

**THE EFFECT OF GAMMA RADIATION UPON THE DISPERSE DYE  
ADSORPTION OF TRIACETATE, POLYESTER, AND POLYANIDE FIBERS**

**A THESIS**

**Presented to  
the Faculty of the Graduate Division  
by  
William Wayne Bailey**

**In Partial Fulfillment  
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## SUMMARY

An investigation was made of the effect of gamma radiation upon the disperse dye adsorption of triacetate (Arnel-60), polyester (Dacron-64), and polyamide (nylon-66) fibers. The fibers, in the form of spun yarns, were knitted into fabrics and samples of the fabrics were irradiated in the Cesium-137 Research Irradiator located in the Radioisotopes and Bioengineering Laboratories on the campus of the Georgia Institute of Technology. After irradiation, the dye adsorption characteristics of the fibers were determined through carefully designed and controlled experiments.

The fabric samples were irradiated for one, two, three, six, and twenty-four hours and received irradiation doses of  $1.07 \times 10^6$ ,  $2.14 \times 10^6$ ,  $3.21 \times 10^6$ ,  $6.42 \times 10^6$ , and  $2.57 \times 10^7$  roentgens per gram respectively. Specimens taken from the samples were dyed, along with specimens of the same size fibers. After dyeing, the specimens were dissolved in appropriate solvents and absorbance values of the colored solvent-fiber dispersions were obtained through the use of a Beckman D U spectrophotometer.

The absorbance values obtained for the irradiated and nonirradiated specimens were plotted as a function of dyeing time for each of the irradiated and nonirradiated samples which had been dyed with one of the three aminoazobenzene type dye-

stuffs employed in the investigation. Each of the triacetate, polyester, and polyamide fibers, therefore, was analyzed for differences in dye adsorption both from the standpoint of a variable irradiation dose and from the standpoint of the ability of the irradiated fibers to adsorb dyes which differed in chemical structure, solubility, size of molecule, and saturation value, i.e. maximum adsorption on the fiber at a given temperature. No attempt was made to convert the absorption values obtained to actual amounts (in terms of weight of dye per unit weight of fiber) of dye adsorbed by the fiber. Instead, the fact that an increased absorbance value (defined as a function of per cent transmittance) indicating an increased amount of dye was adsorbed by the fiber, was used as the criteria for determining whether the dye adsorption of one specimen was greater than the dye adsorption of another specimen.

It was found that the gamma radiation emitted by the cesium-137 source had only a small effect upon the three disperse dyes (C.I. Disperse Red 1, C.I. Disperse Red 17, and C.I. Disperse Red 32) employed in the investigation. The effect on the polyamide fibers, however, was more pronounced in that the ability of the polyamide fibers to adsorb all three disperse dyes was greatly increased at irradiation doses up to  $6.42 \times 10^6$  roentgens per gram or six hours' irradiation in the Cs-137 Irradiator. The adsorption of C.I. Disperse Red 1 and C.I. Disperse Red 32 on the polyamide specimens was increased only slightly, however, after the specimens had been irradiated for

twenty-four hours and had received a total irradiation dose of  $2.57 \times 10^7$  roentgens per gram. At this irradiation dose, C. I. Disperse Red 17 was adsorbed by the fibers rapidly at the beginning of the dyeing cycle and then appeared to be desorbed as the time of dyeing was increased.

## CHAPTER I

## INTRODUCTION

The first comprehensive account of radiation induced polymer crosslinks and polymer chain cleavage was given by Charlesby (1)<sup>1</sup> in 1952. Charlesby's original work was done on polyethylene, but his investigations were soon extended to other long-chain polymers and, as a result of Charlesby's investigations, much interest was generated in the effects of ionizing radiation<sup>2</sup> on natural and synthetic high polymers. The catalytic effect of possible improvements in fiber properties by irradiation led to intensive studies on the effects of high energy radiation upon the mechanical properties of various fiber-forming polymers. The fundamental nature of the changes produced in long-chain polymers by irradiation has also been investigated by many workers and a number of theories of irradiation mechanisms have been proposed. Recent investigations of fiber modification using high energy radiation have involved copolymerization of a monomer and a long-chain polymer to produce a polymer with more favorable characteristics.

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<sup>1</sup>The numbers in parentheses refer to the Bibliography.

<sup>2</sup>The terms "ionizing radiation" and "high energy radiation" are used interchangeably throughout the investigation.

Purpose of the Research.--This investigation is directed toward further study of the effects of ionizing radiation on polymers. Changes occurring in the dyeability of three irradiated hydrophobic fibers have been investigated and the changed dyeing characteristics of these fibers when dyed with disperse dyes have been reported.

The investigation is exploratory in nature and the possible value of the study depends upon the extent to which fiber modification through the use of irradiation will advance. Armstrong and Rutherford (2) and more recently, Dasgupta et al. (3) have reported the successful polymerization of various monomers onto and in some of the synthetic and natural fibers with resulting improvements in water resistance, weathering, resistance to mildew, and ease of dyeing. If means are found to further improve the less desirable characteristics of synthetic fibers by graft, in situ polymerization through the use of irradiation, or both, and the practice of fiber modification becomes widespread, a knowledge of the dyeing characteristics of the fabrics containing the irradiated fibers will be essential. This is true because the dyer of a radiation-induced copolymerized fabric would be faced with two problems. One problem would be the effect the added monomer would have upon the dyeability of the fabric and the other would be the change in the dyeing characteristics of the fabric brought about by exposure of the fibers to high energy radiation during the modification process.

Survey of the Literature.--The intense ionizing radiation of nuclear reactors on the materials surrounding the reactor core led to the first investigations of the effects of ionizing radiation upon various materials. Bovey (4) notes that an understanding of the effects of radiation on ceramics, glasses and metals was of the first importance for the successful design and operation of atomic reactors.

The changes in the construction materials used in the first reactors and the exposure to a high flux of neutrons and gamma rays were often detrimental. The detrimental effect, however, was found to be largely caused by energetic neutrons (energies exceeding  $10^5$  ev) rather than by gamma rays since, according to Helvey (5), "gamma rays tend to interact only with the electrons in metallic or crystalline materials producing heat, whereas neutrons frequently knock atoms out of the crystal lattice structure causing a profound change in properties. Metals, for example, become brittle with a consequent decrease in ductility and increase in strength and hardness."

In 1952, some ten years after the advent of the nuclear reactor, Charlesby (6) found that exposure of polyethylene in an atomic pile led to a crosslinked polymer. He noted that the crosslinking appeared to arise from the removal of hydrogen atoms, leaving unsaturated bonds on the carbons of the chain. Charlesby further explained that the gamma radiation from the pile seemed more effective in producing crosslinks than did the associated neutron radiations. This author's work was not

the first to describe the effects of radiation on polymers<sup>1</sup> but it was the beginning of a series of studies by various workers to determine whether polymer properties could be altered by irradiation as the properties of polyethylene were altered by irradiating the polymer.

In 1953, Charlesby and Hancock (7) reported the effect of irradiation-induced crosslinking on the elastic modulus of polyethylene. It was found that in addition to crosslinking, the crystallinity of polyethylene was destroyed when irradiated. At a dose below eight pile units the polymer became flexible as a result of a greater reduction in crystallinity than an increase in crosslinkage formation. This resulted in a decrease in Young's modulus of the fiber. At a dose between eight and twenty pile units increases in crosslinkage more than compensated for the further loss in crystallinity and the polymer became more rigid and glass-like with a consequent increase in Young's modulus. At about 25 pile units the crosslinkage and the reduction in crystallinity offset each other and the irradiated and nonirradiated polyethylene were found to have similar moduli.

Also in 1953, Charlesby (8) reported that polymers other than polyethylene could be crosslinked by exposure to high energy:

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<sup>1</sup>J. G. Burr and W. M. Garrison investigated the effects of irradiation on various plastics in 1948 and in that same year W. L. Davidson and G. Beib reported their investigations on the effects of pile radiation on rubber. In 1951 O. Sisman and C. D. Bopp investigated the change in the physical properties of irradiated plastics.

radiation. He listed polystyrene, Terylene<sup>1</sup>, nylon, and unvulcanized rubber as those materials which would undergo crosslinking while methyl methacrylate was said to undergo degradation after a very short irradiation period.

Charlesby (9) reported in 1954 that polystyrene required a much higher irradiation dose than did polyethylene before the former would show crosslinkage. He attributed this effect to the benzene ring in styrene, the resonant levels of which acted as an energy "sink", thereby dissipating the added energy that might otherwise have produced crosslinking. Evidence to support Charlesby's conclusion that the resonant levels of the benzene ring tend to act as an energy sink to high energy radiation has been reported by McGrath and Johnson (10). McGrath and Johnson's investigations were conducted primarily to obtain data on the change in breaking strength of nylon and Dacron<sup>2</sup> fabrics when exposed to gamma radiation. The authors irradiated dyed and undyed nylon samples and then compared the strength loss of the dyed samples with that of the undyed samples. The dyed fabrics showed a consistently higher breaking strength than the undyed fabrics irradiated for equal period of time in the same Cobalt-60 source. This effect, according to McGrath and Johnson, was probably due to the organic dye (a benzene ring-containing compound) acting as an energy sink. The principle of the benzene ring acting as an energy sink is

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<sup>1</sup>I. C. I. trademark for polyester fiber.

<sup>2</sup>du Pont trademark for polyester fiber.

further reinforced by the behavior of Dacron when exposed to radiation. Dacron, a benzene ring containing compound, exhibits far less loss in strength when irradiated than any of the other synthetic or natural fibers exposed to the same irradiation dose with the possible exception of Orlon<sup>1</sup> acrylic fiber.

Little (11) investigated the effects of pile irradiation on nylon and Terylene in 1954 and Todd (12) reported the results of an investigation on Terylene that same year which supported the work done by Little. Both investigators disagreed with Charlesby's views that irradiation caused crosslinking to predominate in Terylene.

By 1955 the distribution of radioisotopes by the Atomic Energy Commission in the U. S. A. had reached a sufficient magnitude that the isotopes were available in sizeable quantities for use outside the field of medicine. The isotope gave the research worker a ready source of high energy radiation with a minimum of capital outlay. The first important isotope, Cobalt--60, also gave the radiation worker a relatively pure gamma emitter; thus the effects of slow and/or fast neutrons (which are present along with gamma rays in the atomic pile) could be discounted as a factor in irradiation experiments.

Gilfillan and Linden (13) investigated the effects of both gamma and neutron radiation on the strength of cotton,

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<sup>1</sup>du Pont trademark for acrylonitrile fiber.

rayon, nylon and Orlon in 1955. They concluded that all the yarns were injured at the level of gamma irradiation used ( $8.4 \times 10^6$  roentgen). After irradiation cotton lost approximately one-half its strength when tested for tensile strength in both the dry and wet conditions. Rayon lost about the same as cotton except that the break in the wet state was very low. Nylon showed a reduction of about one-half in strength when tested dry but exhibited no loss in strength when tested in a wet condition. Orlon was only marginally affected by the gamma irradiation. The paper by Gilfillan and Linden is of particular importance because it was one of the first attempts in this country to evaluate the effects of gamma rays on fibrous materials. It is of interest to note that Gilfillan and Linden employed both gamma and neutron radiation in their investigation. They noted, however, that no comparisons should be made between the losses in yarn strength produced by gamma irradiation and those produced by neutrons.

In 1956, Teszle and Rutherford (14) published a paper on the effects of gamma irradiation on Dacron polyester fibers. The total dose received by the polyester samples was  $5 \times 10^7$  roentgens. It was noted that orientation influenced the behavior of the fiber toward irradiation, with fibers of low draw ratio tending to show more crosslinkage than those of high draw ratio. The authors noted that very little change was observed in softening point and solubility of the irradiated

fibers (a result reported by Todd in 1954). Teszle and Rutherford concluded, therefore, that the crosslinks were probably of a low order of magnitude.

McGrath and Johnson (15) investigated the effects of gamma radiation on various fabrics in 1956 and in 1957. Harmon (16) made a closely related investigation of the effects of gamma radiation on textile cords.

The purpose of McGrath and Johnson's study was to obtain data on the effect of high energy radiation on parachute fabrics. The fabrics were exposed to a total irradiation dose of  $7.4 \times 10^6$  roentgens, and at this dose undyed nylon fabric retained only 60 - 75 per cent of its original strength. Dacron, on the other hand, exhibited a strength loss of only 2 - 7 per cent thereby retaining 93 - 98 per cent of its original strength. Further experiments by McGrath and Johnson indicated that Dacron gained in strength at lower levels of irradiation (up to  $1.8 \times 10^6$  roentgens). Nylon exhibited slightly less than 10 per cent loss in strength up to  $1.8 \times 10^6$  roentgens, and at a dose of  $4.6 \times 10^5$  roentgens, the loss was about 2 per cent. The authors also found that oven aging (for two hours at 300° F.) of the test fabrics before irradiation had little effect on the change in the strength of the fabrics after irradiation. If the test fabrics were aged in the oven after they were irradiated, however, the degradative action of the irradiation was magnified and the fabrics showed a greater loss in strength.

Three of the textile cords included in Harmon's investigation were Nylon 66, Dacron, and Celanese X-36 (Fortisan). Harmon irradiated the cords at dose rates of  $1.08 \times 10^5$  roentgens,  $1.08 \times 10^6$  roentgens,  $3.24 \times 10^6$  roentgens, and  $1.08 \times 10^7$  roentgens respectively.

