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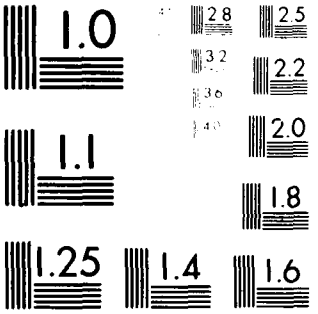


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Technical Report No. 13

# OXIDATIVE STABILIZATION OF ACRYLIC FIBERS
# PART V. THE DECOLORATION REACTION

by

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When acrylic fibers are heat treated for various times at 220-250 C, they form dark, insoluble structures of uncertain chemical character which are inert to many strong oxidizing and reducing agents. The heat-treated fibers are, however, rapidly decolored by warm alkaline hypochlorite solutions. When fibers which have undergone short time heat treatment are subjected to the hypochlorite, incubation periods are observed before decoloration is noted; and a swollen acrylic network remains after


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decoloration is complete. The acrylic network is primarily unreacted precursor units save for a small amount of hydrolyzed material. The decoloration reaction is zero order, indicating a reaction at the surface. Prior to the decoloration reaction, there is a penetration or plasticization of the subsurface material by elements of the solution, as indicated by the presence of chlorine atoms in the interiors of exposed fibers. The rate of the decoloration reaction increases with increasing duration of the stabilization heat treatment.

In fibers which have undergone partial diffusion-controlled stabilization, a dark mantle surrounds a lightly colored core. A previous model suggested that prefatory reactions had occurred throughout the fiber and that sequent reactions occurred only in the mantle. The rate of decoloration is unaffected as the decoloration interface passes from the mantle to the core, indicating that the decoloration reaction is not influenced by the occurrence of the sequent reactions. The existence of the acrylic residue indicates that the prefatory reactions are continuing in both mantle and core during the course of stabilization.

The overall rate of prefatory reactions is controlled by the rate of formation of nitrile initiators, the initiation of nitrile polymerization, and the rate of propagation. Fibers may already contain initiators, such as itaconic acid, or initiators can be formed at reaction temperatures under oxidative or inert conditions. The rates of formation of the various initiating species and the rates of initiation of polymerization are largely unknown.

$^{13}$C-NMR spectra of the acrylic residue shows the same triad methine peak areas as those obtained on the untreated fiber; hence the stereoregularity of the nitrile groups has no influence on the rate of nitrile polymerization.

The mechanism of decoloration is postulated to involve electrophylic scission of the chlorine-oxygen bond, adding chlorine to the pyridine-like nucleophile of the acrylic chromophore. The adduct thus formed rapidly undergoes ring opening followed by hypochlorite attack on the remaining unsaturation,

Hot aqueous sulfuric acid dissolves the unreacted fiber and solubilizes that portion which has undergone only the prefatory reactions, whereas hypochlorite treatment removes those portions which have undergone the prefatory and sequent reactions. The present results therefore suggest that during the early-to-intermediate stages of stabilization, the fiber consists of interpenetrating networks of original material, that which has undergone only the prefatory reactions and that which has undergone the sequent reactions. On further stabilization, the fiber is transformed into a structure dominated by material which has undergone the sequent reactions. The precise structure of the final material depends therefore on the original fiber composition and the processing variables.

# OXIDATIVE STABILIZATION OF ACRYLIC FIBERS

## PART V. THE DECOLORATION REACTION

by

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When acrylic fibers are heat treated for various times at 220-250 C, they form dark, insoluble structures of uncertain chemical character which are inert to many strong oxidizing and reducing agents. The heat-treated fibers are, however, rapidly decolored by warm alkaline hypochlorite solutions. When fibers which have undergone short time heat treatment are subjected to the hypochlorite, incubation periods are observed before decoloration is noted; and a swollen acrylic network remains after decoloration is complete. The acrylic network is primarily unreacted precursor units save for a small amount of hydrolyzed material. The decoloration reaction is zero order, indicating a reaction at the surface. Prior to the decoloration reaction, there is a penetration or plasticization of the subsurface material by elements of the solution, as indicated by the presence of chlorine atoms in the interiors of exposed fibers. The rate of the decoloration reaction increases with increasing duration of the stabilization heat treatment.

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## I. INTRODUCTION

It has been known for a long time that acrylic fibers can be converted into carbon fibers (1). The first step in this conversion involves heating the PAN fibers at 220 to 290 C in air for several hours. This process is usually termed stabilization. The stabilized fibers are then converted into carbon fibers by subsequent thermal treatment under inert conditions. Although the subsequent reaction conditions have some effect on the properties of the final carbon fibers, it is accepted that the initial stabilization step has a more dominant effect on the properties of the product.

Previous papers in this series have addressed various facets of the stabilization process: the kinetics of stabilization, oxygen uptake, and a general model of stabilization (2); the dynamics of stabilization (3); a new model for the morphological structure of polyacrylonitrile (4); and the moisture uptake of stabilized fibers (5). The present paper will consider several low temperature chemical reactions of stabilized acrylic fibers which demonstrate the existence in the fibers of interpenetrating networks of reacted and unreacted material during portions of the stabilization process.

One phenomenon accompanying the stabilization reaction has been noted for a long time. That is, the color of the fiber changes from white to yellow, to orange, to brown, and finally to black. Many possible mechanisms have been suggested to explain this phenomenon and the related question of how oxygen is incorporated in the fiber during stabilization in air (1, 6, 7, e.g.). The precise nature of the reactions involved

in stabilization and the structure of the stabilized material remain, however, to be elucidated satisfactorily.

Several reasons for this difficulty in characterizing the reactions and structure may be given: First, the stabilized product is insoluble in any known solvent, and hence normal chemical tests cannot be used. Second, the commonly used technique of IR absorption for structural characterization--although quite useful for low molecular weight compounds--is not very helpful in analyzing the stabilized fibers (the stabilized fibers give broad, intense absorptions, which are very difficult to identify unequivocally).

This requires new methods to obtain information about the stabilized fiber. It has been found that a reaction can cause the color of the black, partially stabilized fiber to change back to light yellow. This reaction, called a decoloration reaction, involves the reaction of the stabilized fiber with warm aqueous alkaline sodium hypochlorite solutions. In addition, treatment of the partially stabilized fibers with hot aqueous sulfuric acid will dissolve portions of the fiber, with the shape of the residuum depending upon the limiting conditions of stabilization. The observations made in studying these reactions are presented in this paper and are used to develop an improved model of stabilization.

## II. EXPERIMENTAL PROCEDURE

### A. Materials

#### 1. Acrylic Fibers

Commercially available Courtelle and Orlon fibers were respun by C. B. Brogna and R. Ruleson at Fiber Research Laboratory to eliminate gross variations in spinning conditions (8). These fibers, as well as other commercial and experimental acrylic fibers used in the present investigation, are described in Table I. The fibers were partially or completely stabilized by heat treatment under a variety of conditions (see Tables II and III below).

#### 2. Decoloration Reagent

Commercially available alkaline sodium hypochlorite, Chlorox, was used as received. The available chlorine is 5.25% by weight, which is equivalent to 0.76 mole liter$^{-1}$. The pH of the solution is 11.4. In addition to sodium hypochlorite, 0.76M sodium chloride is present (9). Hypochlorite will disproportionate into chloride and chlorate above room temperature (10), will decompose in the presence of metal ions to chloride and oxygen (11, 12), with the ionic species present depending on the pH.

In the present work, a large excess of hypochlorite relative to the fiber mass was used for the decoloration reaction. The possible species present in the warm alkaline solutions employed include $Na^+$, $ClO^-$, $ClO_3^-$, $OH^-$, and $Cl^-$.

### B. Observation of the Decoloration of Stabilized Fibers

Acrylic fibers given various heat treatments were used as starting materials for qualitative and/or quantitative examination using a variety

of techniques. These include:

1. Direct Method Observations

A few individual filaments of heat treated fibers were immersed in a shallow reservoir filled with alkaline hypochlorite solution. The fibers were pinned between two pieces of 50 mesh platinum gauze to discourage fiber movement yet allow adequate diffusion of reactant and observation of the fibers. The reservoir was closed with a cover slip. The reservoir/slide assembly was then placed on a pre-heated microscope hot stage to raise the temperature rapidly to the test condition. Color photographs of the decoloration process of an individual filament were taken using transmitted light from a Xenon arc lamp.

2. Indirect Method Observations

The stabilized fibers were cut into 1 inch long pieces, and about 100 pieces were reacted with 20 ml of reactant in a capped Erlenmeyer flask. The temperature was kept constant by a water or oil bath. Several fiber lengths were removed after selected time periods, rinsed with distilled water, and examined through a Zeiss Universal Research Microscope. The diameters of the fibers were either determined indirectly from photomicrographs or directly by means of a Filar eyepiece. In both cases, the diameters of the colored zone and the decolored zone were noted.

3. Infrared Spectroscopy

KBr disks of processed fibers were prepared by standard methods. Only the occurrence and location of certain bands are reported here because the spectra were quite similar to those already published (7, 13-16, e.g.).

4. Proton Nuclear Magnetic Resonance (H-NMR)

Approximately 40 mg of sample was mixed with 0.5 ml deuterated dimethylsulfoxide (DMSO-$d_6$) and allowed to stand for several days to effect dissolution without application of heat. A small quantity of insoluble material was removed prior to examination with a Varian T-60 NMR spectrometer.

5. $^{13}$C-Nuclear Magnetic Resonance (C-NMR)

Approximately 100 mg of sample was mixed with 3 ml of DMSO-$d_6$ and allowed to stand for several days. The filtered material was examined at 100 C with a Bruker 250 MHz spectrometer.

6. Energy Dispersive X-Ray Analysis

C-805 fibers were pyrolyzed in air at 225 C for 180 min., decolored in the hypochlorite solution for various times at 40°C in an unstirred solution to prevent removal of the residue phase. The fibers were mounted in a polyester potting compound and polished with 60, 320, and 600 grit sand paper then $Al_2O_3$ polishing compound. The samples were coated with gold to reduce charging, and examined in a Cambridge Stereoscan scanning electron microscope with a KEVEX attachment for energy dispersive chemical analysis. This device was used to measure the radial variations in the concentration of chlorine atoms across the fiber. The accumulated intensity over 60 sec. was taken as proportional to chlorine concentration at each location.

## III. RESULTS

### A. Direct Observations of the Decoloration of Individual Filaments

When a single filament of C-type yarn (such as CHT) which has been stabilized at 225°C is immersed in hypochlorite solution at 50°C, two types of behavior are observed. The first, termed Type I, is observed for CHT fibers stabilized for 127 min. Following an incubation time, an optically-distinct clear zone is seen around the perimeter of the fiber; this clear zone subsequently increases in size at the expense of the central colored zone. As illustrated by the data in Fig. 1, the diameter of the colored zone decreases linearly with increasing decoloration time. A representative black-and-white photomicrograph of such a fiber in the partially-decolored state is shown in Fig. 2. An inner colored zone is seen surrounded by an outer swollen, clear or pale yellow residue. The perceived color of the central phase changes with time as indicated in Fig. 1.

With increasing time of stabilization and the same decoloration conditions, the fibers are observed to decolor at a faster rate, and the amount of clear residue following decoloration decreases. After long stabilization times, the color of the central phase also changes after decoloration, but no residue is observed. This is termed Type II behavior.

Although direct observation of the decoloration of individual filaments appears fairly straightforward, the technique presented a number of difficulties. The fibers tended to break up in the later stages of decoloration; the fibers tended to move about in the field of

view throughout the reaction; and bubbles--which may be decoloration reaction products, hypochlorite decomposition product(s) or water vapor-accumulated on the fibers and under the cover slip as decoloration proceeded. In many runs, these phenomena prevented adjustments of focus for photography or direct measurements of diameter; and it was only possible to determine the time required for complete disappearance of the colored phase. In a few cases, these problems did not occur, and it was possible to follow the course of the decoloration reaction throughout the entire regime (as shown in Fig. 1 and reported in Table II).

