to their pure forms; whereas, Orthene, and Dursban LO, with a few exceptions, exhibited lower  $\Delta E$  values compared to acephate and chlorpyrifos. Eastman Acid Red KSC and 2BDR, and C.I. Acid Yellow 151 exhibited greater color change when treated with the commercial form of these insecticides. Both Pyroicide Fogging Concentrate 7192 and Syntox increased the amount of light fading in all dye types compared to technical form. Based on the results obtained for the technical grades of pyrethrum and resmethrin, Pyroicide Fogging Concentrate 7192 caused greater fading than Syntox on the dyed nylon samples. However, the Syntox was applied at a 2.5% (active ingredient) concentration, while resmethrin was applied at 5% concentration.

#### Statistical Analysis

An analysis of variance statistical test was used to evaluate further the effects of the independent variables (exposure conditions, dye types, and insecticide products) on the

dependent variable ( $\Delta E$  = total color difference) (see Table XXIX). Because all of the independent variables and second order interactions (exposure x insecticide, exposure x dye, and insecticide x dye) were significant, Duncan's Multiple Range Tests were used to determine the significant differences and nonsignificant groupings within each of the above second order interactions. Hence, the significant effects of the independent variables on color difference were confounded by the interactions among these variables and are discussed accordingly.

In general, xenon light exposure produced significantly higher  $\Delta E$  values, followed by ozone, high temperature and humidity, and standard temperature as indicated in the Duncan's Multiple Range Test on mean color difference values for exposure conditions (see Table XXX). During xenon light exposure, the dyed samples were subjected to the combined effects of light, heat, and humidity which often accelerate insecticide discoloration of dyes. Many of the insecticides appreciably reduced the lightfastness of selected acid and disperse dyes. The standard temperature conditions induced the least amount of color change, as was expected. The mean color difference values associated with each exposure condition differed significantly.

The results of the Duncan's Multiple Range Test performed on the mean color difference values associated with the 16 insecticide treatments are given in Table XXXI. Averaged across all dye types and test conditions, the mean  $\Delta E$  value for Sevin SL was

TABLE XXIX

## Analysis of Variance Test

Independent Variables	Degree of Freedom	Sum of Squares	PR > F	F value
Dye	28	31290.47	0.0001	29.98
Insecticide	15	65493.44	0.0001	117.15
Exposure	3	10970.06	0.0001	98.11
Dye x Insecticide	420	87706.20	0.0001	5.60
Dye x Exposure	84	10593.15	0.0001	3.38
Insecticide x Exposure	45	27976.87	0.0001	16.68



Table XXX

Duncan's Multiple Range Test For Exposure Conditions

Exposure	Mean $\Delta E$	Groupings *
Xenon Light	13.4	A
Ozone	11.1	B
High Temperature and Humidity	8.9	C
Standard Temperature	6.9	D

\* Means with the same letter are not significantly different.

Table XXXI

## Duncan's Multiple Range Test For Insecticide Products

Insecticide	Mean $\Delta E$	Groupings*
Sevin SL	20.5	A
Dylox	18.7	B
Vaponite 2	17.8	B C
Ficam W	16.9	C
Prentox Malathion	15.1	D
Pyrocide Fogging Concentrate 7192	14.1	D
Baygon	10.7	E
Syntox	8.8	F
Orthene	7.1	G
Dursban L0	6.0	G H
Safrotin	5.1	I H
Diazinon 4E	4.7	I H
Evercide Concentrate 2362	4.6	I H J
Multicide Concentrate 2154	4.4	I H J
Bonide House Hold Flea Killer	3.9	I J
Untreated Controls	2.9	J

\* Mean with the same letter are not significantly different.

significantly higher than the mean associated with the other insecticide products. Dylox and Vaponite 2 produced the second and third highest mean  $\Delta E$  values, although the value for Vaponite 2 was not significantly different than that of Ficam W. The untreated samples exhibited the lowest mean  $\Delta E$  value which was not significantly different from the values for Bonide House Hold Flea Killer, Multicide Concentrate 2154, and Evercide Concentrate 2362. The rank orders of the mean  $\Delta E$ 's for the insecticide treatments within each of the four exposure conditions are presented in Table X, XIV, XVIII, and XXII, and have been discussed previously. Compared to the mean  $\Delta E$  values in the combined analysis, the rank order and significant differences among the insecticides within each exposure conditions differed somewhat. For example, in the standard temperature and xenon test, Sevin SL and Vaponite 2 produced the greatest amount of color change. In the high temperature and humidity test, unlike the result of two previous tests, Prentox Malathion and Dylox had the highest mean  $\Delta E$  values; however, the mean  $\Delta E$  values of Dylox was not significantly higher than that of Ficam W, Vaponite 2, and Pyroicide Fogging Concentrate 7192. In ozone test, Dylox, Sevin SL, Ficam W, and Vaponite 2 had significantly higher color difference values. In all of the test conditions, the untreated samples had the lowest mean  $\Delta E$  values. The ozone test caused the greatest amount of color change on the untreated controls because

some of the blue acid and disperse anthraquinone dyes were sensitive to ozone.