Harmon's investigations revealed that nylon cords irradiated in air, suffered a 10.5 per cent strength loss at a dose level of  $1.08 \times 10^5$  roentgens. At a dose of  $1.08 \times 10^6$  roentgens the loss was slightly over 25.5 per cent. Dacron was found to increase in strength at a dose of  $1.08 \times 10^5$  roentgens. The increase was slightly over 6 per cent. At a dose of  $1.08 \times 10^6$  roentgens the strength of the Dacron cords decreased by 4 per cent.

Fortisan cords were found to increase very slightly in strength at a dose of  $1.08 \times 10^5$  roentgens and to decrease 3.6 per cent when irradiated at a dose of  $1.08 \times 10^6$  roentgens.

At a maximum irradiation of  $1.08 \times 10^7$  roentgens nylon cords irradiated in air showed a 52 per cent decrease in strength. Dacron cords irradiated under the same conditions lost 9.4 per cent strength while the Fortisan cords lost 21.6 per cent of their original strength.

As work in the field of textile fiber irradiation progressed, it became apparent that fibers could not be improved materially by simple exposure to high energy radiation. Although polyester fibers generally showed a slight increase in tensile strength and nylon exhibited less creep under tension

when the irradiation dose was relatively low, the improvement was only slight and soon gave way to degradation as the irradiation dose was increased.

The improvement of fiber properties by the use of high energy radiation has now taken the form of in situ and/or graft polymerization of various monomers on fibers, yarns, and fabrics. The polymerization of monomers, brought about through the use of gamma radiation, has recently been reported by the Textile Research Center at North Carolina State College (17), by Armstrong and Rutherford (18) of that institution, and by Dasgupta et al. (19) of Atomic Energy of Canada, Ltd.

Armstrong and Rutherford carried out their studies by irradiating the samples in glass drying tubes in the presence of the monomer vapors. Oil-pumped nitrogen was used as the carrier gas. Various monomer vapor concentrations were obtained by passing the nitrogen through two gas bubble towers containing aqueous solutions of varying monomer concentration. The monomer and water vapors were then passed through a glass drying tube containing 1 - 2 grams of fiber during irradiation.

In their studies on the properties of modified fibers, Armstrong and Rutherford noted that cotton was made resistant to attack by microorganisms after poly-acrylonitrile has been deposited onto the fiber by the method of irradiating the fiber while passing acrylonitrile and water vapors over it. The authors also found that the addition of vinyl acetate to polypropylene allowed the modified polypropylene fiber to be dyed

to deep shades with good penetration using disperse dyes.

Dasgupta et al. recently reported the results of an investigation concerned with the graft copolymerization of styrene and nylon. Dasgupta et al. investigated the graft copolymerization of styrene and nylon using gamma radiation from Cobalt -- 60 to derive the optimum conditions for the grafting process and to obtain a modified nylon fabric suitable for testing.

The authors employed the simultaneous and the pre-irradiation methods to graft the styrene monomer to nylon fabrics. The simultaneous methods, which involved irradiation of the fabric while passing monomer vapor over it, or while the fiber was immersed in a solution of the monomer, was primarily the method used by Armstrong and Rutherford in their investigations. The pre-irradiation method of Dasgupta et al. involved irradiating weighed samples in water for known lengths of time before addition of the monomer solution. After addition of the monomer solution, the mixture was given a low dose of radiation to initiate grafting and the solution mixture was then set aside for aging.

Dasgupta et al. noted that the properties of the grafted nylon fabric were drastically altered after copolymerization with styrene. For example, the fabric became insoluble in all the common solvents. Water spray resistance experiments indicated water resistance had been increased 100 per cent in one of the modified fabrics (coarse weave) and 20 per cent in

the other (fine weave). Stretching strengths (i.e., per cent increase in length until break of warp and filling and breaking strength of warp and filling) was considerably increased in the modified fabrics. A measure of the water permeability of the modified fabrics by the Static Head Penetration test indicated an approximate increase in resistance to penetration (measured in height of water column in cms) of 125 per cent for the coarse fabric at a 49.5 per cent add-on of monomer and almost a 400 per cent increase for the fine fabric at a 47.2 per cent add-on of monomer. Tests of the grafted nylon in the Weather-Ometer indicated that the modified fabrics were more resistant to weathering than heavier fabrics such as army duck.

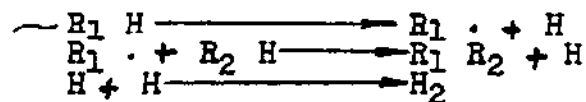
## CHAPTER II

FUNDAMENTAL STUDIES OF IRRADIATION  
MECHANISMS AND DYE - FIBER REACTIONS

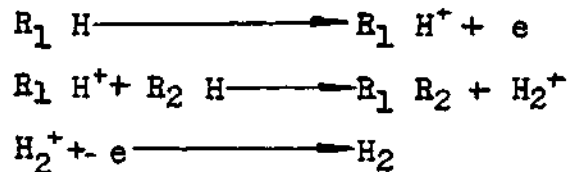
Theories of Irradiation Mechanisms.--Numerous theories have been proposed over the past few years to account for the reactions observed in irradiated polymers. Charlesby (20) has observed that this is an indication of the uncertainty which prevails in the subject and that, "While the information already available concerning the effects of radiation on polymers is adequate for many practical purposes, it is not sufficiently accurate for many theoretical studies."

Some of the theories listed by Charlesby (21) of reaction mechanisms in irradiated polymers are as follows:

1. Reaction of a highly energetic radical molecule with a neutral molecule, forming a crosslink.

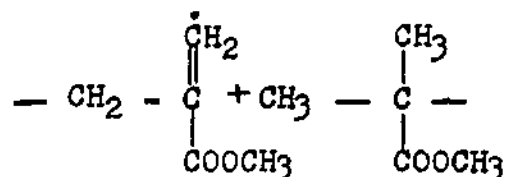


or alternatively, the ejection of a proton or electron and the reaction of the remaining ionized molecule with a neighboring neutral molecule.



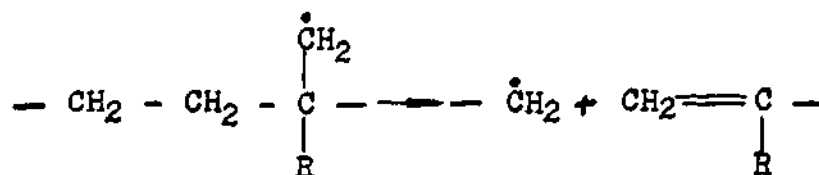
2. The formation of free radical centers by irradiation which are capable of moving along the polymer chain as well as from one polymer chain to another to form crosslinks.

3. The operation of the cage effect to prevent direct decomposition of an excited polymer molecule into two radical chains. Thus, following the loss of a hydrogen atom a slow re-arrangement of the molecule takes place to give a stable structure.

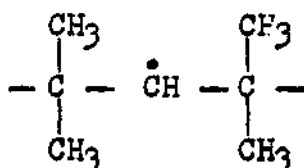


Where no such stable re-arrangement can be obtained by a disproportionation reaction following loss of a hydrogen atom, crosslinking is assumed to occur.

4. Resonance stabilization in which the removal of an  $\alpha$ -hydrogen atom by radiation in a molecule containing one side group per monomer ( $\text{---CH}_2\text{-CHR-}$ ) which is resonance stabilized with the side group of the monomer, causes the hydrogen atom to abstract a similar  $\alpha$ -hydrogen atom from a neighboring molecule giving a second resonance stabilized molecule. These two being in close proximity can interact very readily to form a crosslink. In molecules with a tertiary carbon ( $\text{---CH}_2\text{-CR}_1\text{R}_2$ ) the abstraction of a hydrogen from the side group  $\text{R}_1$  or  $\text{R}_2$  does not produce any such resonance stabilization and the molecule fractures to give an unsaturated molecule and a polymer radical:



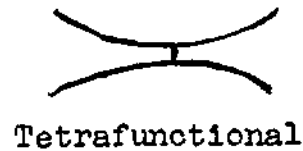
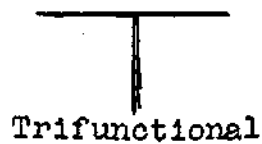
5. Another theory similar to No. 4 assumes that hydrogen liberated by radiation always abstracts hydrogen from a neighboring molecule; this second hydrogen can either be an  $\alpha$ -hydrogen or a hydrogen from  $\alpha$ -methyl. In the first case, crosslinking takes place between two molecules as suggested above whereas in the second case steric hindrance prevents crosslinking, and the radical molecules decompose to give unsaturated end-groups and fractured molecules. It has further been suggested that, instead of the secondary hydrogen being removed from the  $\alpha$ -methyl group, it is more likely to be removed from the main chain to give



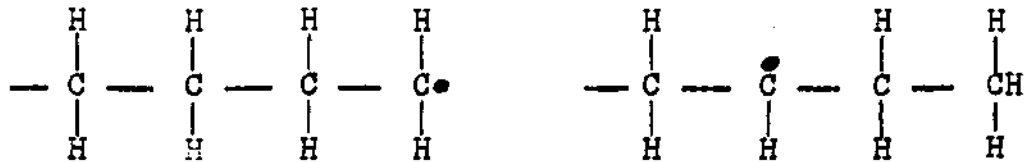
in which case steric hindrance by methyl groups prevents recombination.

6. According to the existing theories the formation of an insoluble, three-dimensional network indicates the presence of crosslinking. Each crosslink is formed by the formation of a lateral bond between two polymer molecules, this bond requiring the removal of at least two side groups or atoms. It has further been shown that an insoluble network can be formed by main chain fracture if it is assumed that each

fractured end can link itself to a neighboring neutral molecule. This process is termed endlinking and the function points formed in this way are trifunctional, as compared with the tetrafunctional junction points involved in the formation of a lateral bond between two polymer molecules.



7. If hydrogen mobility along the polymer chain is permitted, crosslinking may result from main chain fracture. Main chain fracture of a polyethylene molecule, for example, leaves two radicals with free valences.

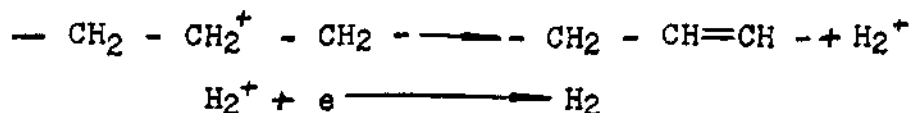


Hydrogen mobility along the chain can saturate these ends leaving radical molecules which are exactly like those formed directly by the breaking of C — H bonds.

8. The theory that a single ionization leads to a crosslink, or to unsaturation, has been advanced and, along with this view, the assumption has been made that the location of ionization is mobile since an electron can move through an irradiated plastic quite readily. Thus, according to the theory, crosslinking takes place only when the ion (or electron deficiency) is approached closely by a neutral carbon.



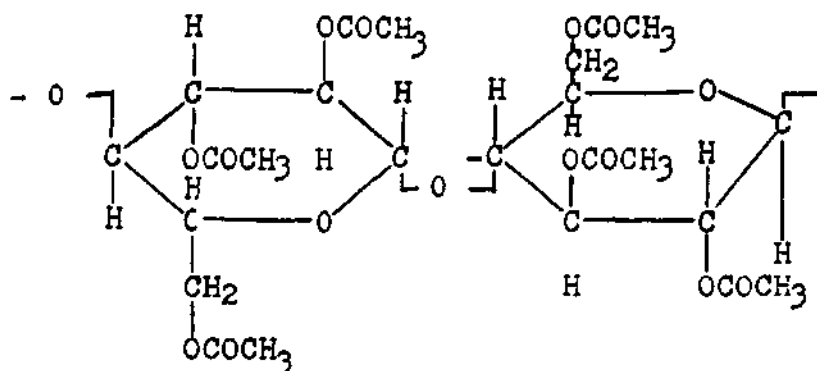
A somewhat similar explanation can account for the formation of unsaturation followed by neutralization of the H<sub>2</sub> ion.



The theory stresses the need for C atoms to be close together for a link to form. With increasing temperature it should therefore become easier for crosslinking to occur in competition with other processes, and such an increase is in fact observed.

Effects of Irradiation on Triacetate, Polyester, and Polyamide Fibers.--Arnel triacetate fiber has received no attention directly in regard to the effects of irradiation upon the polymer. The probable reason for this is that the raw material for Arnel is cellulose and cellulose as well as the secondary acetate made from cellulose has been reported to suffer chain scission when exposed to high energy radiation. Thus, it is reasonable to conclude that the triacetate polymer in which all of the three hydroxyl groups in each glucose residue have been acetylated (as compared with a ratio of acetyl to hydroxyl groups of 23:7 for the secondary acetate) probably suffers main chain scission just as does secondary acetate.

The repeating unit of Arnel is as follows:

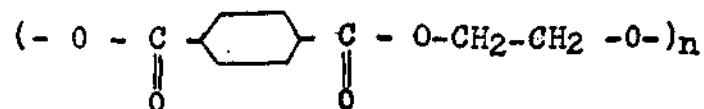


Bovey (22) has reported work done by various workers on the irradiation of cellulose and cellulose derivatives. Cotton fibers as well as ethyl cellulose, cellulose 2, 6 - dipropionate, cellulose 2, 6 - diacetate, and cellulose 2, 6 - dinitrate have been found to degrade rapidly when exposed to pile radiation and to high speed electrons. For example, exposure to  $0.5 \times 10^{18}$  nvt caused the cellulosic polymers to become crumbly, to develop cracks and a yellow to brown discoloration.

Further work reported by the author indicated that a dose of one megarep was found to fracture 0.16 per cent of the bonds in a cellulose chain and that a dose of 100 megarep might be expected to fracture about 14 - 15 per cent of the bonds. Bovey reported that Saeman et al. found that 100 megarep caused a 14 per cent loss in the potential glucose content (measured by reducing power) of cotton linters and it appeared likely that for each chain fracture one glucosyl unit was destroyed. Bovey noted it also was likely that the 1, 4 - acetal bond must be among those broken, if not the chief site of scission, since it would be necessary to break particular pairs of ring bonds

in order to achieve scission if the acetal bonds did not break.