As indicated above, the kinetics of the decoloration reaction are characterized by an incubation period followed by a steady decrease in the diameter of the colored phase. The time at which the diameter of the colored phase extrapolates to zero thickness is taken as the decoloration time. The reciprocal of the decoloration time is proportional to the reaction rate (diameter = a - kt, $t_{dec} = a/k$). The logarithm of the decoloration time at other temperatures relative to that at 50 C is plotted against 1/T in Fig. 3. From the slope of the line, an activation energy of about 6 kcal $mol^{-1}$ is obtained.

The temperature of the decoloration reaction also influences the quantity of residue remaining after completion of the reaction: more residue remains at lower temperatures, and at sufficiently high decoloration temperatures, no residue remains. The existence of residue phase also depended upon the degree of agitation of the fiber-reactant mixture. The residue phase is rather fragile, and is removed from the fiber if the mixture is stirred during the decoloration reaction.

For lightly stabilized fibers (e.g., 127 min. @ 225 C), the diameter of the residue phase after decoloration is larger than the diameter of the fiber before decoloration (by about 25% in a typical case). That is, the residue phase is swollen by the reactant solution. For longer stabilization times (e.g., 185 min @ 227 C), the diamter of the residue phase is less than that of the initial colored fiber (by 34% in a typical case). At still longer times (more than 212 min @ 225 C), no residue phase remains after decoloration.

The residue phase apparently presents no significant barrier either to diffusion of the reacting species to the reaction front or of reacted species (if any) from the front: a linear decrease in the diameter of the colored phase is observed whether or not the residue phase is present. Furthermore, there is no detectable optical orientation anywhere in the residue phase; the birefringence of the colored phase is completely destroyed by passage of the reaction front.

Fibers which yield a residue phase develop cracks during the course of decoloration at 50 C. These cracks appear towards the end of the reaction and tend to cause the fiber to break up into small pieces or chaff. The crack formation observed here takes place under much milder conditions than the cracking observed when non-stabilized acrylic fibers are subjected to boiling alkaline hypochlorite solutions (17).

The rate of decoloration increases with increasing stabilization time. Indeed, the fiber reacted for 4300 min at 226 C had to be examined at 21 C in a 12.5% solution of hypochlorite in order to obtain a measurable rate of decoloration. The measured decoloration time for this sample can be

adjusted for comparison with other measurements using the kinetic data in Fig. 3 with a direct, but untested, correlation between decoloration time and hypochlorite concentration. In Fig. 4, the logarithm of the decoloration time, $t_{dec}$, is plotted against the logarithm of the stabilization time, $t_{stab}$, for a variety of conditions. Equations for the straight lines are presented in Table III. The parameters for 226 C in air were estimated by least squares procedures whereas those for 226 C in argon and 240 C in air are based on only two data points.

The species which are formed during stabilization react very rapidly with the hypochlorite solution. The higher the concentration of these species, the more rapid is the decoloration rate. High temperature treatment, near the upper end of the stabilization range, tends to decrease the rate of decoloration: See, e.g., in Table II the CHT fiber treated for 4300 min at 226 C followed by heat treatment in argon for 660 min at 400 C, which decolors quite slowly, although the fiber does completely dissolve. Perhaps this fiber has already undergone some small amount of heteroatom release or carbonization. Fibers that have undergone extensive carbonization and high-temperature heat-treatment are not decolorized by the hypochlorite solution. Indeed, warm alkaline hypochlorite solutions can be used to oxidize the outer surface of carbon fibers to improve the interlaminar shear strength in composites (18).

Short time exposure of the same fibers in argon at 226 C gives essentially the same decoloration rate as those treated in air, which suggests that atmosphere does not play an important part in the early stage formation of the groups which are susceptible to hypochlorite attack. Prolonged treatment at the same temperature shows a pronounced effect of atmosphere, with the air-treated fibers decoloring much more rapidly than fibers treated in argon (see Table II).

The CHT fibers considered in Table II contain a weak acid comonomer, which serves as a catalyst for increasing the rate of stabilization (8, e.g.). For such fibers, the initial rate of the prefatory reactions should not require the presence of oxygen; and hence the rate of decoloration for short heat treatment times should not depend on atmosphere. As the catalyst comonomer is used up initiating the prefatory reactions, the effect of oxygen in catalyzing these reactions should become significant; and the extent of the prefatory reactions--and hence the rate of decoloration in hypochlorite solutions--should show a dependence on atmosphere.

B. Indirect Method of Observing Decoloration of Fiber Materials and Individual Filaments.

To obtain rapid results for a variety of stabilization conditions and fiber types, an indirect method of observation was used. Fibers were reacted with warm hypochlorite solution; a small sample was removed and rinsed; and the diameter of the whole fiber, colored phase plus residue phase, $a$, and the diameter of the colored phase, $b$, were determined with a Filar eyepiece. A plot of $b/a$ vs. time is shown in Fig. 5 for C-805 fibers. Although considerable scatter is observed, a distinct incubation period is noted, and the ratio $b/a$ is seen to decrease with increasing time.

The scatter in b/a vs. time may be associated with variations in the initial fiber (due to the fiber formation process), to the stabilization conditions (such as inside vs. outside filaments in the yarn bundle), or to uncontrolled variations in the decoloration reaction. Even more scatter was observed in plots of a vs. time and b vs. time than in b/a vs. time, which suggests the presence of significant variability in the original fibers.

Similar experiments were conducted on C-C fibers (the precursor material for the respun C-805 fibers) which had been treated at 225 C for 210 min. In this case, Type II behavior was observed; i.e. no residue phase remained after decoloration. A plot similar to Fig. 5 was obtained, except that no induction period was noted. During the course of the reaction, the fiber became quite fragile and could not easily be removed from the reaction bath without disintegrating.

The C-C fibers stabilized under milder conditions, e.g., 100 min. at 205 C, exhibited Type I behavior; the parameter b/a again decreased with time, but less scatter was observed relative to that seen in the data for C-805 fibers. The last finding suggests that some of the scatter in the last data may be associated with the respinning conditions.

During the course of these experiments, it was noted that for fibers which exhibited Type I behavior, the color of the supernatant hypochlorite liquid and the fiber remained unchanged for a period of time, after which the fiber started to decolor. No obvious change occurred in the supernatant liquid or in the size of the fiber. For fibers which exhibit Type II

behavior, the color of the supernatant phase became nonuniformly deeper and the fibers tended to break into small pieces. The fibers became uniformly lighter in color and the fiber diameter decreased. Prior to complete dissolution of the fiber, the supernatant phase became less colored and the pieces of the fibers were quite difficult to see.

In both cases, it was easy to distinguish a time after mixing the fiber and hypochlorite solution when a discernable shift in color of the fibers occurred. Lightly stabilized, transparent orange to brown colored fibers also showed a distinct time to affect a color change or lightening, but no residue phase was detected. Microscopic observation of opaque black fibers showed no color change prior a shift in color from black to brown called $t_1$. Following this time, red striations appeared which seemed to correspond to the crenulations on the fiber surface. The outer edges of the fibers became more diffuse during this period, but a distinct change in diameter of the colored phase could not be determined. Fig. 6 shows the time required for an initial color change as a function of stabilization time at 225 C for both C and O fibers. Both Type I and Type II behavior are represented in the figure. The induction period measured by this technique (for the first observable change in color) is far shorter than that determined for the initial formation of a clear outer zone: A change in the color of the fibers was noted after only 20 min. for C-805 fibers stabilized for 180 min. at 225 C (Fig. 6), whereas the residue phase (clear outer zone) was first noted after about 90 min. (Fig. 5).

Although the observations detailed in Figs. 1 through 5 and Table II were made on C-type fibers--that is, fibers which contain itaconic acid and undergo a diffusion-controlled mechanism of stabilization at 225 C--similar observations have been made on all the fibers listed in Table I, with Type I behavior observed for lightly stabilized fibers and Type II behavior for more stabilized fibers. The induction periods for fibers which undergo reaction-controlled stabilization are considerably longer than those for fibers undergoing diffusion-controlled stabilization, and the scatter in the data is far greater.

C. Analysis of Decoloration Reaction Products

To obtain information on the decoloration reaction products, C-805 fibers heated for 180 min. at 225 C were subjected to the decoloration reaction at 50 C with stirring. The color of the solution rapidly changed from light yellow to brown in about five minutes; the color of the fibers changed from black to brown. After about one hour, the color of the mixture became light yellow, but many fibers could readily be seen. The color then changed gradually to golden and the fibers were more difficult to see. The pH of the mixture gradually decreased during the course of the reaction, indicating the production of acid material.

After filtration, the filtrate was light yellow. This indicated that the deep color of the mixture at the later stages of reaction was caused by the suspended colored fibers. The weight of residue was about 35% of the initial weight of stabilized fiber. After seven hours reaction, the final solution color was yellow, the pH was 7.6, and the yield of residue phase was 9% of the initial fiber weight.

The residue phase obtained after one hour reaction was soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO); H-NMR and $^{13}$C-NMR as well as infrared spectra were obtained. The solid residue material did not melt when heated to 220 C, but it turned black at about 140 C. The intrinsic viscosity, [η], of the residue phase in DMF at 20°C is 0.32 which gives an estimated viscosity average molecular weight of 15,000 (19). The original fiber had [η] = 2.19, or $M_v$ = 175,000.

Differential scanning calorimetry was also carried out on the residue phase. Although the IR and NMR spectra show that nitrile groups are present, a distinct exotherm was not observed upon heating. Rather, a general very broad, slightly exothermic deviation from the baseline was observed.

The filtrate remaining after removal of the residue phase produced a yellow green precipitate upon acidification with HCl, with a yield of 13.6-15.5% of the original weight of black fiber. The acid precipitate was soluble in DMSO and DMF. Extraction of the acidified filtrate by ethyl ether or ethyl acetate produced no organic soluble residue. The acidic precipitate did not melt, turned black at about 140 C, and exhibited an uninteresting DSC scan. The $\eta_{sp}c$ plot showed the presence of a poly-electrolyte effect. The estimated intrinsic viscosity and molecular weights are 0.27 and 12,000 respectively.

The H-NMR spectra of the untreated C-805 fibers showed four peaks in addition to the DMSO peak. The chemical shifts on the δ scale were approximately (a) 2.0: (b) 3.1; (c) 3.3; and (3) 3.6 ppm. The relative peak area ratios obtained by integration were 2:1:1:trace. The first two peaks are therefore associated with (a) $-CH_2-$ and (b) -CHR- protons for the structure $-(CH_2CHR)-$, where R represents nitrile or methyl acrylate groups. Peak (c) may be due to the presence of small amounts

of water, since the hydrogen bonding between water and DMSO will give a characteristic peak at this position (20). Peak (d) is associated with the methyl ester protons from the methyl acrylate comonomer present in the fiber. The identification of the peaks was supported by comparison with the H-NMR spectra of polyacrylonitrile homopolymer and of polyacrylonitrile-co-methyl acrylate (O-440).

The H-NMR spectrum of the residue phase was similar to that of the unreacted C-805 polymer. The peaks at 2.0 and 3.2 ppm (area ratio 2:1) indicate that some linear polymer, $-CH_2CHR-$ units still exist. A small peak at 3.4 ppm was difficult to identify, since many types of protons, such as amino, -H in ethers, and -NCH-, may be present in this region. The H-NMR spectra of the acid precipitate also shows the 2.0 and 3.0 ppm peaks (ratio 2:1); but the peak at about 3.4 ppm has almost disappeared.

The IR spectra of the residue phase is very similar to that of the unreacted polymer, including the characteristic 2240 $cm^{-1}$ nitrile peak. Two additional strong bands are present at 1720 and 1620 $cm^{-1}$. The former is very likely a carbonyl or carboxyl oxygen, while the latter is the characteristic infrared adsorption of degraded acrylic polymers. It could be a mixture of C=C, C=O, C=N stretching bands and primary N-H bending (1650-1580 $cm^{-1}$). A very strong NH band is present at 3450 $cm^{-1}$ coupled with a band of medium intensity at 600 $cm^{-1}$.