Results of the Duncan's Multiple Range Tests for each dye type showed that Eastman Acid Red KSC, Eastman Acid Red 2BDR, and C.I. Acid Red 360 exhibited significantly higher mean  $\Delta E$  values overall (i.e., averaged across all exposure conditions) (see Table XXXII), and in the standard temperature, high temperature and humidity, and xenon light tests (see Tables XIII, XVII, XXI, and XXV). Except for these three dyes, there were no significant difference among the mean  $\Delta E$  values for the individual dyes in the standard temperature and high temperature and humidity test. In xenon light exposure, the mean color difference values for the following dyes were not significantly different: C.I. Disperse Blue 3, C.I. Disperse Violet 28, C.I. Acid Yellow 49, C.I. Disperse Blue 3, C.I. Acid Blue 277, C.I. Acid Blue 25, C.I. Disperse Red 340, C.I. Acid Red 57, C.I. Acid Blue 80, C.I. Disperse Red 17, C.I. Acid Blue 324, undyed controls, C.I. Acid Red 361, C.I. Acid Red 377, and C.I. Disperse 309. In the ozone test, C.I. Disperse Blue 3 had the highest mean color difference value which was significantly greater than the means for Eastman Acid Red KSC, 2BDR, C.I. Acid Red 360, C.I. Disperse Blue 7, and 26, and C.I. Disperse Violet 28. Other dyes exhibited similar patterns of significance in ozone test (see Tables XIII, XVII, XXI, and XXV).

Table XXXII

## Duncan's Multiple Range Test For Dye Types

Dye Applied to Nylon	Mean $\Delta E$	Grouping *			
Eastman Acid Red KSC	20.9	A			
Eastman Acid Red 2BDR	19.8	A			
C.I. Acid Red 360	18.9	A			
C.I. Disperse Blue 3	15.9	B			
C.I. Disperse Violet 28	12.3	C			
C.I. Disperse Blue 26	11.9	C		D	
C.I. Disperse Red 17	11.7	C		D	
C.I. Acid Blue 25	11.0	C		D	E
C.I. Acid Blue 324	10.8	C	F	D	E
Undyed Controls	10.7	C	F	D	E
C.I. Disperse Red 340	10.7	C	F	D	E
C.I. Acid Blue 277	10.6	C	F	D	E
C.I. Acid Blue 80	10.2	C	F	D	E
C.I. Acid Yellow 49	10.1	C	F	D	E
C.I. Disperse Blue 7	9.3	H	F	D	E
C.I. Disperse Red 309	8.8	H	F	I	E
C.I. Acid Orange 152	8.3	H	F	I	
C.I. Acid Red 57	8.3	H	F	I	
C.I. Acid Blue 40	7.7	H		I	J
C.I. Acid Yellow 219	7.6	H		I	J
C.I. Acid Red 337	7.6	H		I	J
C.I. Acid Orange 156	7.2	H	K	I	J
C.I. Acid Red 299	7.2	H	K	I	J
C.I. Disperse Yellow 3	7.0	H	K	I	J
C.I. Acid Red 361	6.5	L	K	I	J
C.I. Acid Yellow 151	5.6	L	K		J
C.I. Acid Red 266	5.6	L	K		J
C.I. Acid Red 99	5.2	L	K		J
C.I. Acid Red 114	4.9	L	K		

\* Means with the same letter are not significantly difference.

## SUMMARY AND CONCLUSION

This study investigated the effects of 15 selected commercial insecticides on the colorfastness of 20 acid dyes and eight disperse dyes on nylon carpet yarns. The results also were compared with the data from the AATCC study so the combined effects of insecticidal chemicals and formulation additives could be evaluated. All of the commercial insecticides were approved by the EPA for home use.

With a few exception (i.e., Bonid House Hold Flea Killer, Evercide Concentrate 2362, and Syntox) all dyed samples were treated individually with 5% (w/w active ingredient) concentration of each insecticide products, then exposed to standard temperature ( $21 \pm 3^{\circ}\text{C}$ ) for 1000 hours, high temperature ( $100 \pm 5^{\circ}\text{C}$ ) and high humidity for eight hours, xenon light exposure for 80 AFU's, and ozone for two cycles of fade. The color difference values ( $\Delta E$ ) of the treated and exposed samples were measured instrumentally by using a Hunterlab D25-M colorimeter. The  $\Delta E$  values for the samples were analyzed statistically by using the Analysis of Variance and Duncan's Multiple Range tests. The results of these tests helped to determine further the effects of commercial insecticides on the colorfastness of nylon carpet dyes in each of the four exposure conditions.