The repeating unit of Dacron is:



According to Charlesby (23) the lengths of paraffinic chain and phenyl groups in the molecular structure of Dacron indicate that the polymer would be expected to crosslink but it would also have a considerable degree of radiation protection. A small degree of crosslinking has been observed in Dacron under irradiation, but it has been shown that the changes which occur in the irradiated polymer may be more complex than mere crosslinking.

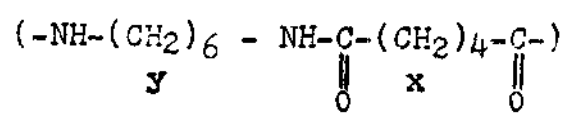
The high irradiation resistance of Dacron is shown by the fact that the polymer was reported to have decreased in tensile strength and elongation by only 50 per cent when irradiated in the Oak Ridge pile for a dose of about  $10^{18}$  nvt. (Approximately 500 megarads).

Polyethylene terephthalate (Terylene) was irradiated in the B. E. P. O. atomic pile at Harwell, England by Little (24). (See above, p. 6). The polymer was given a dose of  $15 \times 10^{17}$  neutrons/cm<sup>2</sup> (about 750 megarads). At this dose the fibers had lost all their strength and begun to powder, while chips of the polymer were brittle. However, little or no change was observed in the crystalline pattern obtained by x-ray diffraction studies.

A contradiction of the rapidity with which high energy radiation affects Dacron has been given by Teszler and Rutherford (25) (See above, p. 6). Appreciable effects were reported after an exposure of the polymer to slow neutron doses as low as  $10^{14}$  nvt (equivalent to 0.1 megarad or less). After a dose of  $10^{17}$  nvt (about 50 megarad) increases in elastic modulus were taken as an indication of crosslinking. It was observed, however, that the few crosslinks that may be produced in Dacron as a result of irradiation is unlikely to result in a significant improvement in mechanical properties.

When irradiated in the absence of oxygen, a number of carboxyl (-COOH) groups have been observed to form in the Dacron polymer, whereas in the presence of air, hydroxyl (-OH) and carbonyl (C = O) groups are formed.

A repeating unit of the nylon polymer may be represented as follows:



When the values of x and y in the formula become large, the properties of the corresponding nylon tend toward those of polyethylene. Thus, many of the changes which take place in the polymer when polyethylene is irradiated may also be expected to occur in the irradiated nylon polymer.

Charlesby (26) has recently given an excellent summary of the present state of knowledge concerning the effects of irradiation on nylon in which he reports the following work

performed by C. W. Deeley et al. in 1957:

In the unirradiated state, nylon shows four absorption peaks in its elastic spectrum, whose positions depend on the temperature and frequency of resonance. These peaks are related to the onset of various degrees of mobility of the molecules. Of these, the highest ( $\infty$ ) peak is due to the melting of crystallites. After the specimen was irradiated in the Brookhaven nuclear reactor for a dose of  $0.3 \times 10^{18}$  nyt the ( $\infty$ ) peak was found to move to lower temperatures, while at higher temperatures the elastic modulus increased. These results are consistent with the conclusions reached from the behavior of irradiated polyethylene, i.e. radiation destroys crystallinity but causes crosslinking, which binds the molecules together even at temperatures above the crystalline melting point. The destruction of crystallinity was also shown by infra-red measurements and by a decrease in density.

Elastic measurements of the irradiated nylon indicate that crosslinking in nylon occurs less readily than in polyethylene. It has been shown, however, that crosslinking of nylon is not proportional to the radiation dose as it is in the case for polyethylene.

Theories of Disperse Dye Adsorption.--The difficulties encountered in dyeing the man-made fibers may be caused: (1) by a lack of sites in the fiber molecule capable of accepting dye molecules; (2) by the extremely compact nature of the fibers, which prevents easy access to dyestuffs or (3) by the hydrophobic nature of the synthetic fibers, which prevents swelling in the aqueous dyebaths normally employed (27).

Giles (28) lists the following mechanisms of adsorption of organic solutes (disperse dyes) by cellulose acetate.

1. Solid solution
2. Polar forces (mainly hydrogen bonds).
3. Nonpolar forces (van der Waals forces).

These mechanisms given by Giles have generally been resolved into two hypotheses. One is the site-dyeing hypotheses and the other is the solution-dyeing hypotheses. The site-dyeing hypotheses depends upon the evidence of hydrogen bonding and van der Waals forces to explain the mechanism of disperse dyeing while the solution-dyeing hypotheses is an important explanation because the dyes often form colloidal solutions within the hydrophobic fiber. Recent data has shown that the two hypotheses are not entirely contradictory and that each may be true in certain circumstances. Vickerstaff (29) states: "the distinction between solid solution and adsorption is very largely unreal."

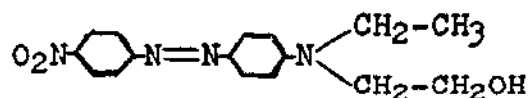
Postman (30) gives the following account of the dyeing of cellulose acetate with disperse dyes:

One picture which emerges is that of a dyebath containing many particles of suspended dye of various sizes, with a small amount of dye in solution, that is, as individual molecules. These molecules of dye in solution enter the very narrow interstitial canals in the fiber and are adsorbed by the fiber and leave the solution, they are replaced by other molecules by dissolution of some of the small particles suspended in the dyebath. In this way, the solution remains saturated with dissolved dye, provided of course, that dissolution of solid particles occurs as rapidly as adsorption of molecules from the solution.

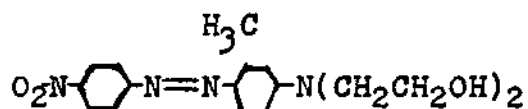
Recent quantitative data of the adsorption of disperse dyes by cellulose acetate has indicated that the disperse dye probably enters the fiber partly in monodisperse and partly

in associated form and penetrates between the fiber chains in regions inaccessible to water. It has been noted by Giles (31), however, that the log saturation adsorption of disperse dye from water by cellulose acetate increases as the log dye solubility of the dye increases. This suggests, according to Giles, that only weak competition for the dye exists between substrate and water and that the dye-fiber attraction is of the same nature as the dye-water attraction, and is therefore mainly polar. Giles further notes that non-polar (van der Waals) forces almost surely contribute to the adsorption energy<sup>1</sup>. The evidence for van der Waals forces is the tendency for the partition coefficient between cellulose acetate and water to rise with molecular weight.

The disperse dyes that were used in the investigation were aminoazobenzene derivatives. The Color Index names and the structural formulas of the dyes are as follows:



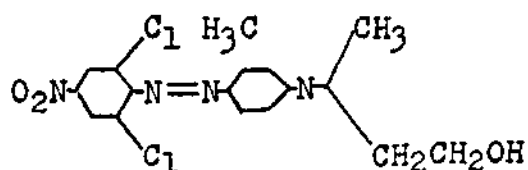
C. I. Disperse Red 1



C. I. Disperse Red 17

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<sup>1</sup>The energy that is required for the dye molecules to break away from their association with water and to become properly oriented to penetrate between the narrow interstitial canals of the fiber.



C. I. Disperse Red 32

The approximate molecular area, the aqueous solubility and the maximum adsorption of these dyes have been compiled from various sources by Giles (32).

Dye	Molecular Area (Relative)	Aqueous Solubility (mg./l.)	Maximum Adsorption (mmol/kg.)
C. I. Disperse Red 1	130	7.7 (80°C)	56(80°C)58(100°C)
C. I. Disperse Red 17	150	45 (80°C)	124 (80°C)
C. I. Disperse Red 32	140	13 (80°C)	70 (80°C)

Giles notes that adsorption normally rises with an increase in the number of hydrogen-acceptor groups (Cl, NO<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>- N=N -) within the dye structure, but if there is a methyl group ortho to the azo group, adsorption, which is at first very high, falls with the increase in the number of hydrogen-acceptor groups. The explanation is that the o-methyl group increases the electron density at the azo group and thus enhances its ability to accept a bonding hydrogen atom. Addition of electron-attracting groups (hydrogen-acceptors) then progressively neutralizes this effect, and adsorption falls, in spite of the hydrogen-accepting power of those groups themselves.

The points made by Giles are clearly recognizable in the dyes used in this investigation. For example, Disperse Red 17 has a much higher adsorption value than the other two

dyes. This high adsorption must be attributed to the fact that a methyl group is ortho to the azo group in the dye. In direct contrast, Disperse Red 32 has a methyl group ortho to the azo group but, as Giles noted, the adsorption of the dye has been greatly decreased due to the chlorine atoms (electron-attracting groups) attached to the dye molecule. It is of interest to note that the adsorption value of Disperse Red 32 is still greater than Disperse Red 1 which has no methyl group ortho to the azo group.

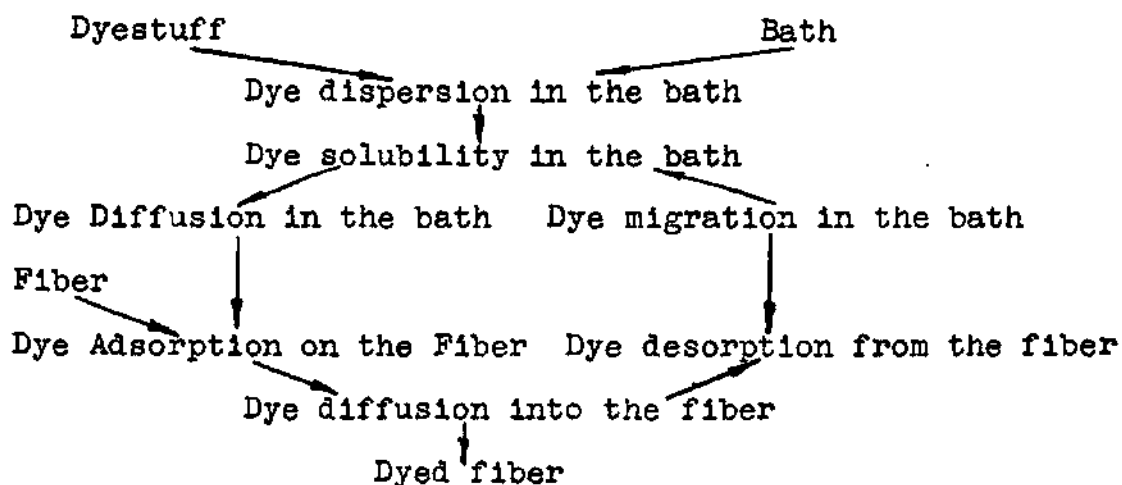
Disperse Dye Adsorption by Triacetate, Polyester, and Polyamide Fibers.--Majury (33) investigated the affinity of secondary acetate and triacetate for certain disperse dyes and found that both fibers had the same affinity for the dyes. From this, he concluded that the origin of the affinity of cellulose triacetate lies in the acetyl rather than in the hydroxyl groups of the fiber and further, the proportion of acetyl groups is evidently not a limiting factor, within the range of acetyl groups between the two acetates (about 2.3 per unit for acetate and 3.0 per unit for triacetate), in determining dye uptake.

Fortess and Salvin (34) have shown that an increase in temperature influences the rate of dyeing of secondary and triacetate by increasing the solubility of the disperse dyes. In their investigation of the adsorption of a red and a violet azo-type disperse dye on secondary and triacetate, the authors concluded that at temperatures of 120-160°F. there was a sig-

nificant increase in diffusion rate and in the solubility of the disperse dyes. At higher temperatures of 160-200°F. the diffusion rate apparently decreased while the solubility of the dyes increased further. Thus, at the higher temperatures, the equilibrium was shifted in favor of the dyebath.

It has been found that hydrogen bonding plays an important role in the dye adsorption of polyethylene terephthalate (Dacron) fibers (35). Hydrogen bonding may take place as the result of hydrogen donation by the dye or through the acceptance by the dye of hydrogen from the ester groups in the substrate. It is also believed that nonpolar forces between aromatic nuclei in dye and substrate must play a significant part in the dyeing process.

Carbonell (36) depicts the dyeing of Dacron with disperse dyes as follows:



Carbonell notes that adsorption is influenced by the dye's solubility in both the bath and the fiber and that low aqueous solubility will reduce the rate of adsorption; but on

the other hand, this does not always mean, according to Carbonell, that a low rate of adsorption is an indication that the dyes have low water solubility. The rate of dyeing, which is controlled by the rate of diffusion, may be influenced by the rate of adsorption of the dye onto the fiber surface. In the normal disperse dyeing process, however, adsorption is always greater than the rate of diffusion. Therefore the rate of adsorption may be said in general to have no influence on the rate of dyeing when hydrophobic fibers such as Dacron are dyed with disperse dyes.

Vickerstaff (37) notes that the mode of attachment of the disperse dye to the nylon fiber has not been studied in detail. He notes, however, that similar mechanisms must operate in adsorption of disperse dyes on nylon as on cellulose acetate with the carbonyl groups of the main polymer chains of nylon playing the same role as those in the ester groups of cellulose acetate. The dyes may become attached by the formation of hydrogen bonds to the amide group in the fiber.

The influence of the crystalline nature of nylon as regards the dyeability of the fiber has been shown by a comparison of the saturation adsorption of disperse dyes on cellulose acetate and on nylon (38). At 85° C. a 10 per cent adsorption on nylon was equivalent to a 25 per cent adsorption of the same dye on acetate, while a 20 per cent adsorption on nylon meant that the acetate had adsorbed almost 55 per cent of the dye.