The $^{13}$C-NMR spectra of the residue phase showed a nitrile triad centered at 119.4 ppm (TMS reference) an unresolved methylene band at 32.6 ppm and a methine triad at 27.4, 27.0, and 26.5 ppm which are identical to those in the unreacted polymer. Based on Schaefer's assignments (21) the methine lines are taken as measures of the syndio-, hetero-, and isotactic placements in the polymer, respectively. The relative concentrations of these placements are given in Table IV.

The infrared spectra of the acid precipitate was almost identical to that of the residue phase. This, coupled with the H-NMR and $^{13}$C-NMR spectra indicate that the two materials are very similar and contain unreacted polyacrylonitrile units.

The residue phase collected from CHT fiber stabilized in air for 197 min. at 221 C and reacted in hypochlorite solution for 85 min. at 45 C was washed and centrifuged. The centrifugate consisted of two sharply demarcated layers. The lower layer, "A" (13% yield,based on the weight of the pyrolized fiber) had a light sandy opaque color when dry. The upper layer, "B" (4% yield) had a dark tan translucent color when dry and was quite brittle. The IR spectra were indistinguishable, except that B had slightly more intense peaks in the carboxylic region.

The viscosity average molecular weights were calculated either from a single specific viscosity or from the intrinsic viscosity by means of the Billmeyer an Onyon equations. The results are shown in Table IV. Because the infrared and NMR spectra show that changes in composition have occurred and there may also have been an alteration in molecular weight distribution through chain scission, the calculated molecular weights for the residue phases may be different from the actual values.

The $^{13}C$-NMR spectra of phases A and B were essentially identical to that of the unreacted CHT fiber, save that the very small methyl ester peak (at 52.1 ppm in the unreacted fiber) has disappeared. Also, the nitrile triad is now resolved into its nine constituent pentad peaks. The peak resolution may have been improved by half an order of magnitude due to an increase in relaxation time resulting from a decrease in molecular weight. The methine triad does not show any further splitting in the degraded polymer. The relative areas of the three methine peaks are given in Table IV.

## D. Sulfuric Acid Etching

Fibers of essentially identical composition save for the presence or absence of itaconic acid were heat treated for various times at 225 C in air or in nitrogen, and then subjected to a 2.5 hour etch in 50 wt % aqueous sulfuric acid at reflux, and the residue was examined in the light microscope.

Fibers treated in air which do not contain the weak acid catalyst left a sponge-like residue, (Table V). The concentration of solid material in the sponge increased with increasing stabilization time; and after long stabilization times, the fibers are unaffected by the sulfuric acid treatment. The sponge-like material was fragile and could not be manipulated to examine its cross-sectional features. Longitudinal observations gave the impression that the solid was continuous across the entire fiber diameter.

The spongy residue observed in this work should be contrasted with the annulus of material which remains after sulfuric acid treatment of fibers containing the catalytic monomer which have been heat treated in air to form the dark mantle. The annulus residue in the latter case, particularly after intermediate times of stabilization, seems unaffected by sulfuric acid. The dimensions of the annulus correspond closely to the dimensions of the dark mantle in the heat treated fibers.

## F. Chemical Analysis of Cross Sections of Fibers Exposed to Hypochlorite Solutions

C805 fibers stabilized at 225° in air for 180 min. were subjected to hypochlorite solution at 40°C for various times without stirring. At present times fibers were withdrawn from the decoloration bath and dried without rinsing to minimize alteration of the chlorine content across the fiber. X-ray analysis for chlorine was preformed at five positions across a fiber radius, taking care to examine surfaces free of debris. The positions were at the fiber center and 1/4, 2/4, 3/4 and the edge position of the fiber radius. Four or five individual fibers were examined for each decoloration time. Fig. 7 shows the chlorine concentration across the fiber radius as a function of decoloration time. The error bars are the standard deviation of the measurement. The circles at each position are based on the "best fit" line when the data was cross-plotted as chlorine content vs. time for each position. Such plots allowed the origin to become a "sixth" point. Independent tests demonstrated that chlorine species will not penetrate unstabilized fibers under the conditions of test.

## IV. DISCUSSION

### A. Review of Models of Stabilization

Previous publications in this series have advanced a model for the stabilization reaction of acrylic fibers. The model as reviewed in Warner et al. (2) is as follows: The reactions involved in stabilization, while too complex to specify in detail, can be divided into two categories: those which occur prior to and including nitrile polymerization, called "prefatory reactions", and those which occur subsequent to nitrile polymerization and involve the newly created species, termed "sequent reactions".

Two limiting mechanisms of stabilization were also described, which represent diffusion-controlled and reaction-controlled kinetic processes. In the reaction-controlled process, the overall reaction rate is limited by the prefatory reactions. The sequent reactions occur sequentially and simultaneously with the prefatory reactions. In the diffusion-limited case, prefatory reactions occur relatively rapidly throughout the fiber, due to the presence of catalyst, to preconditioning steps, or to the heat transfer capability of the fiber bundle with the ambient atmosphere. The sequent reaction follow more slowly as the diffusion of oxygen to reactive sites is limited by previously oxidized material.

The model further suggests that fibers which undergo reaction-limited stabilization exhibit a uniform darkening of the fiber cross-sections with time, and the rate of oxygen uptake is linear with time. In contrast, fibers which undergo diffusion-limited stabilization typically show a two-zone morphology of a lightly colored core, a deeply colored outer mantle, and

a sharp interface between the two zones. Movement of the zone interface towards the fiber center and oxygen uptake both depend linearly on the square root of time, at least for times greater than some initial time required for establishment of the two-zone morphology.

Fibers which exhibit reaction-limited stabilization are not etched completely by hot aqueous sulfuric acid, nor are the mantle regions of fibers undergoing diffusion-limited stabilization. The light-colored cores of the latter fibers are, however, completely dissolved by the sulfuric acid treatment (2). The finding that stabilized fibers are decolored by alkaline hypochlorite solutions and the further examination of fibers undergoing sulfuric acid etching has led to a number of modifications and refinements of the above model as will become apparent from the ensuing discussion.

B. Incubation Time and Chlorine Penetration

The process of the decoloration reaction for lightly stabilized fiber is characterized by two incubation periods. During the first incubation period, no change in the color of the fiber was noted. Then during a relatively short time interval, beginning approximately at a time designated $t_1$, a color change was determined in the fiber-hypochlorite solution mixture. After $t_1$, small changes in color were observed but the diameter of the fiber did not change. After the second incubation period, designated $t_2$, the diameter of the colored phase decreased linearly with increasing time. The length of the incubation periods $t_1$ and $t_2$ and the scatter observed in determining $t_1$ depended upon the fiber type and the stabilization conditions. Fibers undergoing diffusion-limited stabilization

generally show shorter $t_1$ values and less scatter than fibers undergoing reaction-limited stabilization. With increasing stabilization time the incubation periods decreased and the variation in measured values of $t_1$ also decreased.

When both incubation periods were observed, then an acrylic network residue phase was also observed whose diameter and density depended upon the stabilization conditions. When the incubation times and the residue phase were not observed, the fibers simply decreased linearly in diameter with reaction time coupled with an apparent color change.

Prior to the incubation time $t_2$, chlorine species were observed to diffuse into the fiber interior, with the chlorine profile depending upon the exposure to decoloration agent. Significant penetration of chlorine sopecies occurred at 13 min. even though the first observable color change occurred at $t_1$ = 20 min. The chlorine content at the outer edge at first increased then later decreased suggesting that some chlorine species are soluble in fiber containing prefatory and sequent groups. The decoloration reactions form species in which the total chlorine solubility is lower. Thus at later stages of decoloration, the chlorine content is greatest in the center of the fiber. It is anticipated that the chlorine gradient across the fiber would depend not only on the exposure time and temperature of the decoloration reagent but also on the extent of stabilization. The technique used to measure the distribution of chlorine in the fibers cannot distinguish between chloride, hypochlorite, or chlorate ions. These ions differ in oxygen content, but the technique cannot measure oxygen concentrations. In any case, the presence of hydrolysis products would render difficult any determination of the ion structure.

The broader variation in measured $t_1$ values in the reaction-limited case reflects different fibers in the mixture undergoing color changes at different times. This effect may be the result of inhomogeneities within the individual fibers prior to stabilization or it may be due to inhomogeneous stabilization, perhaps caused by oxygen attacking outside filaments of the yarn bundle before it attacks the more centrally located filaments.

Both incubation times very likely result from a combination of the denser surface texture of the acrylic filaments, the presence of non-reactive groups initially blocking ingress of the ions into the fiber interior, to the establishment of a boundary layer. Once the residue phase is present, the stresses at the interface due to the swollen phase precludes the blocking action.

## C. Kinetics of Decoloration

The zero order kinetics, as shown in Figs. 1, 3, and 4, and the results given in Table II relate to the changing diameter of the colored zone, not to the attack of chromophores. The dissolution of solids into liquids (22) is influenced by processes such as diffusion, concentration gradients, convection, variations in surface energy effects due to variations in radius of curvature, thermal gradients, and heat transfer. In the absence of these effects, the process of dissolution should depend

only on the concentration of soluble material per unit area exposed to the solvent and the energetics of transfer from the solid to the solution phase (23, 24).

The weight of material dissolved from a fiber (or a long cylinder) in a given time will depend on the surface area, i.e., $2\pi rdr$; and the diameter of the dissolving cylinder at a given time will depend on the surface concentration of dissolving material. Thus, the rate dependence shown in Fig. 1 related to the concentration of active material at the surface. Because the diameter of the colored zone decreases linearly with time, the surface concentration of reactive groups must be independent of radius. Suppose now that the concentration of active material depends on the stabilization time and the active material is reasonably homogeneously dispersed in an inert matrix. As the concentration of active material at the surface increases, and in the absence of complicating factors such as those cited above, the rate of dissolution should increase in proportion.

The action of hypochlorite on stabilized fiber to produce a swollen decolorized residue phase appears to be a zero order attack on chromophores at the interface between the colored phase and the decolored phase. Although it has already been shown that chlorine species have penetrated to the fiber center before the decoloration reaction starts, the identify of the ionic species in the fiber center is not known. Because only hypochlorite ions will cause decoloration, it is assumed, but not demonstrated, that a sharp gradient in hypochlorite ion concentration exists at the decolored-colored phase interface. The decrease in diameter of the colored zone is linear with time and can be represented:

$$d = d_o - k(t-t_2) \qquad (1)$$

where $d_o$ is the diameter of the particular fiber investigated; $t_2$ is the incubation time; and $\underline{k}$ is the kinetic constant represented by the slope of the diameter of colored zone vs. time relation. The constant $\underline{k}$ is proportional to the concentration of active species at the boundary between the colored and decolored zones. The time when d goes to zero, $t_{dec}$, is equal to $(d_o + kt_2)/k$, i.e., inversely proportional to the rate constant. Because of the difficulties in following the decoloration reaction in a quantitative manner, as noted in Section III above, some of the data are reported only as the time for complete decoloration, $t_{dec}$. Thus the activation energy for the decoloration process obtained from Fig. 3, as well as the effect of stabilization time on decoloration time (Table III), may include a contribution from the $(d_o + kt_2)$ term if it varied from test to test.

If the data point at 226C, 4300 min. is eliminated because of the uncertain effect of the hypochlorite concentration on decoloration rate, there appears to be a one-to-one inverse relation between decoloration and stabilization times (Fig. 8). There is insufficient data to test whether or not the correlation exists over sufficient times for fibers with and without the catalytic comonomer. However, if the correlation is assumed to hold for the CHT type fiber at both 226 C and 240 C, then an activation energy of about 42 Kcal $mol^{-1}$ is obtained.

One remarkable result of the decoloration studies is that no obvious discontinuity in the rate of decoloration occurs as the diameter of the colored zone passes from the dark mantle into the lightly colored case of fibers exhibiting a two-zone morphology. The existence of the residue phase in fibers exhibiting the two-zone morphology indicates that prefatory continue to take place within the dark mantle. Sequent reactions take place in the dark mantle, but not the lightly colored core.