Color difference values of commercial insecticides, except

for Multicide Concentration 2154 and Evercide Concentration 2362, were compared with the  $\Delta E$  values of AATCC Midwest study to evaluate the combined effects of active and inactive ingredients of each insecticide product on the acid and disperse dyes.

The mean color difference values of the insecticide products in all of the four exposure conditions are shown in Figure 7. Fifty-nine of the 64 mean color difference values were above 3.5  $\Delta E$  units. Specifically, the greatest amount of discoloration occurred during xenon light exposure. Sevin SL and Vaponite 2 caused the greatest amount of fading, although other insecticide products including Baygon, Dylox, Ficam W, Prentox Malathion, Pyroicide Fogging Concentrate 7192, and Multicide Concentrate 2154 also reduced the lightfastness of many of the dye types. Bonide House Hold Flea Killer, Dursban LO, Evercide Concentrate 2362, and Syntox, with a few exceptions, decreased the lightfastness of all of the acid and disperse dyes. Diazinon 4E, Orthene, and Safrotin caused the least amount of fading in this test. However, the lightfastness of more than half of the dyed samples were reduced when treated with these insecticides. Dyes treated with Dylox and Prentox Malathion exhibited the highest mean  $\Delta E$  values in high temperature and humidity test. In standard temperature test, Baygon, Dylox, Ficam W, Orthene, Prentox Malathion, Pyroicide Fogging Concentrate 7192, Sevin SL and Vaponite 2 discolored the majority of the dyed samples. Bonide House Hold Flea Killer, Dursban LO, Evercide Concentrate 2362 and

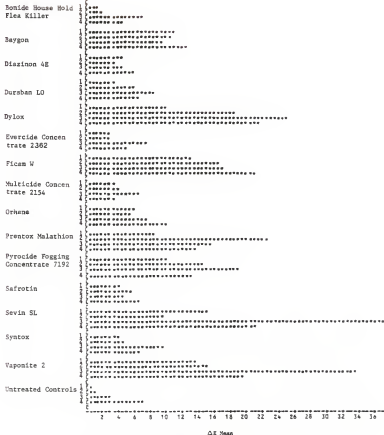


Figure 7. Bar Chart Comparison of Mean Color Difference Values ( $\Delta E^*$ ) for Insecticides in All Four Different Exposures

Key:

- 1 Standard Condition Test
- 2 High Temperature and High Humidity Test
- 3 Jenon Light Test
- 4 Ozone Test



Multicide Concentrate 2154 had the least amount of color change.

In general, the carbamate insecticide products [Baygon (propoxur), Ficam W (bendiocarb), and Sevin SL (carbaryl)] discolored the majority of the acid and disperse dyed samples in all four exposures. Discoloration was mostly due to the white "chalky" residue which was left on the surface of the samples after treatment.

Among the organophosphate insecticide products evaluated, Vaponite 2 (dichlorvos) and Dylox (trichlorfon) obtained the highest mean  $\Delta E$  values, although Orthene (acephate) and Prentox Malathion also caused a great amount of color change on majority of disperse and acid dyes, compared to the other organophosphate products. Certain dyes (C.I. Acid 360, Eastman Acid Red KSC, and 2BDR, C.I. Disperse Red 17, and 340) always exhibited a great amount of color change ( $\Delta E > 20.0$  units) and/or hue shift in treatment with these insecticide products under each exposure condition. Diazinon 4E, Dursban LO (chlorpyrifos), and Safrotin (propramphos) caused the least amount of color change among the organophosphate insecticides.

The pyrethroid insecticide products [Evercide Concentrate 2362 (fenvalerate), and Multicide Concentrate 2154 (phenoxybenzyl), and Syntox (resmethrin)] caused considerably less color change on the dyed samples, compared to the carbamate and organophosphate insecticides. The mean  $\Delta E$  values of all of pyrethroid insecticides were less than 3.5  $\Delta E$  units in high

temperature and humidity and standard temperature tests; whereas, in xenon light exposure test all of the dyed samples faded appreciably. The majority of acid and disperse dyes discolored in ozone test when they were treated with these insecticide products.

Pyrocide Fogging Concentrate 7192 (pyrethrum) discolored all dyed samples in high temperature and humidity, xenon, and ozone tests. Twenty-four of the 29 dyed samples also were discolored with this insecticide in standard temperature test. Due to the yellowish oily color of this insecticide, all disperse and acid blue dyes had a hue shift to greenish blue which resulted in appreciable color difference values. The undyed controls also exhibited a considerable amount of color change when treated with Pyrocide Fogging Concentrate 7192.