## CHAPTER III

## EXPERIMENTAL PROCEDURE

Irradiation of Samples.--Arnel, Dacron, and nylon fabrics were knitted on a 32-feed circular knitting machine and test samples were taken from the knitted fabrics to be irradiated in the Cesium-137 Research Irradiation (See Appendix I). Each sample was so positioned in the sample carrier of the Irradiator that it received a uniform dose.

The fabric samples were placed under constant conditions of temperature and humidity for forty-eight hours prior to irradiating. The samples were accurately weighed after conditioning and prior to irradiation. After the samples were irradiated they were again placed under constant conditions for 24 hours.

Dyeing the Specimens.--The irradiated and the non-irradiated samples were scoured before dyeing. An attempt was made in the investigation to keep the per cent dye on the weight of the fabric (o.w.f.) the same for all three of the experimental fabrics. In order to accomplish this, ten Arnel, ten Dacron, and ten nylon specimens, which were taken from the original non-irradiated and scoured samples of these three fabrics, were placed under standard conditions for approximately 64 hours. The specimens were then weighed on a precision balance and, with an allowance for a standard per cent

Table 1. Irradiation Record

Fabric	Sample Weight Grams	Time of Irradiation Hours	Total Dose Roentgen/Gram <sup>1</sup>
Dacron	6.0884	1	1.07 x 10 <sup>6</sup>
Dacron	5.6522	2	2.14 x 10 <sup>6</sup>
Dacron	6.0091	3	3.21 x 10 <sup>6</sup>
Dacron	5.9232	6	6.42 x 10 <sup>6</sup>
Dacron	6.1216	24	2.57 x 10 <sup>7</sup>
Arnel	6.7752	1	1.07 x 10 <sup>6</sup>
Arnel	6.7286	2	2.14 x 10 <sup>6</sup>
Arnel	6.3898	3	3.21 x 10 <sup>6</sup>
Arnel	6.3476	6	6.42 x 10 <sup>6</sup>
Arnel	6.6355	24	2.57 x 10 <sup>7</sup>
Nylon	8.0208	1	1.07 x 10 <sup>6</sup>
Nylon	5.9981	2	2.14 x 10 <sup>6</sup>
Nylon	7.9255	3	3.21 x 10 <sup>6</sup>
Nylon	7.2126	6	6.42 x 10 <sup>6</sup>
Nylon	7.7337	24	2.57 x 10 <sup>7</sup>

<sup>1</sup>See Appendix II.

moisture regain for each fabric, the average weight of each of the Arnel, Dacron, and nylon fabric specimens was obtained. This average specimen weight was consequently used in the determination of the weight of dye required for each dyebath and in the calculation of the amount of the various dyeing assistants, dispersing agents, acids, and alkalis that were used in the individual dyebaths.

Three dyebaths were used for all dyeings of each of the fabric specimens. Thus, each fiber (Arnel, Dacron, and nylon) was dyed with disperse dyes which differed somewhat in their chemical structure, solubility, and molecular area (Chapter II should be consulted for a discussion of the dyes used in the investigation). The dyes used were C. I. Disperse Red 1, C. I. Disperse Red 17, and C. I. Disperse Red 32. Table 4 lists the dyebath formulas, the per cent o.w.f. and the total weight of each ingredient used.

Tap water deionized with an ion exchange unit was used to make up all dye baths.

Specimens 3.3 cm x 0.9 cm were taken from the scoured irradiated and non-irradiated fabrics to be dyed with dispersed dyes. The Arnel fabric irradiated 24 hours was totally degraded after scouring; therefore, this sample could not be used in any of the dyeing investigations. Neither the Dacron nor the nylon fabrics, however, showed excessive degradation after 24 hours irradiation and both the Dacron and nylon specimens that were irradiated 24 hours were used in the investi-

Table 2. Scour Formulas

Fabric	Per Cent on Weight of Fabric	Formulas
Arnel	2.0 per cent 2.0 per cent 0.5 per cent	Neutral Soap Duponol RA Tetrasodium Pyrophosphate
Dacron	2.0 per cent 1.0 per cent	Duponol RA Tetrasodium Pyrophosphate
Nylon	1.0 per cent 1.0 per cent	Duponol RA Tetrasodium Pyrophosphate

Table 3. Average Specimen Weight

Fabric	Weight of 10 Specimens (grams)	Less Moisture Content (grams)	Average Speci- men Weight (grams)
Arnel	0.7381	0.7123	0.0712
Dacron	0.7228	0.7192	0.0719
Nylon	0.8163	0.7296	0.0729

gation. All specimens were dyed in test tubes using 5 ml. dyebath. Each test tube with the 5 ml. dyebath was properly identified and placed into a temperature-controlled waterbath. A device was fashioned out of heavy aluminum stock to hold the test tubes in position in the waterbath. The water was heated to a constant temperature of 96° C. The test tubes containing the dyebaths were then placed into the tube holder in the hot-water bath and were covered with glass slide covers to reduce evaporation of the dye solution. (Tests indicated that approximately 1 ml. of water was lost from the dye solution due to evaporation when the 5 ml. bath was heated to 95° C. for 6 hours).

After the dyebaths had reached a constant temperature of 95° C., the specimens were added. All specimens were dyed for a minimum time of five minutes and a maximum time of 120 minutes. Table 5 lists the details of the irradiation and dyeing times for the Arnel, Dacron, and nylon specimens.

Two heating mantles and two "Powerstats" were used in the investigation. The dyeing experiments were so arranged that 12 specimens could be dyed at one time (i.e., spaces for 12 test tubes were available in the water bath heated by the two mantles - six for each mantle).

After the dyeings were completed, the specimens were rinsed in two 10 ml. portions of deionized water. The dyed specimens were then dried at room temperature.

Spectrophotometric Measurements of Dyed Specimens.--The Arnel

Table 4. Dyebath Formulations for Arnel, Dacron, and Nylon

Fabric	Average Specimen Weight (grams)	Bath Volume (ml)	Bath Ratio	Dyebath Ingredients	Per Cent Dye and Chemicals (o.w.f.)	Total Dye and Chemical Weight for 500 ml. Bath (grams)
Arnel	0.0712	5	70:1	Dye <sup>1</sup>	1.21	0.0914
				Duponol RA	3.60	0.2700
				Product BCO <sup>2</sup>	5.00	0.3700
				Soda Ash	0.20	0.0160
Dacron	0.0719	5	70:1	Dye	1.21	0.0869
				Alkanol HC <sup>3</sup>	1.67	0.1200
				Avitone T <sup>4</sup>	7.00	0.5000
				Acetic Acid	1.60	0.1140
Nylon	0.0779	5	65:1	Dye	1.21	0.0943
				Avitone T	6.40	0.5000
				Neutral Soap	1.28	0.1000
				T.S.P.P.	0.64	0.0500

<sup>1</sup>Either Disperse Red 1, Disperse Red 17, or Disperse Red 32.

<sup>2</sup>du Pont trademark for a Nonionic surfactant.

<sup>3</sup>du Pont trademark for Cetyl betaine.

<sup>4</sup>du Pont trademark for a Sodium hydrocarbon sulfonate.

specimens were dissolved in methylene chloride at room temperature, the Dacron specimens in o-chlorophenol at 80° C., and the nylon specimens in hydrochloric acid at room temperature.

The procedure used for dissolution of the Arnel and nylon specimens consisted of dissolving the fabric specimens in 10 ml. of the solvent. The fibers were completely dissolved after five minutes with constant agitation. A portion of the solution was then poured into a 12 mm. x 12 mm. x 46 mm. cortex spectrophotometer cell and an absorbance value for the colored solution was obtained by use of the Beckman D U, Spectrophotometer<sup>1</sup>.

The Dacron specimens were dissolved in 5 ml. portions of o-chlorophenol which were heated in the constant temperature apparatus that was used for dyeing the fabric specimens. After dissolution (which required approximately one-half hour) the solution was allowed to cool to approximately 40° C. before absorbance measurements were made.

The Beckman D U Spectrophotometer was used for colorimetric measurements. A "blank" which consisted of a fabric specimen undyed and irradiated 6 hours of either Arnel, Dacron or nylon dissolved in the proper solvent, was used for the standard.

All colorimetric measurements were made using the same Spectrophotometric absorption cell thus eliminating a variable in the measurements which the different cells themselves would

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<sup>1</sup>D U Spectrophotometer Model 2400, Serial 160102. Beckman Instruments, Inc., Fullerton, California.

Table 5. Dyeing Record

Fabric	Irradiation Time (Hours)	Dyeing Time (Minutes)			
		Red 1	Red 17	Red 32	
Arnel	0, 1, 2, 3, 6	5	5	5	
	0, 1, 2, 3, 6	10	10	10	
	0, 1, 2, 3, 6	15	15	15	
	0, 1, 2, 3, 6	25	25	25	
	0, 1, 2, 3, 6	45	45	45	
	0, 1, 2, 3, 6	65	65	65	
	0, 1, 2, 3, 6	85	85	85	
	0, 1, 2, 3, 6	105	105	105	
Dacron	0, 1, 2, 3, 6, 24	5	5	5	
	0, 1, 2, 3, 6, 24	10	10	10	
	0, 1, 2, 3, 6, 24	15	15	15	
	0, 1, 2, 3, 6, 24	25	25	25	
	0, 1, 2, 3, 6, 24	45	45	45	
	0, 1, 2, 3, 6, 24	65	65	65	
	0, 1, 2, 3, 6, 24	85	85	85	
	0, 1, 2, 3, 6, 24	105	105	105	
	0, 1, 2, 3, 6, 24	120	120	120	
Nylon	0, 1, 2, 3, 6, 24	5	5	5	
	0, 1, 2, 3, 6, 24	10	10	10	
	0, 1, 2, 3, 6, 24	15	15	15	
	0, 1, 2, 3, 6, 24	25	25	25	
	0, 1, 2, 3, 6, 24	35	35	35	
	0, 1, 2, 3, 6, 24	45	45	45	
	0, 1, 2, 3, 6, 24	55	55	55	
	0, 1, 2, 3, 6, 24	65	65	65	
	0 (Red 1)	24 (Red 1)	75		
	0 (Red 1, 32)	24 (Red 17, 32)	85	85	85
	0 (Red 1)	24 (Red 1)	95		
0 (Red 1)	24 (Red 17, 32)	105	105	105	

introduce.

Before individual absorbance measurements were made of each of the dyed specimens, an absorbance curve for the visible spectrum was drawn for each of the nine dye-fiber combinations (three disperse dyes and three fibers). Dyed, non-irradiated fabric specimens were dissolved in the appropriate solvents and the absorbance values of the colored solutions were obtained with the spectrophotometer at frequent wavelength intervals throughout the visible spectrum (400-700 m $\mu$ ).

## CHAPTER IV

## DISCUSSION OF RESULTS

The data have been summarized in Figures Four, Five, and Six. The numerical values for the relative amount of dye adsorbed by the triacetate, polyester, and polyamide fibers, as given in Figures Four, Five, and Six are direct absorbance readings taken from the Spectrophotometer. Therefore, the readings are not absolute measurements of the amount of dye on the fibers (in terms of weight of dye per unit weight of fiber). The absorbance, as given, is defined as a function of per cent transmittance. Thus, as the absorbance readings increased the percent transmission of light through the solution of the fiber specimens decreased, indicating that an increased amount of dye had been adsorbed by the specimens.

Triacetate Fibers.--Figure 1 indicates that the triacetate (Arnel) specimens adsorbed Disperse Red 1, Disperse Red 17, and Disperse Red 32 at different rates. Disperse Red 1 was adsorbed most readily while the adsorption of Disperse Red 17 was next followed by Disperse Red 32 which was adsorbed the least.

It has been indicated that the origin of the affinity of cellulose triacetate for dyestuffs lies in the acetyl groups of the fiber molecule. It has also been noted that the acetyl bonds in the cellulosic polymer (and very likely in the tri-

acetate polymer) are probably the chief sites of scission when the polymer is irradiated.

The non-irradiated Arnel specimens were found to adsorb slightly more dye than the irradiated specimens (Figure 4). The difference in adsorption was slight but it was apparent that the degradative action of the gamma radiation affected the acetyl bonds in the triacetate molecule and thereby tended to lessen the amount of disperse dyes which could be adsorbed by the triacetate fibers.

Polyester Fibers.--Figure 2 indicates that polyester (Dacron) specimens show an affinity for Disperse Red 1, Disperse Red 17, and Disperse Red 32 similar to that shown by the Arnel specimens for those dyes. The change in the dye adsorption of the Dacron specimens after irradiation was, however, the exact opposite of the change in dye adsorption that occurred in the Arnel specimens after irradiation (Figure 5). The amount of dye that was adsorbed was slightly greater for all three dyes in the Dacron specimens after an irradiation of one, two, three six and twenty-four hours respectively.

It has been noted that hydrogen bonding plays an important role in the dye adsorption of Dacron and that hydrogen bonding may take place as the result of hydrogen donations by the dye and/or through the acceptance by the dye of hydrogen from the ester groups in the substrate. Dacron has also been noted to have an inherent radiation protection mechanism in the form of the aromatic groups within the polymer. Therefore,

the polymer should be changed very little by irradiations of dose rates below  $2.57 \times 10^7$  roentgens per gram.

Polyamide Fibers.--Figure 3 indicates that the adsorption of Disperse Red 1 and Disperse Red 17 by the non-irradiated nylon specimens was about the same. Disperse Red 32 was also adsorbed to about the same extent after a sufficient dyeing time.