The major differences between groups that have undergone prefatory reactions and those that have further undergone sequent reactions involve the removal of hydrogen and the addition of oxygen. The concentration of nitrogen atoms within prefatory-reacted and sequent reacted groups should, however, be the same. One explanation for the lack in specificity of hypochlorite reaction with prefatory and sequent groups is that the specific unit being attacked is identical in the two cases. This explanation further requires that the reactivity of the specific unit is unaffected by (a) the presence or absence of oxygen atoms covalently bound to nearby atoms in the polymer chain, and (b) the occurrence or non-occurrence of dehydrogenation or aromatization. These conditions seem reasonable if the rate of reaction with the specific group is sufficiently fast. An alternate explanation is that the prefatory groups are rapidly oxidized by hypochlorite to form sequent groups, which then undergo the decoloration reaction. The conversion of prefatory to sequent groups can also occur during a portion of the incubation period prior to $t_2$ when the fiber is being penetrated by chlorine containing species.

Additional evidence for the equivalent reaction rates of prefatory and sequent groups to hypochlorite attack is found by comparing the rate of decoloration of C-type fibers stabilized for 127 min at 226 C in air and in argon. The air-stabilized fibers have a fully developed two-zone morphology, while the argon-stabilized fiber exhibits only a uniform pumpkin-orange color. Both fibers decolor at essentially the same rate.

This is consistent with the model provided the bulk of the prefatory groups have been formed (within the time considered) by the initial content of residual initiators and very few are formed by the results of oxidation in the mantle. Fibers which do not contain the weak acid comonomer are only lightly colored and have undergone only a small amount of oxygen uptake when stabilized under these same conditions (2, 8).

Fibers which contain the weak acid comonomer, heat treated in air and argon for 562 min. at 226 C, both show enhanced rates of decoloration compared with the same fibers treated for shorter periods of time. This indicates that oxygen-initiated and inert-initiated prefatory reactions have occurred. The rate of decoloration of the air-stabilized fibers is, however, about 2.5 times faster than that of the argon-treated fibers.

Given the premise that prefatory- and sequent-reacted groups react at the same rate with hypochlorite solution, the lack of a discontinuity in decoloration rate between the two zones of a fiber stabilized under diffusion-controlled conditions may simply reflect the differences in concentration of prefatory-reacted groups between the two zones being too small to be observed using the present techniques. Specifically, the concentration of prefatory-reacted groups initiated by the comonomer initiation apparently exceeds considerably the concentration initiated by oxidation products.

## D. The Existence of the Residue Phase

The existence of the residue phase in lightly stabilized fibers, especially in those displaying diffusion-limited kinetics, demonstrates

that the prefatory reactions are not complete prior to the onset of the sequent reactions. Thus, the prefatory reactions are a slow process and are still ongoing after the dark outer mantle has formed and is encompassing greater portions of the fiber cross-section. The prefatory reactions involve in part the creation of initiators for nitrile polymerization, the initiation thereof, and nitrile polymerization. The latter reaction produces much heat which must be adequately removed in order to prevent destructive runaway reactions, e.g., the characteristic acrylic exotherm. Therefore, the prefatory reactions must be controlled to avoid the exotherm, yet be fast enough to result in an economical process.

The catalyst content of the C-type fiber, represented by the itaconic acid comonomer, is only present at an adventitious level. The comonomer is incorporated into the commercial acrylic yarn in order to improve the basic dyeability of the textile. For economic reasons, a portion of the production of this acrylic polymer has been diverted to product of carbon fibers. Hence the content of the weak acid comonomer has very likely not been optimized for the most efficient production of stabilized yarn.

The C-type fibers are apparently wet spun from an aqueous solution of approximately 50% sodium thiocyanate at a pH of 5.3-6.5 into a coagulation bath of approximately 11% sodium thiocyanide, and the resultant fibers may be washed at a pH of 5.7 (25). At a pH of 5.3, the degree of dissociation is about 69%; at pH=5.7, about 81%; and a pH=6.5, about 96%, based on pKa values of 3.85 and 5.45 (26). Thus

four different types of initiator groups exist in the copolymer that contains itaconic acid. These are two non-ionized and two ionized carboxyl groups. The ability of these groups to initiate nitrile polymerization certainly is not identical.

The modest concentration of weak acid comonomer in the C-type fibers leads to the expectation that they will initiate polymerization of only a portion of the nitrile groups in the fibers. Subsequent initiation of nitrile polymerization (and occurrence of the prefatory reactions more generally) should take place more rapidly in the dark mantle than in the core. Hence further prefatory and sequent reactions will take place in the mantle while the mantle-core boundary advances toward the center of the fiber with sequent reactions taking place at the boundary. This effect is expected to produce a pronounced concentration dependence of the oxygen diffusivity in the mantle.

The initiators for nitrile polymerization include three separate forms: those initially present in the fiber before stabilization temperatures are attained (27); those which are created under inert stabilization conditions; and those which are created under oxidative stabilization conditions (28). The overall rate of nitrile polymerization is very likely rapid for initiators initially present in the fibers, slow for those which are created by oxidative attack, and very slow for those created under inert conditions.

The attack of warm aqueous sulfuric acid on lightly reacted fibers undergoing diffusion-controlled stabilization is consistent with the prefatory and sequent reactions occurring simultaneously in the dark

mantle. Brogna (8) has shown that the core material is completely dissolved away, leaving a thin collapsed ribbon of outer material. The surface topology of the outer material is unchanged from that of the unetched fiber.

The transport of sulfuric acid in such etching apparently takes place through the outer mantle, since the collapsed ribbons show no evidence of etching only from the fiber ends. If the latter process were the primary mechanism, one would expect to see fibers (after recovery and drying) exhibiting collapsed ends and unattacked centers--similar to a straw which has been flattened at the ends.

Fibers stabilized for short times under reaction-controlled conditions exhibit a swollen foam-like residue following sulfuric acid attack. The density of the foam increases with increased stabilization time. The evidence provided by Warner et al. (2) was based on fibers stabilized for sufficiently long times that the foam structure after sulfuric acid etching was quite dense.

The structure in these cases, with modest but definite porosity, is at least qualitatively similar to that inferred for the mantles in fibers stabilized under diffusion-controlled conditions. In the latter case, sufficient porosity exists to permit the transport of sulfuric acid to the centers of the fibers. A given stage of development occurs at much earlier times in the mantles of the catalyst-containing fibers than in the volume of fibers without the catalyst.

Based on the evidence that the residue phase is present at early stages of stabilization in fibers which exhibit both diffusion-limited

and reaction-limited kinetics, and that the sulfuric acid etch produces a porous structure in both cases, it seems that at least three types of sequences are present in the fibers: unreacted acrylic sequences, those which have undergone only the prefatory reactions, and those which also have undergone the sequent reactions. These sequences must exist as interpenetrating networks. In the swollen state the networks are sufficiently open to allow diffusion of aqueous sulfuric acid thru the sequent phase to attack the unreacted and prefatory reacted segments and to allow diffusion of hypochlorite solution to attack the prefatory-and sequent-reacted segments.

## E. Color Changes During Decoloration

During the course of the decoloration reaction, the fibers undergo visual color changes. Quantitative spectra of fibrous material is difficult to obtain, requires a considerable quantity of carefully prepared sample, and special equipment to record the reflectance spectra. Quantitative transmittance spectra on fiber dispersions require special care to maintain homogeneity and correction for the amount of scattered light and other effects.

Such measurements were beyond the scope of this study. Unpublished studies on solutions of acrylic polymer which had undergone various extents of base degradation exhibited various shades of color from deep brown to light yellow and had attained color equilibrium, all had the identical visible ultraviolet spectra (29). There were no bond shifts towards the visible as a function of coloration reaction. Instead, the existing characteristic ultraviolet bonds merely increased in intensity.

The reported bleaching of these solution upon addition of acid is incorrect--the solutions were merely diluted, as demonstrated by quantitative spectral studies. Apparently the human eye is quite sensitive to small changes in concentration in the blue-violet region which do indicate major color changes, but cannot be interpreted a significant changes in molar extinction coefficients. Kubasova et al (30) shows ultraviolet spectra of polyacylonitrile homopolymer prepared either by radical polymerization or in urea canal complexes by γ-irradiation, dissolved in dimethyl formamide, then thermally degraded. Again, there is no obvious shift in band structure towards longer wavelengths, only an intensification of the spectra as a function of degradation time. Similar results have also been obtained by other investigators (31, 32).

The reduction in diameter of the colored zone can also lead to confusing perception of color. Because the diameter decreased linearly with time during the decoloration reaction and because no plasticized zone could be discerned ahead of the interface--even though chlorine species were found to have penetrated the interface--it is suggested that the observed color changes of the central colored zone are due to changes in the physical size of the colored zone or by dilution of the fiber chromophores by chlorine atom solution rather than to chemical action taking place within the colored zone. A discontinuous jump in apparent color does occur during the decoloration reaction on C-type fibers as the reaction front traverses the original mantle-core interface.

## F. Fiber Cracking and Break-up

Fibers pyrolyzed in air at 226 C for short periods of time develop cracks in the residue phase during the course of the decoloration reaction. These cracks appear towards the end of the reaction when the dimension of the colored core is rather small. The majority of these cracks are longitudinal and extend along the fiber axis for sizable distances (up to 100 μm). Some circumferential cracks and a few oblique cracks have also been noted. The development of large, wide cracks is more extensive for less stabilized fibers which, according to Table II, yields a residue phase whose diameter exceeds that of the original stabilized fibers. The cracks described here are produced under much milder conditions than the circumferential cracks produced in untreated acrylic fibers exposed to boiling hypochlorite solutions (17). In isotropic hollow cylinders, the hoop strength is one-half that of the axial strength (33). Hence the longitudinal cracks are very likely caused by the swelling of the residue phase coupled with its fragile character. As noted above, there is no obvious change in length of the fiber with decoloration time for fibers which exhibit Type I behavior. In contrast, for Type II behavior the fiber tends to break up into small pieces; and the fiber-reagent mixture appears to become colored. Upon filtration, a fine colored chaff is collected along with an essentially colorless filtrate.

## G. Mechanism of Decoloration

It has been seen that stabilized acrylic fibers are rapidly decolored by warm alkaline hypochlorite solution. The same fibers are not decolored by weak alkaline solutions, alkaline solutions of sodium chloride or sodium chlorate, or by acid solutions of hypochlorous acid. Hence the active species in decoloration must be the hypochlorite ion.

According to Chakrabartty (34) pyridine is a highly oxidative-resistant organic solvent that is also attacked by alkaline hypohalite solutions. These rather mild oxidants rapidly reduce pyridine to ammonia and carbon dioxide. Attempts to characterize the intermediate products by rapid quenching and combined gas chromatography-mass spectroscopy were not successful.