Bonide House Hold Flea Killer (lethane 384), caused the least amount of color change among all of the insecticides in the high temperature and humidity and standard temperature tests. Conversely, the samples treated with Bonide House Hold Flea Killer exhibited appreciably greater color change in the xenon light and ozone tests. However, the majority of the individual  $\Delta E$  values (except C.I. Disperse Blue 3 in the ozone test) of the samples treated with this insecticide did not exceeded 10.0 units.

Compared to the technical grade of the insecticidal chemicals, the formulation additives in the commercial products

influenced the amount of color change that occurred in the acid and disperse dyes. For example, the  $\Delta E$  values of all dyed samples treated with propoxur in the standard temperature test were less than 3.0 units, whereas, all the samples treated with Baygon were discolored noticeably in this test. Other insecticides such as Ficam W, Sevin SL, Diazinon 4E, Dursban LO, Dylox, Prentox Malathion, Pyroicide Fogging concentration 7192, Safrotin, Orthene, and Vaponite 2 also caused greater color change as compared to the technical grade forms (5% insecticide/acetone solutions) of the insecticidal chemicals.

Bonide House Hold Flea Killer and Syntox were the only insecticides that had similar  $\Delta E$  values for both the commercial formulations and the insecticide/acetone solutions. These results may be due to, in part, the lower concentrations that were used in applying these two insecticides.

Certain dyes were equally sensitive to both the commercial and pure form of the insecticidal chemicals, and the amount of discoloration was greater in the high temperature and humidity test. For example, C.I. Acid Red 360, Eastman Acid Red KSC, Eastman Acid Red 2BDR, C.I. Acid Orange 152, C.I. Acid Orange 156, C.I. Disperse Red 17, C.I. Disperse Red 309, C.I. Disperse Red 340 exhibited the highest  $\Delta E$  values in both studies within the four exposure conditions. Other dye types had similar color difference values for the majority of insecticides in this test. High temperature and humidity often will accelerated the

deleterious effects of the active and inactive ingredients.

For some of the dyes, the technical grade of the insecticidal chemicals such as lethane 384, acephate, and chlorpyrifos exhibited higher  $\Delta E$  values, compared to commercial forms when exposed to xenon light; whereas, commercial products such as Syntox (resmethrin), Pyroicide Fogging concentration 7192 (pyrethrum), Prentox Malathion, Baygon (propoxur), Ficam W (bendiocarb), Sevin SL (carbaryl), and Vaponite 2 (dichlorvos) caused greater color change during xenon light exposure compared to the the technical grade of the insecticidal chemical.

In summary, many of the commercial insecticide products caused appreciably greater color change in the acid and disperse dyes applied to nylon than did the 5% insecticide/acetone solution. However, these differences may be attributed to both the inactive ingredients in the insecticide products and variations in the percent wet pick up during application. Even though some of the formulated insecticide products caused appreciably greater color change, compared to the solutions prepared from the technical grade of the insecticides, similar changes were observed in both studies in terms of the dyes that were the most susceptible to insecticide discoloration and the insecticides that had the greatest effect on the dyes.

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THE EFFECTS OF COMMERCIAL INSECTICIDE PRODUCTS  
ON ACID AND DISPERSE DYES ON NYLON CARPET FIBER

BY

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B.s., Frozan Pahlavi University. 1976

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AN ABSTRACT

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It has been recognized for many years that certain commercial insecticide products may cause color change in dyed carpeting. This study builds upon the research conducted by the AATCC Midwest study. Investigate herein were the effects of 15 commercial insecticide products on the 20 acid and eight disperse dyes applied to nylon carpet yarns. In addition, the results of this study were compared with the data from the AATCC Midwest study in order to assess the influence of formulation additives on dye discoloration by insecticide products. Dyed and undyed nylon samples were treated with the commercial insecticides and then exposed to standard temperature, high temperature and high humidity, xenon light, and ozone. The treated/exposed samples were measured instrumentally for color change in  $\Delta E$  (CIEL\*a\*b\*) color difference units.

Among the four test conditions, xenon light exposure caused the greatest amount of color change, followed by ozone, high temperature and humidity, and standard temperature. C.I. Acid Red 360, and Eastman Acid Red KCS and 2BDR were the dyes most sensitive to insecticides in all four exposures and C.I. Disperse Blue 3 exhibited the greatest amount of ozone fading.

The formulated carbamate insecticide products (Baygon, Ficam W, and Sevin SL) contained additives (inactive chemical ingredients) that accelerated color change in the dyed and undyed nylon carpet yarns. The majority of commercial organophosphate

insecticides also caused greater color change than did the technical grade of the insecticide applied in an acetone solvent. However, the differences between the technical grade and formulated products were influenced by exposure condition. In general, the commercial formulations of the insecticidal chemicals caused significantly greater color change than did the 5% insecticide/acetone solutions that were used in the AATCC Midwest study.