The major change that takes place in the nylon fiber exposed to high energy radiation is reported to be the destruction of the crystalline areas of the fiber. It has been noted, however, that the polymer tends to crosslink and the crosslinks bind the molecules of the fiber together even at temperatures above the crystalline melting point. Figure 6 indicates that a significant increase in the adsorption of Disperse Red 1 occurred after the nylon specimens had been irradiated one, two, three, and six hours. After an irradiation of 24 hours, however, the increase in adsorption was only slight compared with the non-irradiated specimens. It is also shown that Disperse Red 17 was not absorbed as readily as Disperse Red 1. Nevertheless, the increase in adsorption was very high for the specimens irradiated one, two, three, and six hours. The specimens irradiated 24 hours showed an initial high adsorption followed by desorption as dyeing continued, indicating that the saturation point of the dye in the irradiated specimen was reached very quickly probably because of the reduced crystalline nature of the fiber. Disperse Red

32, as shown by Figure 6, was adsorbed at about the same rate by both the irradiated and non-irradiated specimens. The irradiated specimens, however, adsorbed more dye than did the non-irradiated specimens at all irradiation dose levels.

## CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

Conclusions.--Irradiated specimens of Arnel triacetate fibers adsorbed less of the disperse dyes employed in the investigation than the non-irradiated specimens of Arnel. The decreased adsorption of Disperse Red 1, Disperse Red 17, and Disperse Red 32 on Arnel was apparent at irradiation dose levels which varied from  $1.07 \times 10^6$  roentgens per gram to  $6.43 \times 10^6$  roentgens per gram.

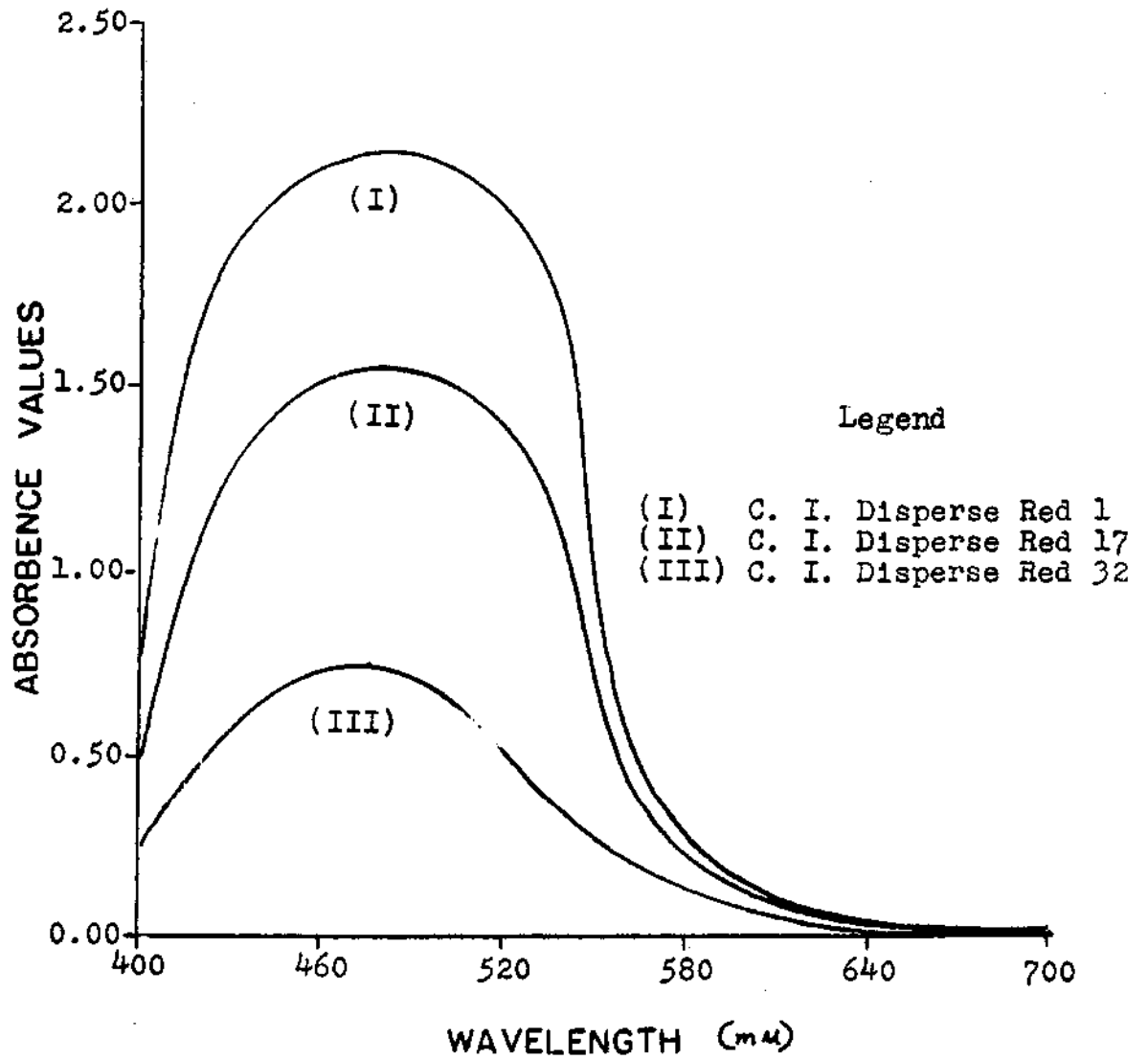
Irradiated specimens of Dacron polyester fibers adsorbed slightly more of the disperse dyes employed in the investigation than the non-irradiated Dacron specimens. An increase in adsorption was noted at all irradiation dose levels.

The disperse dye adsorption of the irradiated nylon polyamide fibers was much greater than the dye adsorption of the non-irradiated fibers. Increases in dye adsorption occurred at all irradiation dose levels (from one to twenty-four hours irradiation in the Cs-137 Irradiator).

Recommendations.--The increase in dye adsorption exhibited by irradiated nylon offers an interesting area for further investigation. It is apparent from the present investigation that dose rates lower than  $1.07 \times 10^6$  roentgen per gram (one hour irradiation in the central position of the Cs-Irradiator at Georgia Tech) may be used to affect an increase in the dye

adsorption of C. I. Disperse Red 1, C. I. Disperse Red 17, and C. I. Disperse Red 32 on nylon. It is also very likely that most disperse dyes will show an increased adsorption on the irradiated nylon fibers. Any investigation along these lines should include a study of the fastness properties of dyed irradiated nylon fibers.

Recent research efforts concerned with the application of high energy radiation to textile problems have been directed toward fiber modification through copolymerization of a monomer onto a long chain polymer by the use of irradiation to effect the copolymerization reaction. It has become apparent from the investigations thus far that many characteristics of a fiber may be altered by radiation-induced copolymerization. One very promising type of alteration is the dye adsorption properties of the hydrophobic fibers, and it is suggested that work be initiated along the lines of evaluation of monomer and difficult to-dye-synthetic fiber combinations which may be copolymerized through the use of irradiation to produce a fiber with improved dyeing characteristics.