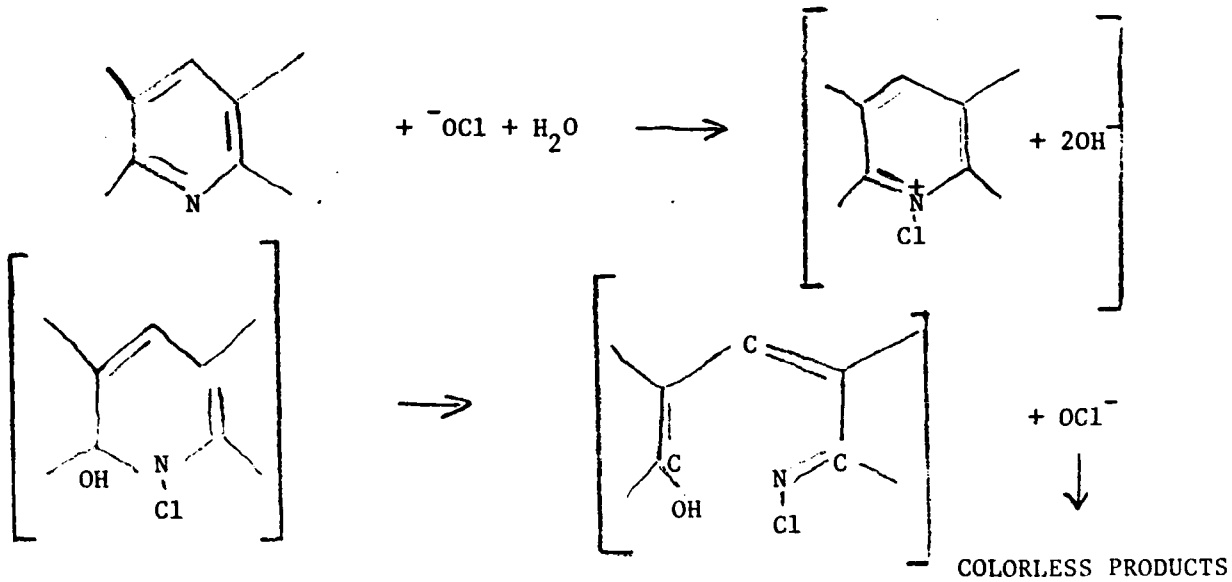
Previous studies (35) showed that polyenes could be distinguished from polyimines by use of basic hydrogen peroxide, but that stabilized acrylic fibers were not decolored by this reagent. The stabilized fiber is unaffected by reagents such as strong acids, strong bases, many strong oxidizing agents (perchlorate, peroxide, permanganate, dichromate) and strong reducing agents (various hydrogenation procedures, sodium borohydride, diborane, lithium aluminum hydride). Therefore the structure of the chromophores must be of a type susceptible primarily to hypochlorite attack, such as the nucleophillic pyridine-type structure.

The hypochlorite ion reacts rapidly as an electrophile in the presence of a nucleophile due to the facile cleavage of the O-Cl bond:

$$\text{O-Cl}^- + \text{Nucleophile} + H_2O \rightarrow 2OH^- + \text{Cl-}\overset{+}{\text{N}}\text{ucleophile} \qquad (2)$$

The activated $\text{Cl-}\overset{+}{\text{N}}\text{ucleophile}$ product can then undergo rapid hydrolysis

or other degradative reactions (36, 37). Thus:




The non-aromatic bonds in the last postulated structure should be rapidly attacked by the hypochlorite ion. If the nitrile group undergoes basic hydrolysis to the amide, the latter should rapidly be reduced to an amine plus $CO_2$ by the Hoffman reaction.

Polyacrylonitrile is slowly attacked by mild base to undergo prefatory type reactions with the formation of reddish chromophores. Such reactions should also occur in warm alkaline hypochlorite reagent, but any prefatory products so produced would rapidly undergo the decoloration reaction. Perhaps the gradual disappearance of the residue phase upon prolonged exposure to hypochlorite solution is due to the latter set of actions. In contrast, acetonitrile is one of the few solvents stable to hypochlorite solutions (38).

## B. Nitrile Polymerization and Stereoregularity

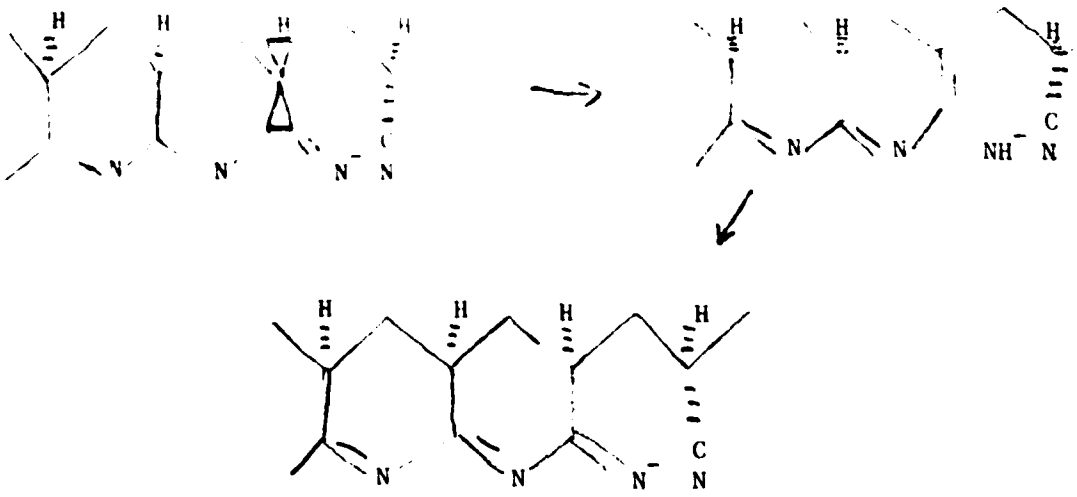
Examination of Table IV shows that the methine tacticity of the original polymer is essentially identical to that of the residue phases collected after stabilization and decoloration. This information can be used to elucidate the microstructure of the fibers and how the microstructure influences the nitrile polymerization reaction. Thus, in a purely heterotactic polymer, some 12.5% of the polymer must be in syndiotactic sequences equal to or greater than three units in length; and a similar amount must be in isotactic sequences equal to or greater than three units in length. Thus, if there is a greater tendency for isotactic units to be incorporated into the polymerized nitrile chain, there should be an enrichment of syndiotacticity in the residue phase. Since this was not observed, then syndiotactically placed nitrile groups must have equivalent reactivity with isotactically placed groups.

This conclusion is not in accord with other work in the literature, which examined the thermal stability--considered equivalent to nitrile polymerizability--of PAN homopolymers prepared under conditions expected to enhance the isotactic content of the polymer. Dinh (39), Kubasova (30) and Griderickh (40) studied polymers of enhanced isotactic content, prepared using urea-canal complexes. They found that the isotactic-rich polymers have enhanced rate of color formation, a higher concentration of paramagnetic centers, and less weight loss than more normal free radical polymerized material: while the polymer prepared in the urea canal complexes did exhibit enhanced reactivity and enhanced isotactic content,

it is not established the two materials tested had approximately the same initiator content. Furthermore Minagawa (27) shows that the free radical polymerization recipe can have marked influence on the peak temperature of the nitrile polymerization exotherm which is due to variations in polymer uniformity.

Some authors claim that syndiotactically placed nitrile groups cannot be incorporated into a polymerized chain because studies with molecular models indicate a high degree of strain (30, 39). It should be noted, however, that cyclobutane and cyclopropane cannot be formed with some models. Further, the space filling LKB molecular models and the skeletal Drieding models allow long sequences of syndiotactic acrylonitrile units to be cyclized without intolerable strain on the bond angles.

A more realistic [illegible] for the lack of stereospecificity may be obtained [illegible] enamine tautomarism of the ultimate cyclized nitrile [illegible] will [illegible] racemization or scrambling of any possible chiral [illegible] that is:



These scrambling reactions may be quite rapid at 200-300 C. Thus, attempts to improve the rate of stabilization by altering the tacticity of the original polymer would probably not be fruitful.

The precise structures of the residue and acid precipitate polymers have not been determined. Although the polymers so far characterized contain roughly 50-250 repeat units, the relative concentrations of nitrile, acid, ester, and amine units (among others) are not known. If these polymers contain up to 80-85% acrylonitrile, then the average run length would be about four acrylonitrile units. Cook (41) showed that model oligomers of polyacrylonitrile up to the tetramer did not exhibit a sharp exothermic reaction. Neither do the residue or acid precipitate polymers thus far tested. The minimum chain length necessary to cause the violent exothermic reaction has not yet been established. The acid precipitate is very likely the acrylic residue which has undergone a slow attack by the basic hypochlorite solution. Although the acid material does contain an enhanced concentration of carboxylate groups, they do not predominate as the material is soluble in DMSO whereas polyacrylic acid is not.

## V. CONCLUSIONS

1. Alkaline hypochlorite solutions will decolorize partly or fully stabilized acrylic fibers. The decoloration process for lightly stabilized fibers occurs in two distinct steps. After an incubation period, $t_1$, the fibers exhibit a lightening in color as chlorine-containing species diffuse throughout the fiber, but the fiber remains colored. After a further incubation time, $t_2$, the colored zone starts to decrease in diameter. The decrease in diameter of the colored zone is linear with decoloration time. Such zero order kinetics are similar to those observed for the dissolution of a solid under reaction or convection control. For fibers that have been more extensively stabilized, two distinct steps are no longer observed; and it seems that penetration of chlorine-containing species and the decoloration reaction occur simultaneously. Because the penetration of chlorine species was in all cases determined by energy dispersive X-ray analysis, the chemical form of the chlorine species (as chloride, hypochloride or chlorate) could not be determined.

2. The incubation periods decrease with increasing stabilization time. Fibers containing a weak acid comonomer, which acts as an initiator for nitrile polymerization, have shorter incubation times than fibers which do not contain the catalyst. Both incubation periods can be associated in part with the dense outer skin of the acrylic fibers and with the presence of inert material which initially acts as a barrier, in addition to the usual time required for the establishment of boundary layers.

3. The rate of the decoloration reaction, measured in most cases from the time to complete decoloration, increases with increasing

decoloration temperature. The apparent activation energy for this process for one set of conditions (fiber type, stabilization temperature, and stabilization time) was about 6 kcal $mole^{-1}$. Hence decoloration is a facile reaction.

4. The hypochlorite reagent destroys and solubilizes that portion of the fiber which has undergone either prefatory or sequent reactions. If the fiber has been stabilized for only a short time and incubation periods are noted, a porous network of acrylic polymer remains after decoloration. For very short stabilization times, the porous network of acrylic polymer swells during decoloration, the final fiber diameter being greater than the original diameter. Due to internal swelling pressures, the network tends to split axially. For longer stabilization times, the diameter of the final fiber is less than the original diameter. For even longer stabilization times, no porous network remains after decoloration.

5. The existence of the acrylic network after partial stabilization and decoloration demonstrates that the prefatory reactions are not complete under the conditions tested in this work. Even in fibers undergoing diffusion-controlled kinetics, wherein a well-defined dark outer mantle advances inward at a rate proportional to the square root of time, acrylonitrile units in the mantle and core regions continue to undergo the prefatory reactions. It is expected, but not demonstrated here, that the prefatory reactions are faster in the mantle because of the presence of oxygen.

6. The rate of decoloration increases with increasing stabilization time under both oxidative and inert stabilization conditions. For CHT fibers at 226 C in air, the rate of decoloration as measured by the time to complete decoloration at 50 C, $t_{dec}$, depends upon stabilization time, $t_{stab}$, as: $1/t_{dec} = 5 \times 10^{-8} (t_{stab,sec})\ sec^{-1}$. The decoloration rate increases with increasing stabilization temperature and decreases when stabilization is effected under inert conditions. For extended stabilization times, the decoloration rate should go through a minimum and then increase again as the polymer begins to undergo release of heteroatoms.

7. Because the decoloration reaction shows no obvious change in rate as the reaction progresses from the dark outer mantle to the light core of fibers which have undergone diffusion-limited stabilization, the reactivities to hypochlorite of the groups formed from the prefatory and sequent reactions are equivalent. This can occur if: (1) the reactivity of the groups formed by the prefatory reactions is not influenced by the groups formed by the sequent reactions; or (2) the prefatory groups are transformed into sequent groups during the chloride atom penetration and decoloration processes and then undergo the decoloration reaction. Confirmatory evidence for the equivalence of reactivity is obtained by short term stabilization under inert and oxidative conditions.

8. $^{13}C$ NMR spectra of the polymer residue after the decoloration reaction shows that the stereospecificity of the residual acrylic polymer is the same as that of the starting fiber. The rate of polymerization

of nitrile groups is therefore not affected by syndiotactic or isotactic placements, as has been suggested previously. One reason may be the facile rearrangement of the stereostructure of the ultimate units of the growing nitrile chains at the temperatures of stabilization.

9. The penetration of chlorine-containing species, as measured by the incubation time $t_1$, demonstrates a degree of heterogeneity from filament to filament within a treated yarn bundle. The degree of heterogeneity is very high for fibers which do not contain a weak acid comonomer. The effect could be due to variations in fiber formation, the stabilization process, or the decoloration process. It is believed, but not confirmed, that most of the variability results from the stabilization process.

10. Hypochlorite ion is a facile electrophile in the presence of a nucleophile such as pyridine. The relatively oxidative resistant pyridine is rapidly attached by hypochlorite. Similar reactions may occur in stabilized acrylic fibers wherein the nucleophilic nitrogen is attacked, leading to ring opening followed by attack on any residual unsaturation.

11. Nitrile polymerization is initiated by three types of groups: those present in the fiber prior to stabilization, those created under oxidative conditions, and those created under inert conditions. The overall rate of polymerization is greatest when initiator groups are present in the as-formed fiber, for instance fibers that contain catalytic additives. Under the conditions of test examined, these active groups are exhausted before all nitrile units have polymerized. The overall rate of polymerization is slower when initiators must be formed under oxidative stabilization conditions and is slower still when initiators are

formed under inert conditions. Some fibers contain catalytic amounts of itaconic acid, which is present in textile fibers to act as a dye site. The quantity present may not be optimal for efficient stabilization.

12. Hot aqueous sulfuric acid will dissolve the precursor acrylic fiber and will destroy/solubilize that portion of the fiber which has undergone only the prefatory reactions, leaving behind a residue of sequent-reacted material. The residue obtained from sulfuric acid treatment of fibers undergoing diffusion-controlled stabilization is in the form of an annulus which corresponds to the dark mantle. The density of the annulus increases with increasing stabilization time. The residue from fibers undergoing reaction-limited stabilization is distributed throughout the fiber cross section, and also exhibits porosity and a density which increases with increasing time of stabilization.

13. The processes of hypochlorite and sulfuric acid attack on partially stabilized fibers lead to the following model of stabilized fiber microstructure: During stabilization, the morphology changes from the homogeneous chemical composition of ordered and disordered acrylic phases, to interpenetrating networks of reacted and uncreacted material, and finally to a structure dominated by the sequent-reacted material. The interpenetrating networks consist of segments of acrylic molecules unaffected by stabilization, prefatory reacted and sequent reacted material. The composition of the interpenetrating networks and the final sequent structure depend upon process conditions.

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Table I

Acrylic Fibers Investigated

| Fiber Type | Abbreviation | Nominal Denier* of Yarn | No. of Filaments | Denier* per Filament | Manufacturer | Copolymer Composition |
|---|---|---|---|---|---|---|
| Monsanto Experimental Fiber | VA-2 | 1772 | 1440 | 1.2 | Monsanto, USA | 7% Vinyl acetate |
| Respun Orlon 42 | O-440 | 440 | 200 | 2.2 | Du Pont, USA (FRL Respun) | 6% Methyl acrylate |
| Respun Orlon 42 | O-300 | 300 | 200 | 1.5 | Du Pont, USA (FRL Respun) | " |
| Orlon 43 | O-43 | tow | | | Du Pont, USA | " |
| Dralon | D | 800 | 380 | 2.1 | Bayer, Germany | Homopolymer |
| Respun Courtelle | C-805 | 805 | 400 | 2.0 | Courtalds, England (FRL Respun) | 6% Methyl acrylate, 1% itaconic acid |
| Commercial Courtelle | C-C | tow | | 4.5 | Courtalds, England | 6% Methyl acrylate, 1% itaconic acid |
| High tenacity Courtelle | CHT | tow | | 1.5 | Courtalds, England | 6% Methyl acrylate, 1% itaconic acid |

*Denier = number of grams in nine kilometers.

Table II

Decoloration Rate of CHT Fibers Prepared and Reacted Under Various Conditions

| Stabilization Atmosphere | Stabilization Time and Temperature | Decoloration Temperature | Decoloration Rate (μm/sec) $10^3$ | Decoloration Time (sec) | Decoloration Time Corrected to 50°C (sec) | Change in Diameter of Residue Phase |
|---|---|---|---|---|---|---|
| Air | 127 min @ 226 C | 50 C | -6.0 | 2900 | 2900 | + 26% |
| Air | 185 min @ 226 C | 50 C | -12.0 | 1490 | 1490 | - 34% |
| | | 21 C | - 5.5 | 3340 | | - 21% |
| | | 65 C | | 520 | | dissolves |
| Air | 562 min @ 226 C | 50 C | -22.0 | 600 | 600 | dissolves |
| | | 21 C | | 5220 | | + 49% |
| Air | 4300 min @ 226 C | 21 C (12.5% solution) | | 1400 | 20[a] | dissolves |
| Air<br>Argon | 4300 min @ 226 C followed by 660 min @ 400 C | 80 C | | 6300 | $5 \times 10^4$ | dissolves |
| Argon | 127 min @ 226 C | 50 C | -6.7 | 2820 | 2820 | + 28% |
| Argon | 562 min @ 226 C | 50 C | | 1520 | 1520 | + 12% |
| Air | 25 min @ 240 C | 50 C | -4.3 | 4500 | 4500 | + 21% |
| Air | 50 min @ 240 C | 50 C | -6.6 | 2040 | 2040 | + 34% |

a) corrected for low reagent concentration.

## Table III

### Correlation between Decoloration and Stabilization Times Under Various Conditions for CHT Yarns

$$t_{dec} = a(t_{stab})^{-b}$$

| Temperature | Atmosphere | a, $sec^{1+b}$ | b | Remarks |
|---|---|---|---|---|
| 226 C | air | $2.0 \times 10^{7}$ | -1.0 | 3 points, direct measurement |
| 226 C | air | $7.4 \times 10^{8}$ | -1.4 | 4th point corrected, see text |
| 226 C | Argon | $1.2 \times 10^{5}$ | -0.4 | 2 points only |
| 240 C | air | $1.9 \times 10^{7}$ | -1.1 | 2 points only |
| 240 C | air | $(6.2 \times 10^{6})$ | (-1.0) | a calculated with b = -1.0 |

Table IV

Viscosity and $^{13}C$-NMR Triad Tacticity of Original and Reacted Polymers

| | C805 Virgin Fiber | Residue Phase | Acidic Precipirate |
|---|---|---|---|
| Mv | $175 \times 10^3$ | $15 \times 10^3$ | $12 \times 10^3$ |
| i | 26.2% | 23.9% | 27.1% |
| h | 47.8% | 45.3% | 44.8% |
| s | 26.0% | 30.8% | 28.1% |

| | HTC Virgin Fiber | Phase A | Phase B |
|---|---|---|---|
| Mv | $132 \times 10^3$ | $2.6 \times 10^3$ | $4.8 \times 10^3$ |
| i | 25.9% | 25.2% | 24.6% |
| h | 49.7% | 53.0% | 52.6% |
| s | 24.5% | 21.8% | 22.8% |

Table V

Effect of Sulfuric Acid Etching on O-43 Fibers Heat Treated at 225° in Air

| Heat Treatment time, hr. | Color prior to etching | Residue Appearance after 2 1/2 hr. Exposure to Aq. $H_2SO_4$ at Reflux |
|---|---|---|
| 1 | yellow | clear gel, very fragile |
| 2 | gold | clear gel, rough surface |
| 4 | deep brown | open sponge-like texture, brown |
| 8 | black | more dense spongy texture, black |
| 24 | black | no reaction, intact, black, smooth |

## FIGURE CAPTIONS

Fig. 1 - Variation of diameter and color of C-HT fiber stabilized in air at 226°C for 127 minutes, as a function of time in decoloration reagent at 50°C. The dark mantle and core regions of the fiber prior to decoloration are indicated. The color notations are only subjective remarks. O photographic readings + Filar eyepiece readings.

Fig. 2 - Photomicrograph of C-HT fiber of Fig. 1, subjected to decoloration for 26.5 min.

Fig. 3 - Logarithm of the ratio (decoloration time at 50°/decoloration time at temperature) vs. reciprocal temperature for C-HT fiber stabilized at 226° for 127 or 185 min. & 562 min. ⊡ . The activation energy is 5.8 kcal/mole.

Fig. 4 - Logarithm of decoloration time at 50°C vs. logarithm of stabilization time for C-HT fibers stabilized in air at 226° for 127, 185, and 562 min, ○ and 4300 min ● then "corrected" to 50°C (see text); in air at 240°, □ ; and in argon at 226°, △ .

Fig. 5 - Ratio of colored phase diameter to residue phase diameter of C-805 fibers heated for 180 min. at 225°C as a function of decoloration time at 37.8°C. The variability at any selected time includes data taken along the length of a given fiber and between individual fibers.

Fig. 6 - Incubation time, $t_1$, to the first apparent color change of fiber mat in decoloration reagent at 40°C without stirring as a function of stabilization time in air at 225°C. Lower curve C-805 fiber. Upper curve, O-42.

Fig. 7 - Variation of chlorine concentration across a fiber radius as a function of decoloration time at 40°C for C-805 fiber stabilized for 180 min. at 225°. The circles are based on the "best fit" line when data is plotted as chlorine content vs. time for each position. For this fiber, $t_1$ = 20 min., $t_2$ = 90 min.

Fig. 8 - Reciprocal of decoloration time vs. stabilization times under assumption that a 1:1 correlation exists. ○ 226°, □ 240°. The calculated activation energy is 42 kcal/mole.

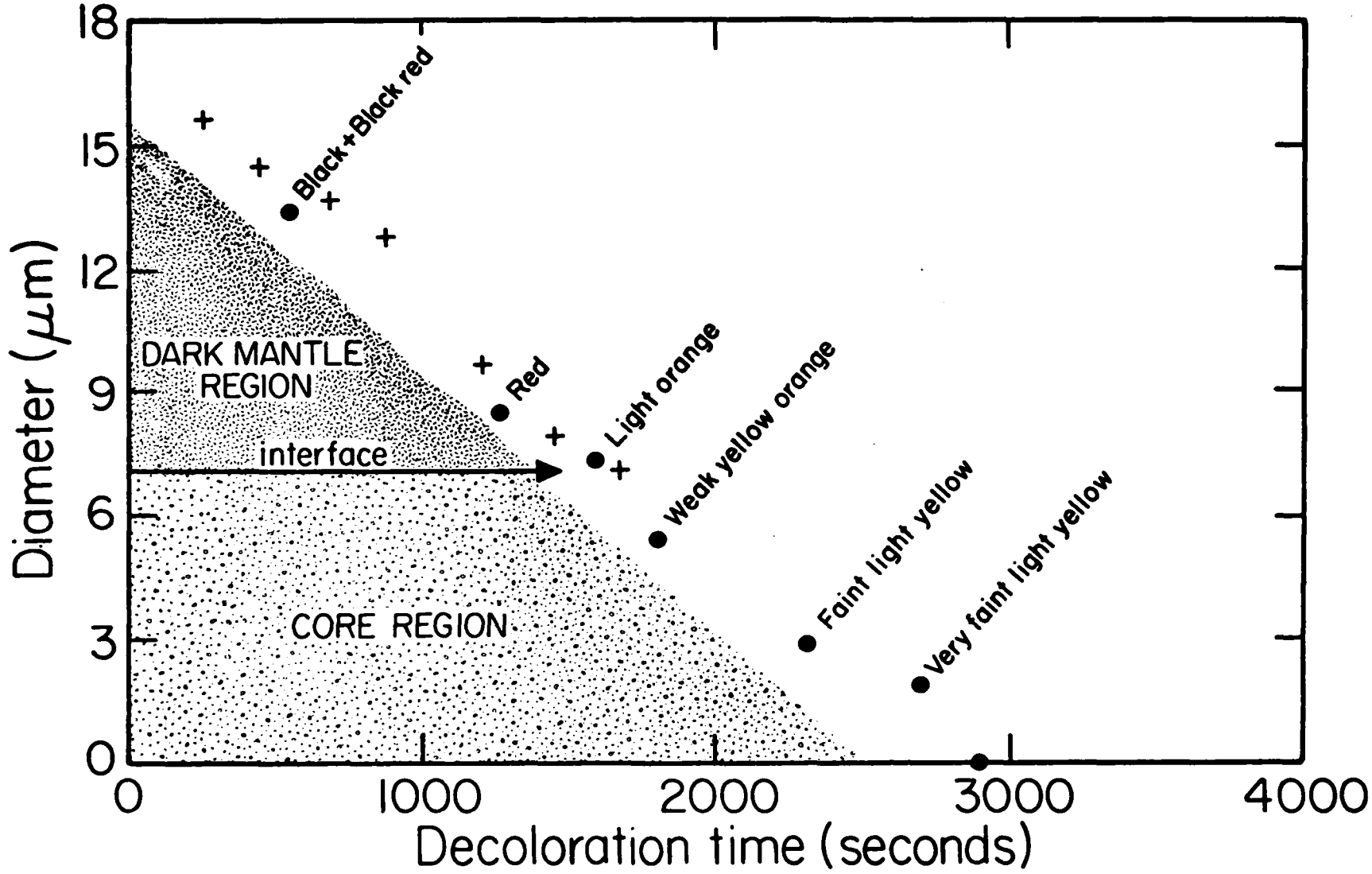

Diameter (μm)
18
15
12
9
6
3
0
0
1000
2000
3000
4000
Decoloration time (seconds)
DARK MANTLE REGION
CORE REGION
interface
Black+Black red
Red
Light orange
Weak yellow orange
Faint light yellow
Very faint light yellow