Irradiation Time: Non-irradiated  
Dyeing Time : Forty-five Minutes

Figure 1. Absorbance Spectrum for Triacetate Fibers

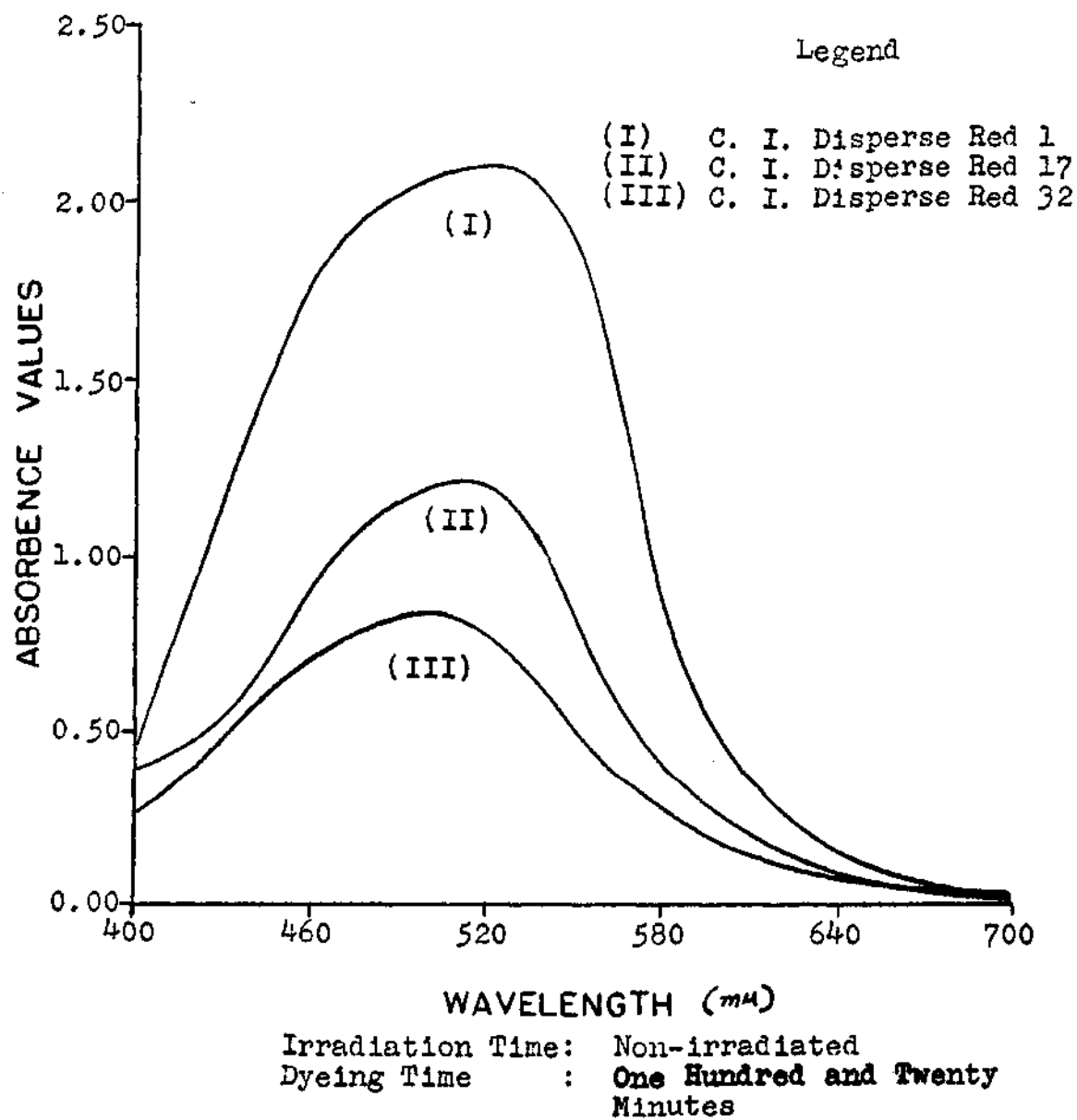


Figure 2. Absorbance Spectrum for Polyester Fibers

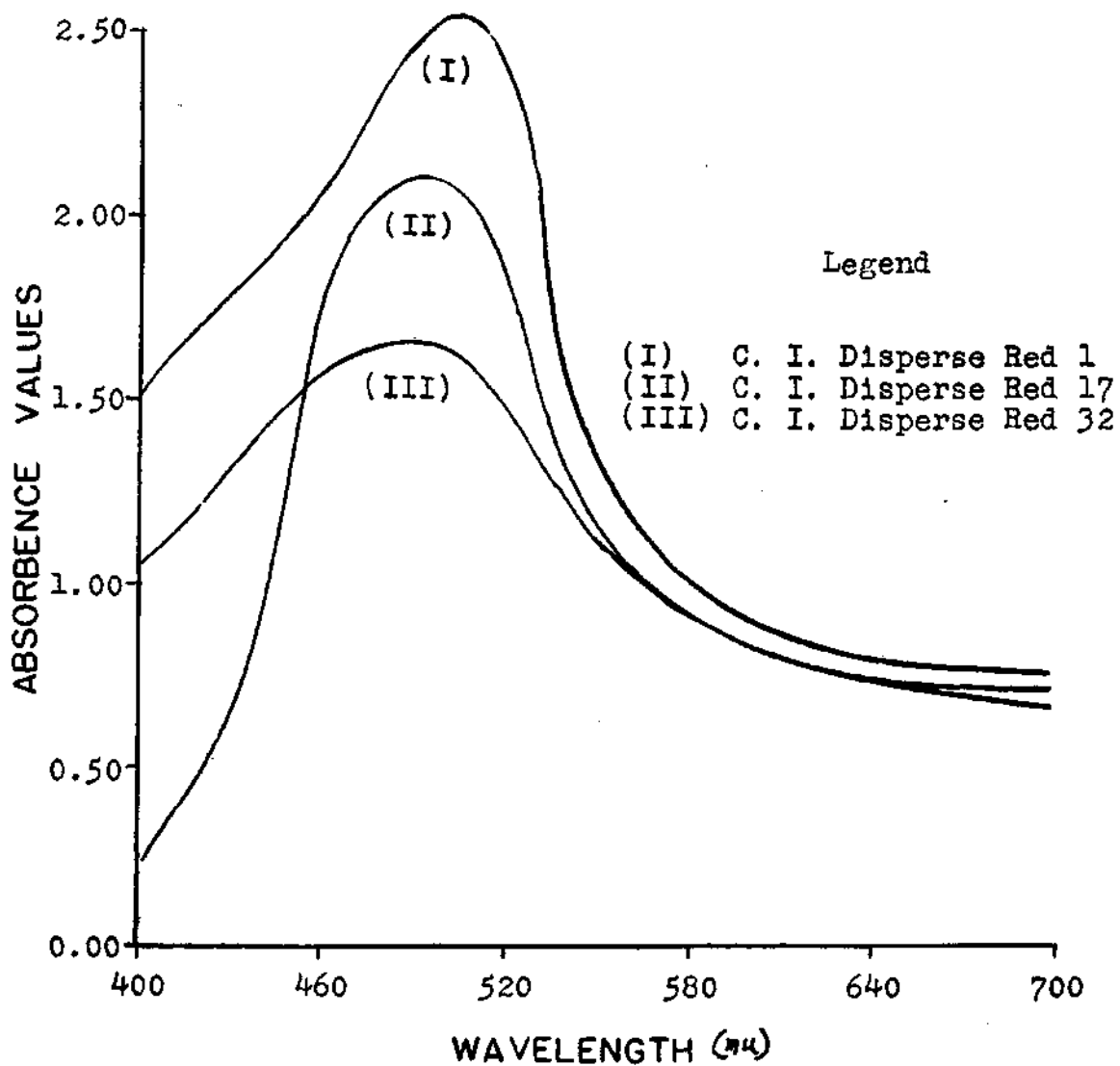


Figure 3. Absorbance Spectrum for Polyamide Fibers

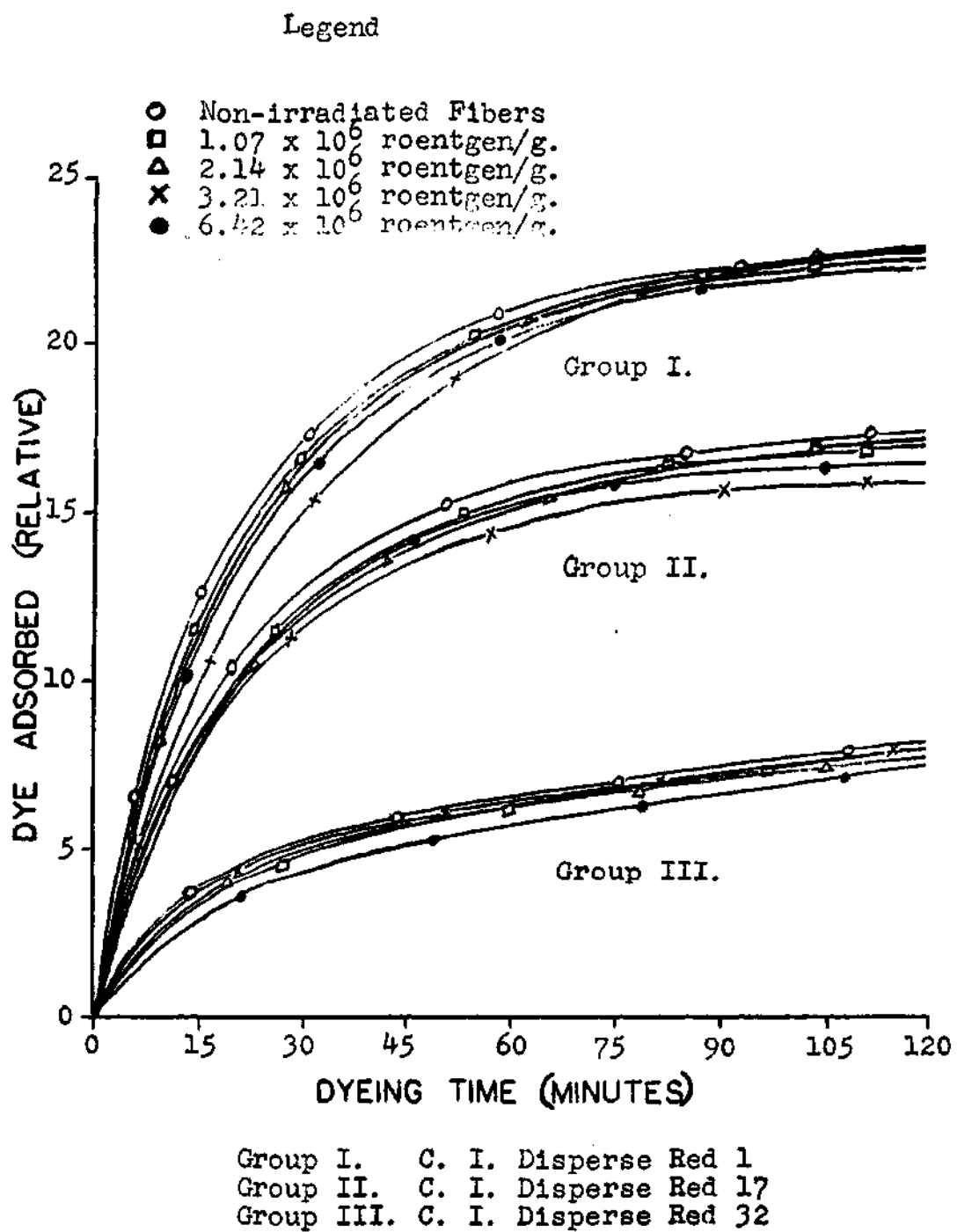


Figure 4. Dye Adsorption vs Dyeing Time for Triacetate Fibers

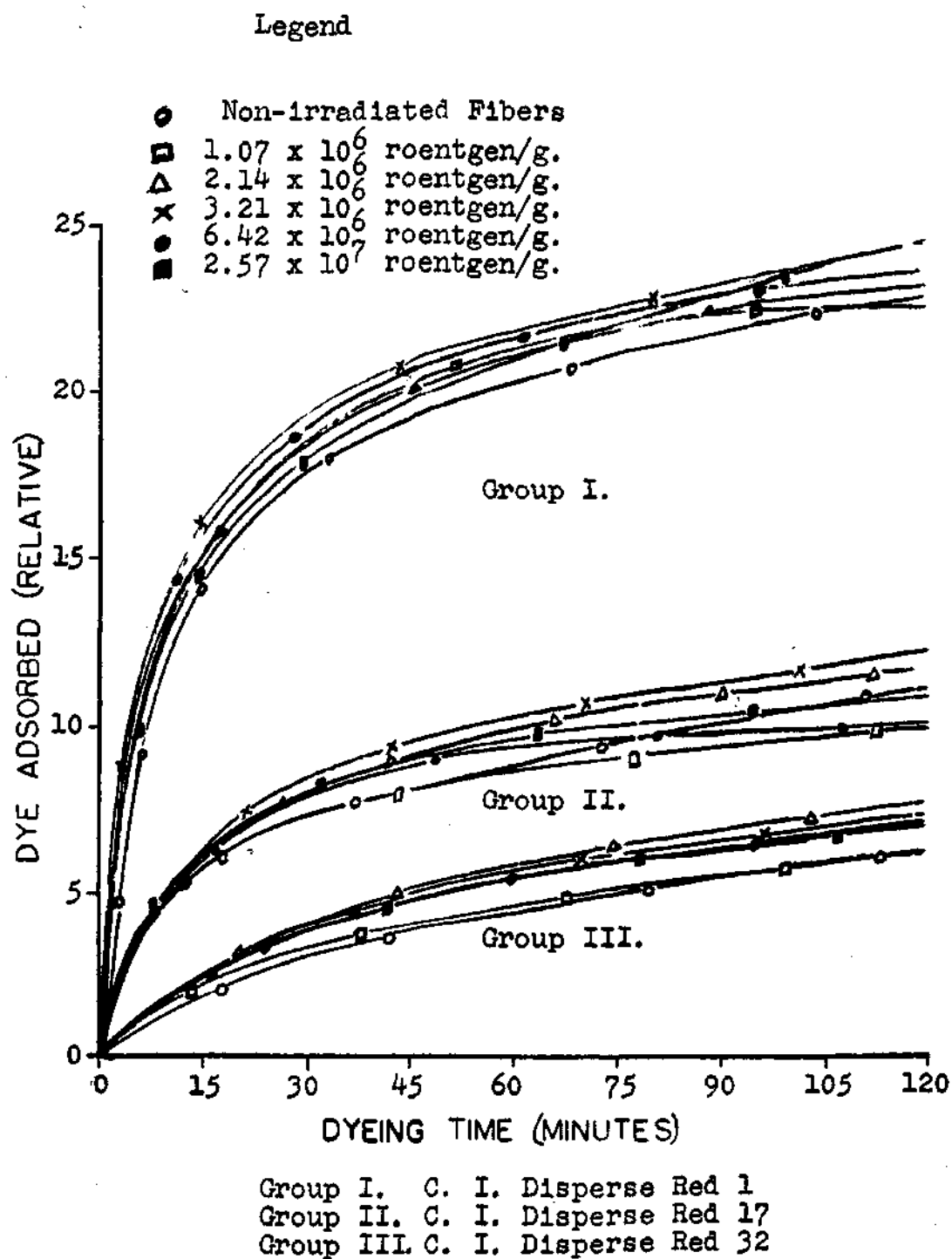
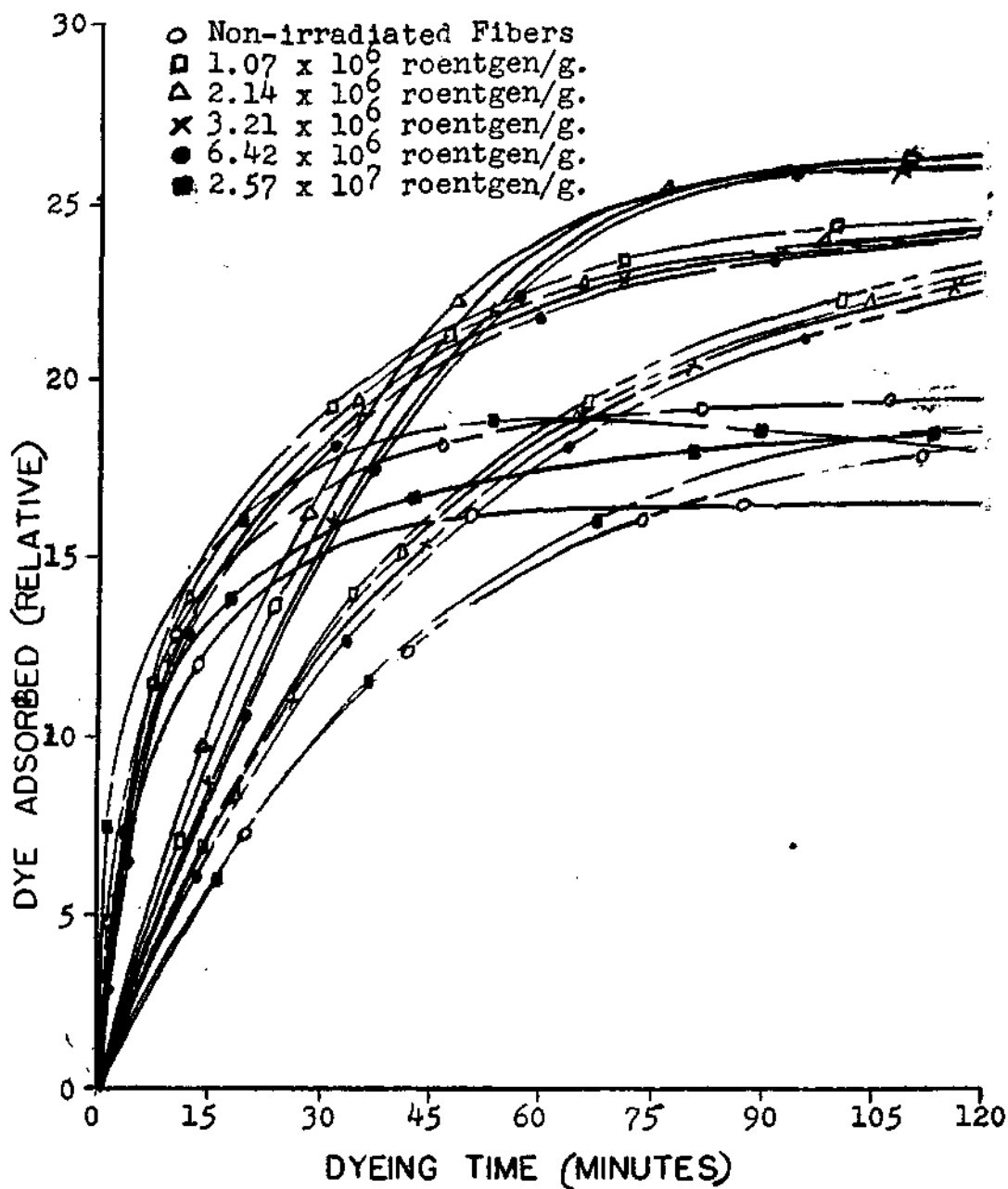