Figure 1

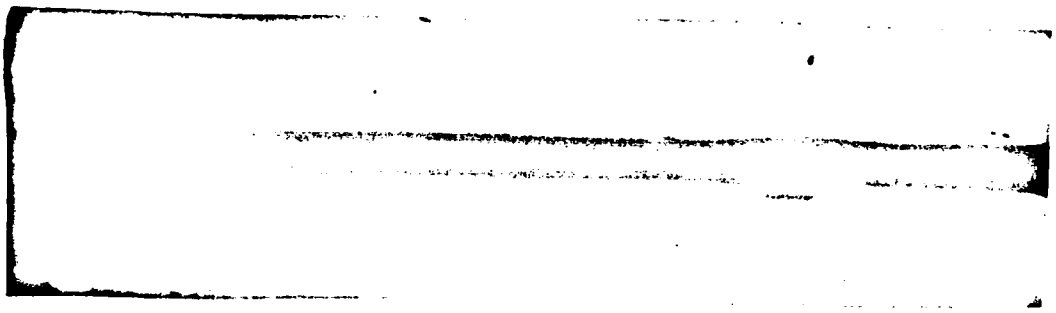


Figure 2

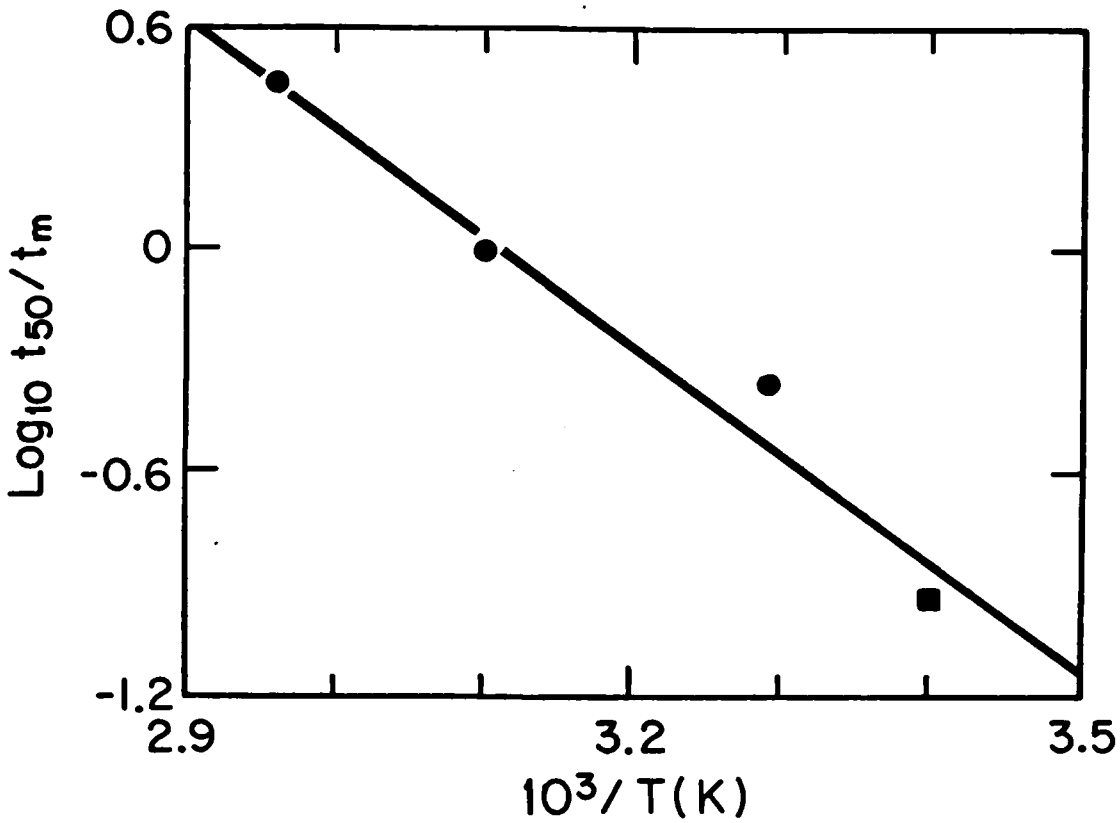



Figure 3

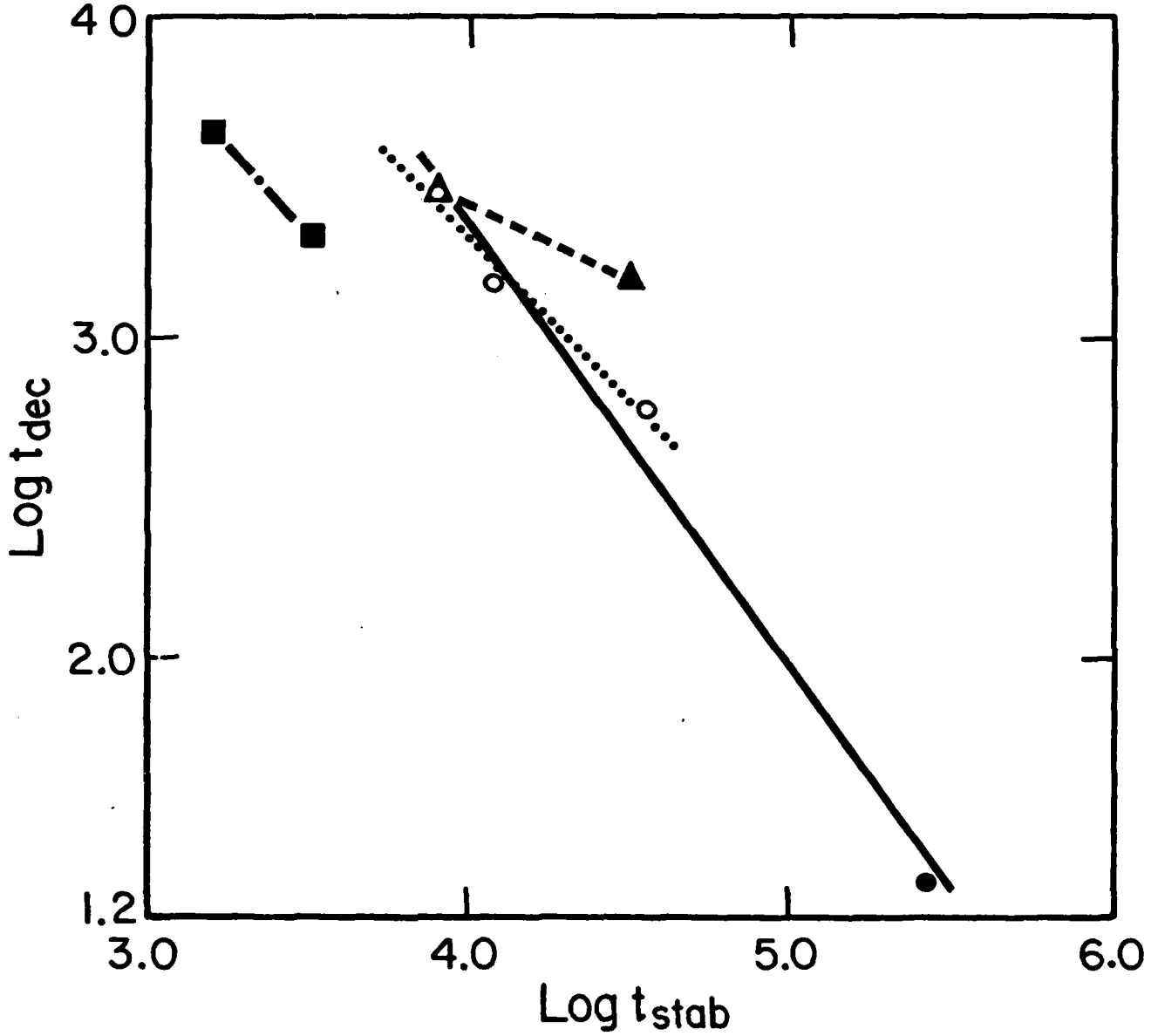



Figure 4

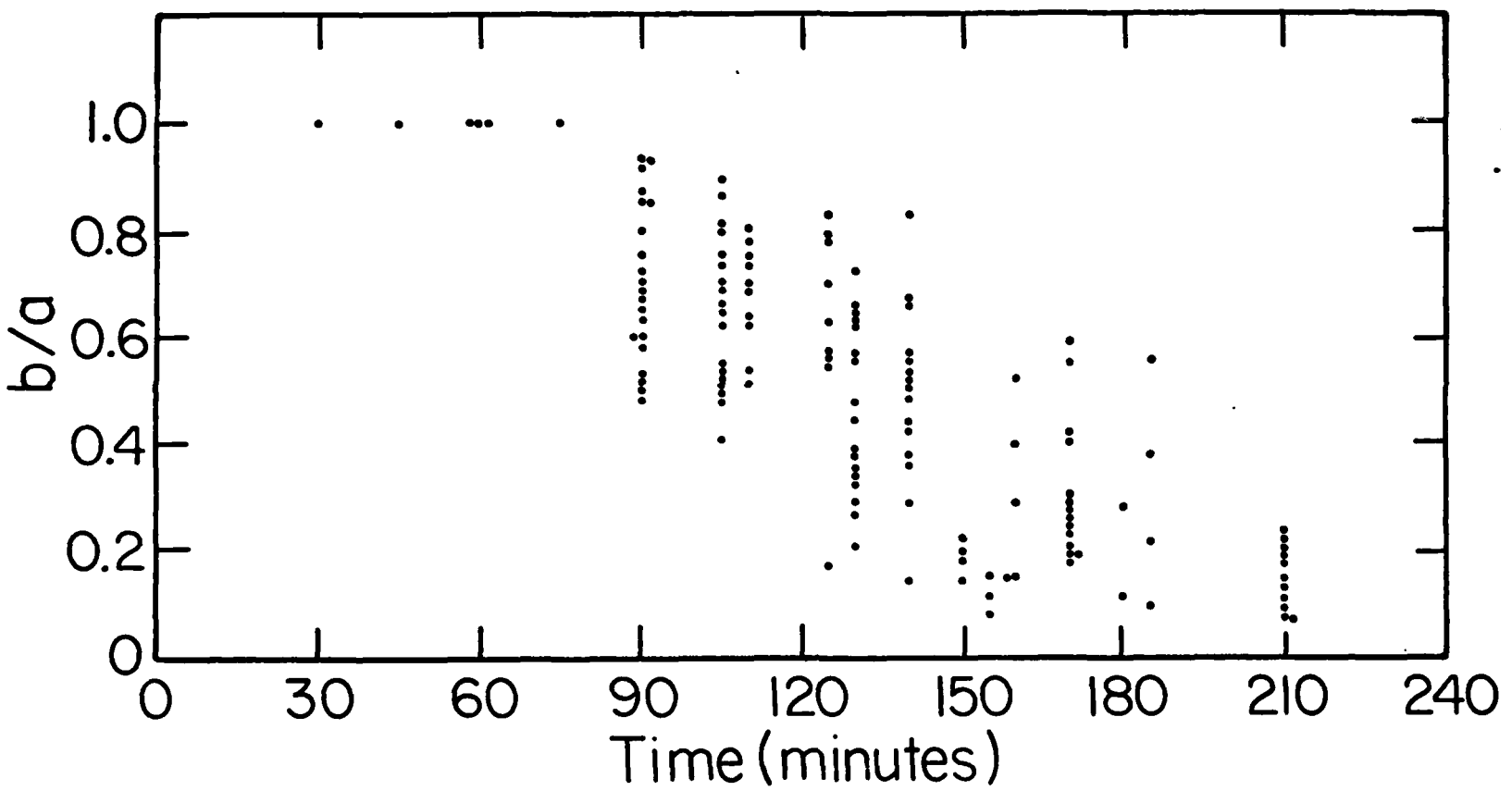



Figure 5

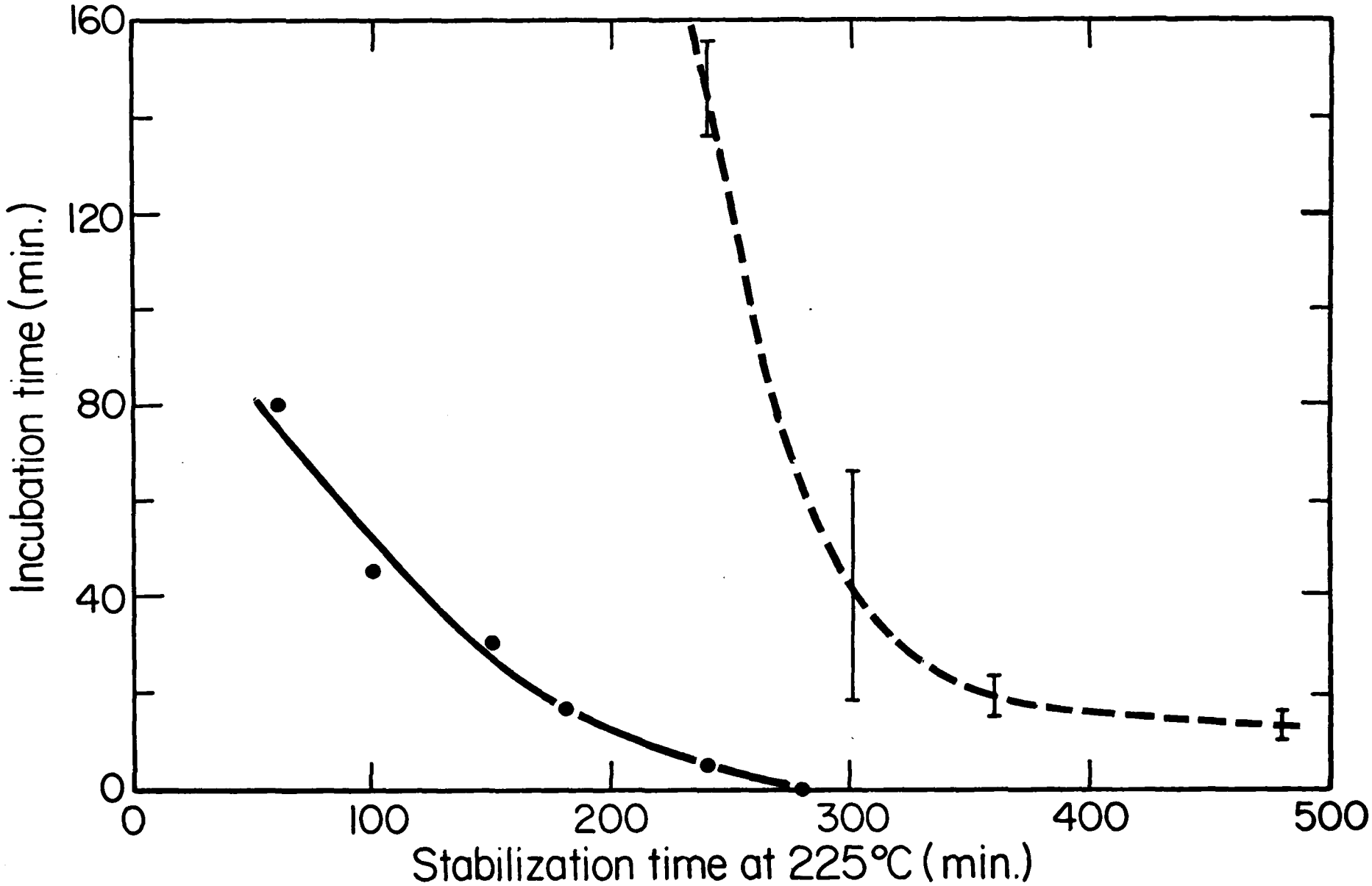

160
120
80
40
0
Incubation time (min.)