Figure 5. Dye Adsorption vs Dyeing Time For Polyester Fibers

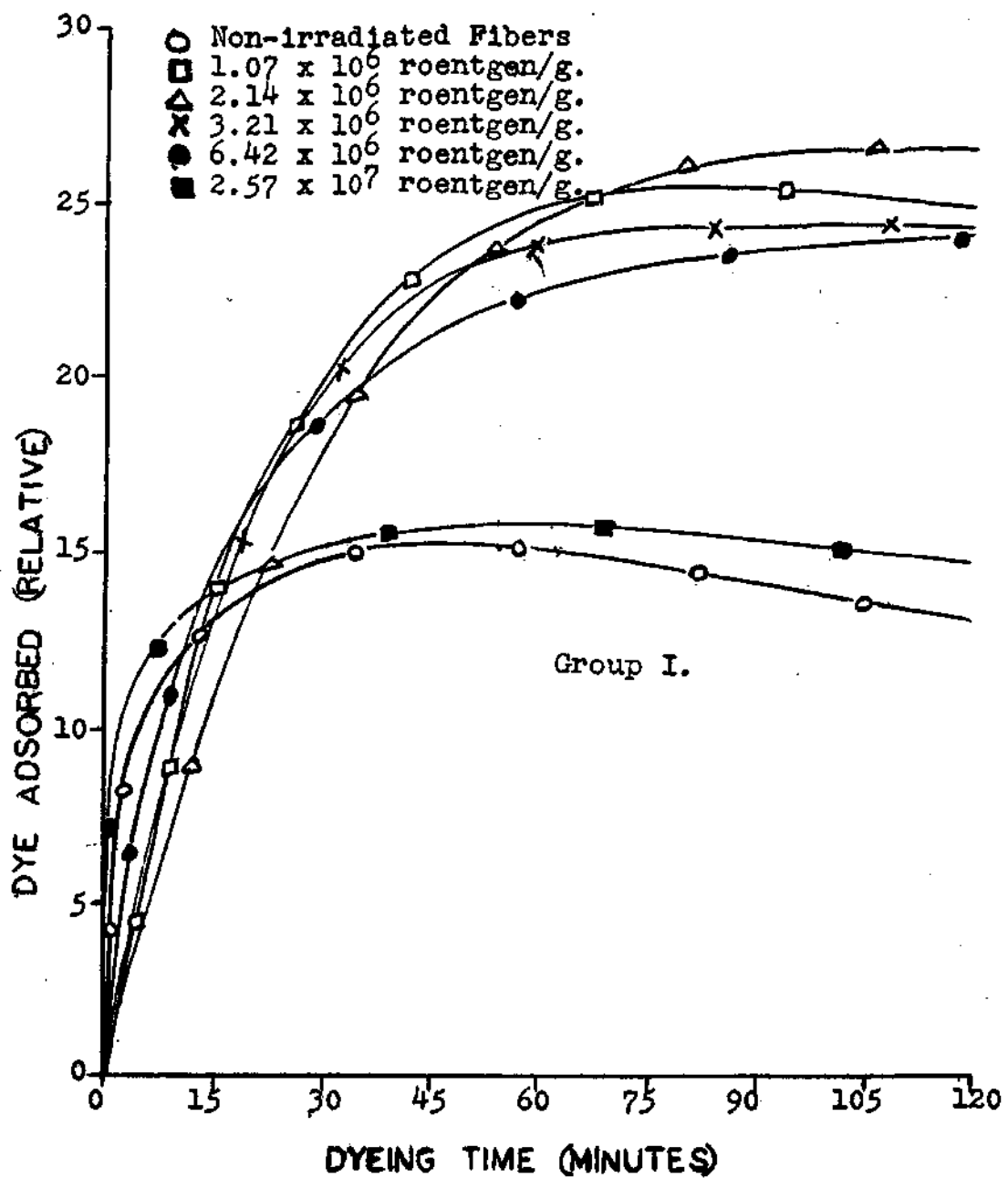
## Legend



Group I. ————— C. I. Disperse Red 1  
 Group II. - - - - - C. I. Disperse Red 17  
 Group III. - - - - - C. I. Disperse Red 32

Figure 6. Dye Adsorption vs Dyeing Time for Polyamide Fibers  
 Dye Adsorption

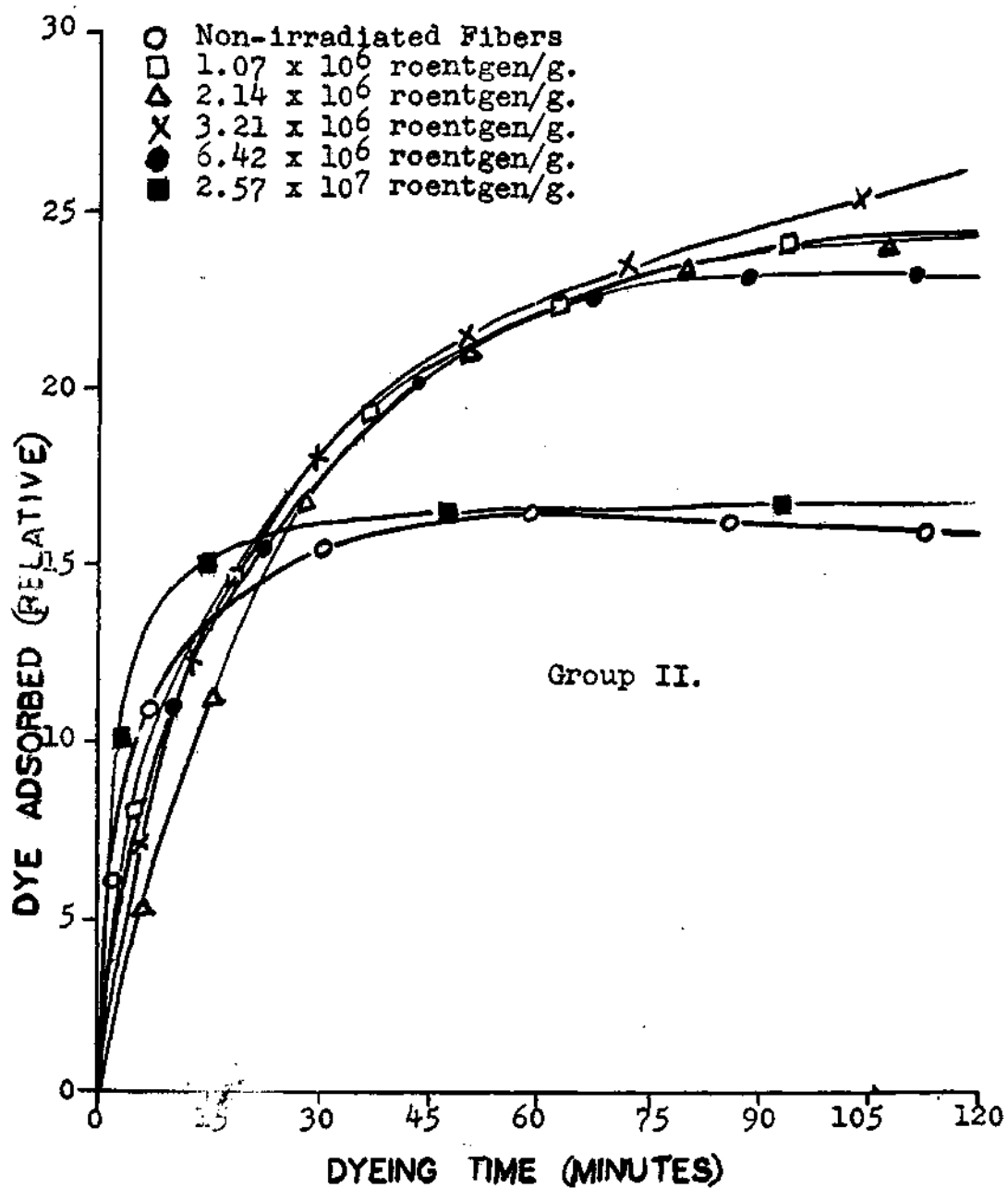
## Legend



Group I. C. I. Disperse Red 1

Figure 6a. Dye Adsorption vs Dyeing Time for Polyamide Fibers

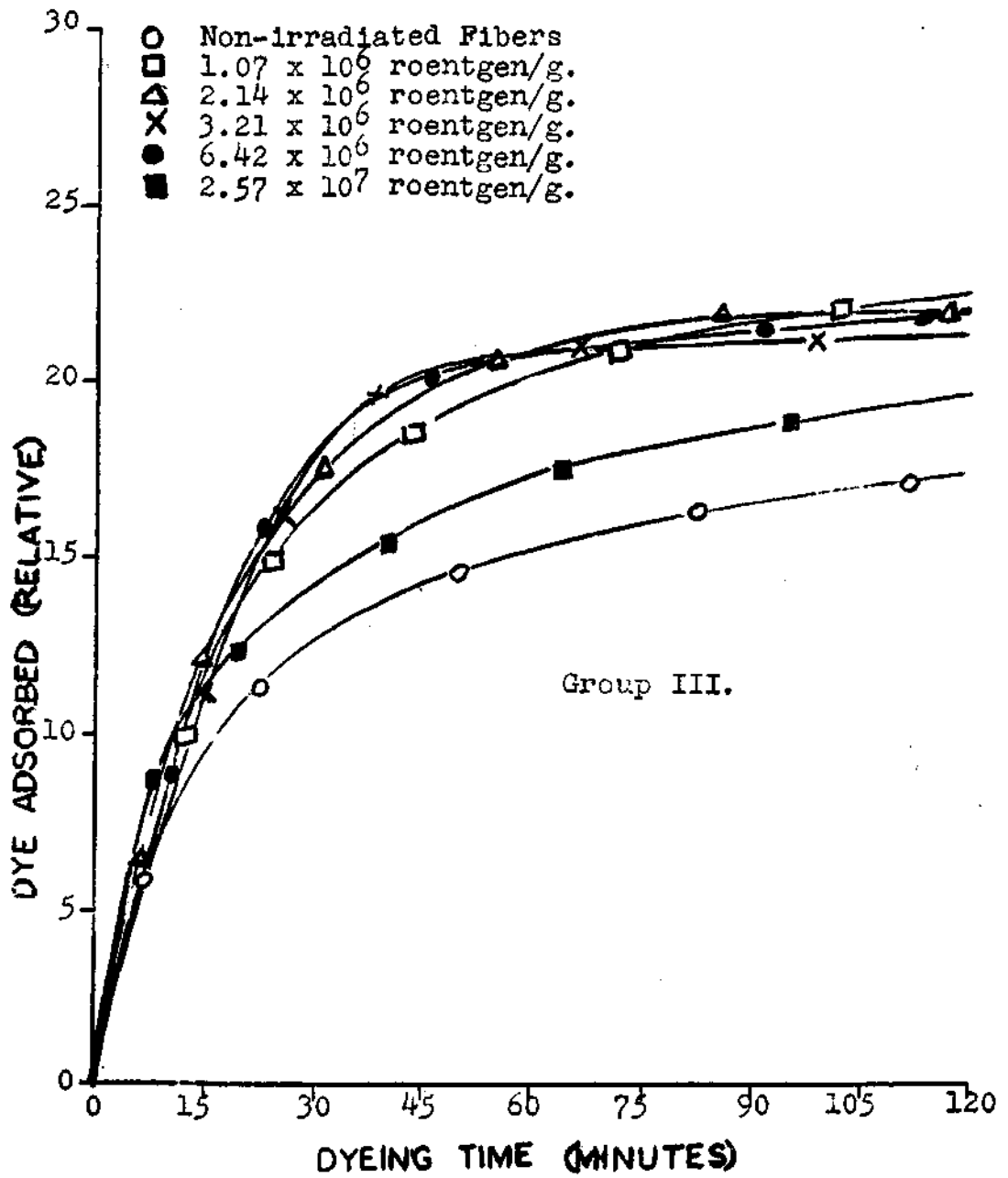
## Legend



Group II. C. I. Disperse Red 17

Figure 6b. Dye Adsorption vs Dyeing Time for Polyamide Fibers

Legend



Group III. C. I. Disperse Red 32

Figure 6c. Dye Adsorption vs Dyeing Time for Polyamide Fibers

## GLOSSARY OF TERMS

1. Radioactive isotopes - Elements, made up of atoms, the nuclei of which are capable of spontaneous disintegration with the emission of corpuscular or electromagnetic radiation. The atoms have slightly different masses though all carry the same charge and hence are chemically identical.
2. High energy radiation - Electromagnetic radiation of a frequency range extending from approximately  $10^{18}$  cycles per second to  $10^{22}$  cycles per second with a wavelength of  $10^{-7}$  to  $10^{-11}$  cm. and an energy of  $10^3$  to  $10^7$  e.v.
3. Gamma rays - A quantum of electromagnetic radiation emitted by a nucleus as a result of a quantum transition between two energy levels of the nucleus. Gamma rays energies range from  $10^4$  to  $10^7$  e.v.
4. Neutrons - Neutral elementary particles of mass number 1. A neutron produces no detectable primary ionization in its passage through matter, but interacts with matter predominantly by collisions and, to a lesser extent, magnetically.
5. Pile unit - Exposure to  $10^{17}$  thermal neutrons per square centimeter, plus associated gamma rays and fast neutrons.
6. Electron volt, e.v. - A unit of energy corresponding to  $1.60 \times 10^{-12}$  ergs.
7. M. e.v. -  $10^6$  e.v.
8. Roentgen, r. - One roentgen produces one e.s.u. of charge in one  $\text{cm}^3$  (0.0012939) of air at  $0^\circ$  C. and 760 mm. or  $2.1 \times 10^9$  ion pairs. Equivalent to absorption of 83 ergs/g. of air, or about 93 ergs/g. of water and many organic molecules.
9. Roentgen equivalent physical, rep. - The quantity of radiation of any kind producing 83 ergs/g. of body tissue or water.
10. Megarep -  $10^6$  rep.
11. Rad. - The quantity of radiation of any kind producing 100 ergs/g. of the absorber concerned.

APPENDICES

## APPENDIX I

## THE CESIUM-137 RESEARCH IRRADIATOR

The basic design of the Georgia Tech Cesium-137 Research Irradiator is a slight modification of the Notre Dame Cobalt-60 Irradiator with cesium-137 as the active material rather than cobalt-60. The Cs-Irradiator contains twelve units (approximately 1,000 curies each) of cesium-137, in the form of CsCl, of specific activity in the range of 17 to 21 curies per gram. The sources are encapsulated in stainless steel slugs, and the slugs are in turn encased in brass tubing. As encapsulated in the stainless steel slugs, the sources measure one-half inch in diameter by thirteen inches in length, the active material length being six inches.

The center sample hole of the Cs-137 Research Irradiator has a homogenous radiation field through a vertical movement of three inches, which will give a homogenous dose of  $6.2 \times 10^6$  ev/hr.g. to approximately 150 grams of material of bulk density of one. Twelve outside sample holes have been positioned around the center sample hole in the Cs-137 Irradiator. Approximately 40 grams with a bulk density of one can be exposed in any one of the twelve outer holes to a homogenous radiation field of approximately  $4.00 \times 10^{19}$  ev/hr.g.

## APPENDIX II

## DOSIMETRY OF THE CESIUM-137 IRRADIATOR

The irradiation dose adsorbed by a sample placed into the Cs-Irradiator may be determined by the ferrous-sulfate-sulfuric-acid system. In principle the application of this dosimeter involves irradiating a known quantity of 0.01N ferrous sulfate which is 0.8N with respect to  $H_2SO_4$ . The solution is kept saturated with oxygen and stirred continuously (by the passage of oxygen bubbles through the solution) during the irradiation period. After irradiating for a known time interval, the unoxidized ferrous ion concentration is determined titrimetrically with 0.01N potassium dichromate as the titrant and potassium diphenylaminesulphonate as the indicator. The difference between the initial and final milliequivalents of ferrous ions is a measure of the energy absorbed. The energy absorbed has been reported as electron volts (e.v.) per gram hour.

The dose absorbed by materials irradiated in the Cs-137 Irradiator has recently been reported as follows:

Central Position

$6.2 \times 10^{19}$  ev/hr-g.

Outside Positions  
( $\times 10^{19}$  ev/hr-g.)

No. 1 - 3.82	No. 7 - 3.91
No. 2 - 3.88	No. 8 - 4.17
No. 3 - 3.68	No. 9 - 4.06
No. 4 - 3.93	No. 10 - 4.16
No. 5 - 3.68	No. 11 - 3.79
No. 6 - 4.16	No. 12 - 3.80

All irradiation dose rates in this investigation have been reported in roentgens per hour-gram. Electron voltes (e.v.) per hour-gram were converted to roentgens (r.) per hour-gram as follows:

Dose absorbed by sample in e.v./hr-g. multiplied by  $1.60 \times 10^{-12}$  (ergs/e.v.) equals ergs/hr-g.

One roentgen equals 93 ergs/g.

Thus, for a sample irradiated one hour, the dose absorbed in roentgens/g. may be obtained by dividing the dose absorbed in ergs/g. by 93 roentgens.

Example:

Dose absorbed by sample in Central position of Cs-137  
Irradiator -  $6.2 \times 10^{19}$  e.v./hr-g.

Thus, for an irradiation time of one hour the dose absorbed would be

$$6.2 \times 10^{19} \text{ ev/g.} \times 1.60 \times 10^{-12} \text{ ergs/ev} = 9.92 \times 10^7 \text{ ergs/g.}$$

and

$$\frac{9.92 \times 10^7 \text{ ergs/g.}}{93 \text{ ergs/g.-roentgen}} = 1.07 \times 10^6 \text{ roentgen/g.}$$

## APPENDIX III

DYE ABSORBENCE VALUES FOR TRIACETATE,  
POLYESTER, AND POLYAMIDE FIBERSTable 6. Dye Absorbence Measurements of Disperse Red 1  
Dyeings on Irradiated and non-irradiated Arnel  
Triacetate Fibers

Dyeing Time Minutes	Absorbence at 490 mu
Irradiation Dose: Not Irradiated	
5	0.697
10	0.920
15	1.220
25	1.630
45	2.110
65	2.140
85	2.160
105	2.140
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.639
10	1.030
15	1.230
25	1.570
45	2.020
65	2.060
85	2.170
105	2.220
120	2.180
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.609
10	0.943
15	1.200
25	1.600
45	1.978
65	2.100
85	2.130
105	2.180

Table 6. (Continued)

Dyeing Time Minutes	Absorbance at 490 mu
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.663
10	0.935
15	1.110
25	1.480
45	1.930
65	2.030
85	2.110
105	2.200
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.598
10	0.910
15	1.080
25	1.670
45	1.960
65	2.010
85	2.130
105	2.140
120	2.090

Table 7. Dye Absorbance Measurements of Disperse Red 17 Dyeings on Irradiated and Non-irradiated Arnel Triacetate Fibers

Dyeing Time Minutes	Absorbance at 480 m $\mu$
Irradiation Dose: Not Irradiated	
5	0.420
10	0.542
15	0.668
25	0.903
45	1.320
65	1.380
85	1.460
105	1.500
120	1.520
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.410
10	0.651
15	0.788
25	0.935
45	1.240
65	1.330
85	1.450
105	1.520
120	1.490
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.413
10	0.728
15	0.749
25	0.942
45	1.200
65	1.380
85	1.380
105	1.520
120	1.520

Table 7. (Continued)

Dyeing Time Minutes	Absorbance at 480 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.418
10	0.669
15	0.771
25	0.905
45	1.170
65	1.350
85	1.380
105	1.450
120	1.500
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.401
10	0.596
15	0.710
25	0.955
45	1.240
65	1.310
85	1.380
105	1.380
120	1.470

Table 8. Dye Absorbance Measurements of Disperse Red 32 Dyeings on Irradiated and Non-irradiated Arnel Triacetate Fibers

Dyeing Time Minutes	Absorbance at 450 m $\mu$
Irradiation Dose: No Irradiated	
5	0.167
10	0.186
15	0.252
25	0.366
45	0.560
65	0.610
85	0.660
105	0.709
120	0.703
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.157
10	0.254
15	0.317
25	0.397
45	0.542
65	0.567
85	0.631
105	0.675
120	0.702
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.157
10	0.259
15	0.323
25	0.407
45	0.538
65	0.593
85	0.655
105	0.660
120	0.721

Table 8. (Continued)

Dyeing Time Minutes	Absorbance at 450 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.173
10	0.248
15	0.298
25	0.415
45	0.523
65	0.618
85	0.620
105	0.660
120	0.709
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.158
10	0.351
15	0.342
25	0.426
45	0.506
65	0.560
85	0.624
105	0.658
120	0.676

Table 9. Dye Absorbance Measurements of Disperse Red 1 Dyeings on Irradiated and Non-irradiated Dacron Polyester Fibers

Dyeing Time Minutes	Absorbance at 517 m $\mu$
Irradiation Dose: Not Irradiated	
5	0.728
10	1.030
15	1.260
25	1.600
45	2.000
65	2.050
85	2.080
105	2.150
120	2.150
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.770
10	1.230
15	1.260
25	1.820
45	2.030
65	2.190
85	2.170
105	2.130
120	2.140
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.700
10	1.090
15	1.460
25	1.750
45	2.010
65	2.240
85	2.160
105	2.160
120	2.230

Table 9. (Continued)

Dyeing Time Minutes	Absorbance at 517 $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.728
10	1.250
15	1.570
25	1.920
45	2.110
65	2.210
85	2.210
105	2.130
120	2.210
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.718
10	1.030
15	-
25	1.750
45	2.140
65	2.190
85	2.210
105	2.210
120	2.170
Irradiation Dose: $2.57 \times 10^7$ roentgen/g.	
5	0.734
10	1.030
15	1.570
25	1.760
45	2.010
65	2.170
85	2.180
105	2.180
120	2.200

Table 10. Dye Absorbance Measurements of Disperse Red 17  
Dyeings on Irradiated and Non-irradiated Dacron  
Polyester Fibers

Dyeing Time Minutes	Absorbance at 512 m $\mu$
Irradiation Dose: Not Irradiated	
5	0.364
10	0.469
15	0.579
25	0.673
45	0.830
65	0.890
85	1.070
105	1.200
120	1.120
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.337
10	0.498
15	0.598
25	0.645
45	0.820
65	0.985
85	0.925
105	0.985
120	1.150
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.323
10	0.451
15	0.674
25	0.673
45	0.893
65	1.070
85	1.090
105	1.130
120	1.370

Table 10. (Continued)

Dyeing Time Minutes	Absorbance at 512 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.338
10	0.508
15	0.579
25	0.700
45	0.855
65	0.960
85	1.150
105	1.110
120	1.360
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.335
10	0.444
15	0.617
25	0.638
45	0.918
65	1.060
85	1.030
105	1.080
120	1.140
Irradiation Dose: $2.57 \times 10^7$ roentgen/g.	
5	0.352
10	0.469
15	0.635
25	0.703
45	0.910
65	1.020
85	1.030
105	1.200
120	1.110

Table 11. Dye Absorbance Measurements of Disperse Red 32 Dyeings on Irradiated and Non-irradiated Dacron Polyester Fibers

Dyeing Time Minutes	Absorbance at 465 m $\mu$
Irradiation Dose: Not Irradiated	
5	0.128
10	0.205
15	0.303
25	0.273
45	0.329
65	0.439
85	0.472
105	0.602
120	0.610
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.148
10	0.303
15	0.344
25*	0.346
45	0.417
65	0.478
85	0.548
105	0.491
120	0.565
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.157
10	0.314
15	0.412
25	0.423
45	0.437
65	0.599
85	0.610
105	0.612
120	0.793

Table 11. (Continued)

Dyeing Time Minutes	Absorbance at 465 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.193
10	0.360
15	0.382
25	0.439
45	0.481
65	0.559
85	0.648
105	0.648
120	0.678
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.181
10	0.312
15	0.385
25	0.334
45	0.520
65	0.573
85	0.630
105	0.648
120	0.648
Irradiation Dose: $2.57 \times 10^7$ roentgen/g.	
5	0.222
10	0.297
15	0.350
25	0.411
45	0.461
65	0.502
85	0.652
105	0.643
120	0.612

Table 12. Dye Absorbance Measurements of Disperse Red 1 Dyeings on Irradiated and Non-irradiated Nylon Polyamide Fibers

Dyeing Time Minutes	Absorbance at 525 m $\mu$
Irradiation Dose: Not Irradiated	
5	1.310
10	1.360
15	1.390
25	1.410
35	1.470
45	1.480
55	1.420
65	1.360
75	1.290
85	1.390
95	1.600
105	1.480
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.492
10	1.080
15	1.210
25	1.450
35	1.440
45	2.280
55	2.460
65	2.360
Irradiation Dose $2.14 \times 10^6$ roentgen/g.	
5	0.542
10	1.070
15	1.340
25	1.450
35	1.530
45	2.270
55	2.320
65	2.410

Table 12. (Continued)

Dyeing Time Minutes	Absorbance at 525 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.626
10	1.110
15	1.370
25	1.400
35	1.480
45	2.340
55	2.340
65	2.380
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.715
10	1.270
15	1.330
25	1.400
35	1.500
45	2.190
55	2.180
65	2.380
Irradiation Dose: $2.57 \times 10^7$ roentgen/g.	
5	1.320
10	1.460
15	1.460
25	1.480
35	1.600
45	1.560
55	1.500
65	1.670
75	1.780
85	1.790
95	1.530

Table 13. Dye Absorbance Measurements of Disperse Red 17 Dyeings on Irradiated and Non-irradiated Nylon Polyamide Fibers

Dyeing Time Minutes	Absorbance at 525 m $\mu$
Irradiation Dose: Not Irradiated	
5	0.714
10	1.130
15	1.320
25	1.430
35	1.600
45	1.620
55	1.660
65	1.680
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.701
10	1.110
15	1.320
25	1.400
35	1.510
45	2.080
55	2.160
65	2.230
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.653
10	1.090
15	1.310
25	1.340
35	1.500
45	2.020
55	2.080
65	2.160

Table 13. (Continued)

Dyeing Time Minutes	Absorbance at 525 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.727
10	1.010
15	1.460
25	1.420
35	1.460
45	2.090
55	2.160
65	2.210
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.531
10	1.120
15	1.320
25	1.450
35	1.520
45	2.070
55	2.170
65	2.150
Irradiation Dose: $2.57 \times 10^7$ roentgen/g.	
5	1.570
10	1.470
15	1.580
25	1.460
35	1.530
45	1.600
55	1.570
65	1.540
85	1.470
105	1.480

Table 14. Dye Absorbance Measurements of Disperse Red 32 Dyeings on Irradiated and Non-irradiated Nylon Polyamide Fibers

Dyeing Time Minutes	Absorbance at 485 m $\mu$
Irradiation Dose: Not Irradiated	
5	0.677
10	0.700
15	0.868
25	1.180
35	1.310
45	1.440
55	1.470
65	1.510
85	1.690
105	1.720
Irradiation Dose: $1.07 \times 10^6$ roentgen/g.	
5	0.674
10	0.855
15	1.120
25	1.310
35	1.800
45	1.940
55	1.980
65	2.020
Irradiation Dose: $2.14 \times 10^6$ roentgen/g.	
5	0.680
10	0.919
15	1.330
25	1.310
35	1.690
45	2.000
55	2.020
65	2.000

Table 14. (Continued)

Dyeing Time Minutes	Absorbance at 485 m $\mu$
Irradiation Dose: $3.21 \times 10^6$ roentgen/g.	
5	0.754
10	1.030
15	1.210
25	1.440
35	1.690
45	2.010
55	1.980
65	2.040
Irradiation Dose: $6.42 \times 10^6$ roentgen/g.	
5	0.719
10	0.900
15	1.150
25	1.510
35	1.710
45	2.000
55	2.030
65	1.960
Irradiation Dose: $2.57 \times 10^7$ roentgen/g.	
5	0.702
10	1.040
15	1.230
25	1.340
35	1.430
45	1.520
55	1.570
65	1.630
85	1.830
105	1.730

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