0
100
200
300
400
500
Stabilization time at 225°C (min.)

Figure 6

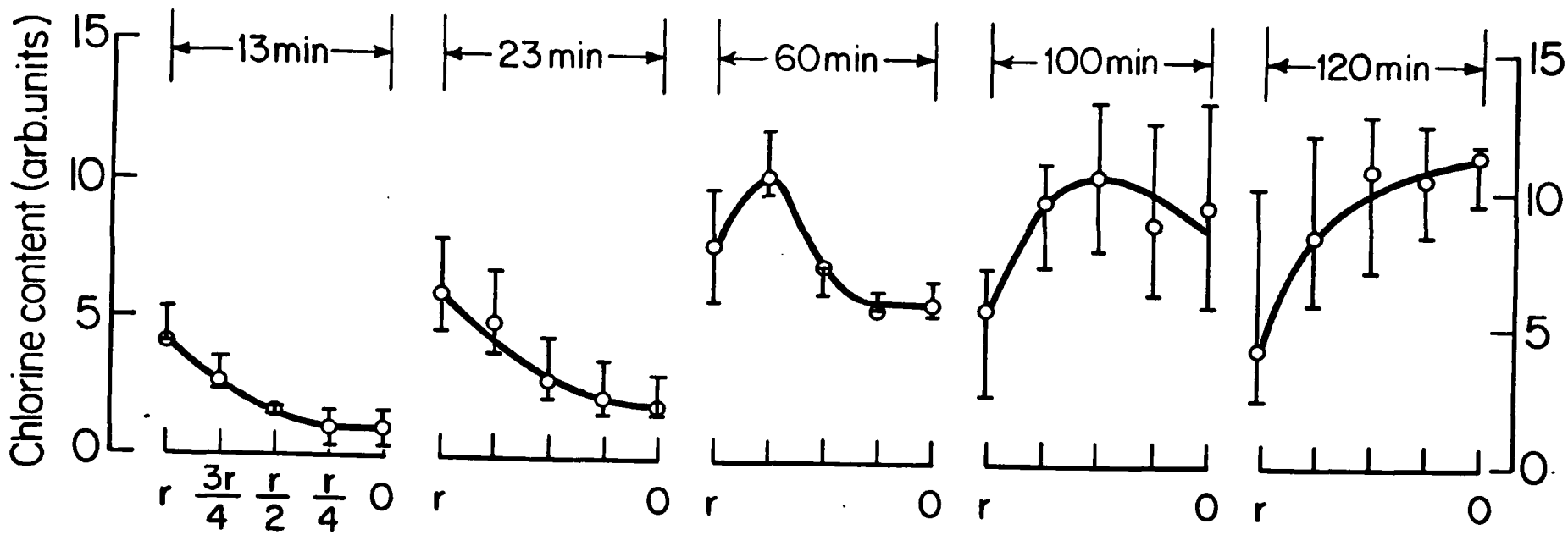
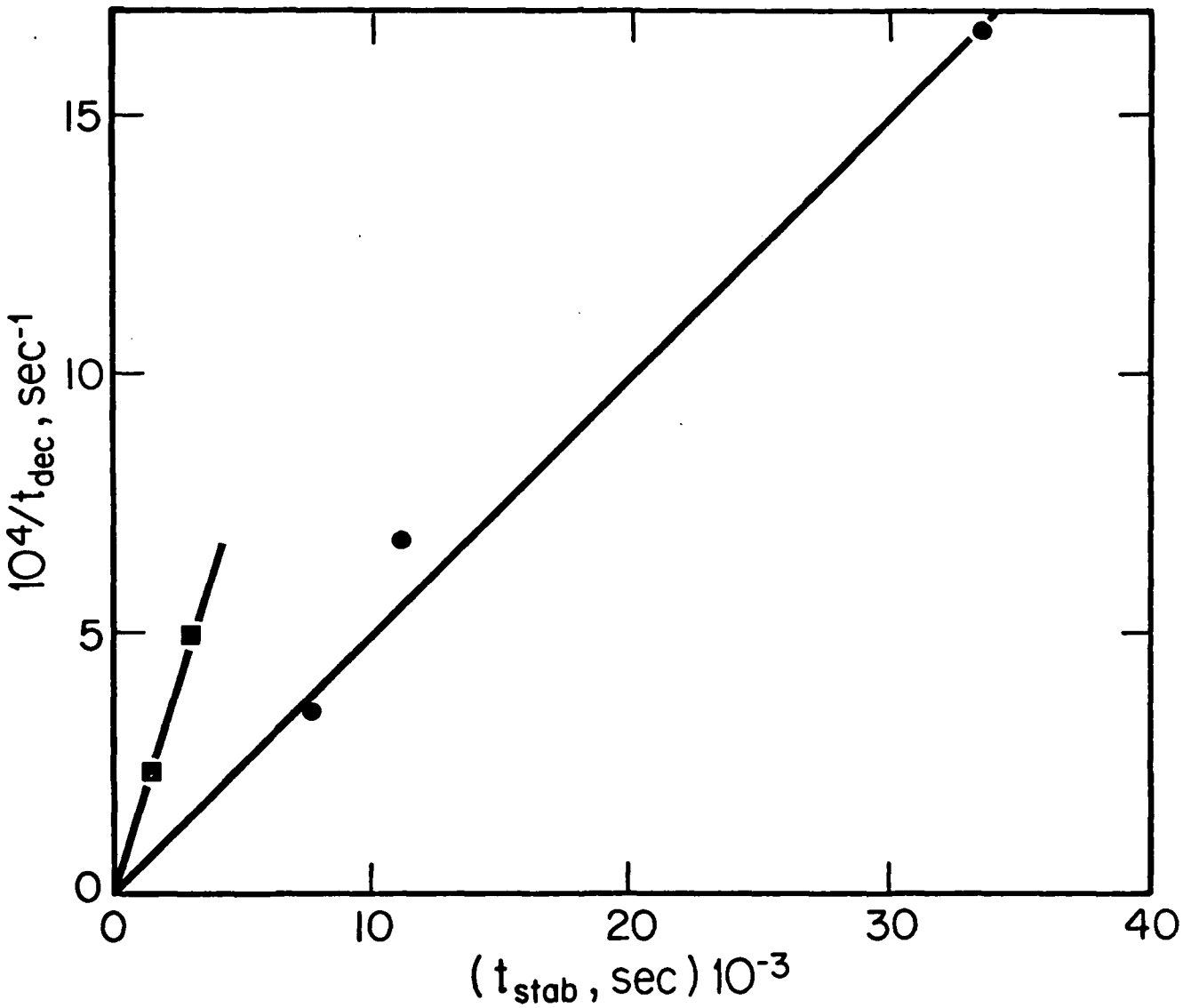

Chlorine content (arb.units)
15
10
5
0
13min
23min
60min
100min
120min
r
3r/4
r/2
r/4
0

Figure 7

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