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PROTECTION OF NOMEX FROM ULTRAVIOLET DEGRADATION

GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF TEXTILE ENGINEERING
ATLANTA, GEORGIA 30332

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SCHOOL OF TEXTILE ENGINEERING
ATLANTA, GEORGIA 30332

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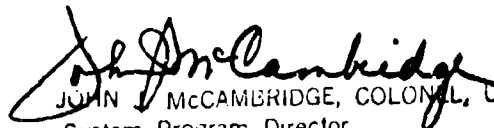
PREFACE

This report was prepared by the School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia under U.S. Government Contract No. F33657-75-C-0716. It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command with Mr. Walter Gloor acting as project engineer.

Dr. Wayne C. Tincher of the Georgia Institute of Technology was the principal investigator for the project. Dr. Walter C. Carter and Dr. David Gentry were responsible for certain phases of the project. The laboratory studies were carried out by Ms. Sandra K. Henson and Mr. Mathew Sikorski.

The authors wish to express their appreciation to the E. I. du Pont de Nemours Company and the Ciba-Geigy Company for many helpful discussions and suggestions during the course of the work and to Celanese Corporation, Monsanto Textiles Company, and Hoechst Company for use of laboratory facilities for production of treated Nomex fabric and webbing samples.

This Technical Report has been reviewed and is approved.


JOHN J. MCCAMBRIDGE, COLONEL, USAF
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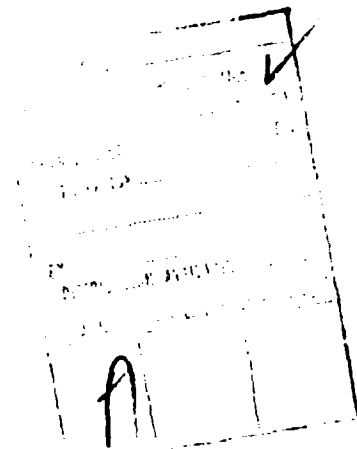


TABLE OF CONTENTS

SECTION		PAGE
I.	SUMMARY	1
	A. Program Objectives and Scope	1
	B. Conclusions	1
	C. Recommendations	2
II.	SELECTION AND EVALUATION OF STABILIZERS	3
	A. Introduction	3
	B. UV Degradation of Nomex	4
	C. Principles	5
	D. Techniques for Addition of Stabilizers to Nomex	14
	E. Exposure and Testing	13
	F. Results of Screening Studies	19
III.	DEVELOPMENT OF STABILIZER SYSTEMS	62
	A. Factorial Experiment	62
	B. Evaluation of Stabilizer Systems	78
	C. Improvement in Treating System	92
	D. The Selected Treatment System	92

TABLE OF CONTENTS (cont'd.)

SECTION	PAGE
IV. PREPARATION AND EVALUATION OF FABRIC AND WEBBING SAMPLES	96
A. Preparation of Fabric Sample	96
B. Preparation of Webbing Sample	98
C. Evaluation of Treated Fabric	97
D. Evaluation of Webbing Samples	107
V. CONCLUSIONS	109
VI. RECOMMENDATIONS	110
REFERENCES	111
APPENDIX A: Literature Survey	112
APPENDIX B: Stabilizers for E-11 Nomex Fabrics	134
APPENDIX C: Fundamental Studies on Nomex UV Degradation	137

LIST OF ILLUSTRATIONS

FIGURE	PAGE
1. Absorption Spectrum of Nomex	11
2. Absorption Spectrum of Uvite.. RBNAD	12
3. Effect of UV Exposure on Nomex Yarn Tenacity	20
4. Effect of UV Exposure on Nomex Yarn Elongation	21
5. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after xenon arc exposure	22
6. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after carbon arc exposure	23
7. Retention of tenacity and elongation of Nomex Type 433 control and blank dyed after xenon arc exposure	25
8. Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control after carbon arc exposure	26
9. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex WGS compared to control after carbon arc exposure	27
10. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after carbon arc exposure	28
11. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control after carbon arc exposure	29
12. Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after carbon arc exposure	30

LIST OF ILLUSTRATIONS (cont'd.)

FIGURE		PAGE
13.	Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after carbon arc exposure	31
14.	Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 327 compared to control after carbon arc exposure	32
15.	Retention of tenacity and elongation of Nomex Type 433 containing Cyasorb UV-800 compared to control after carbon arc exposure	33
16.	Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 770 compared to control after carbon arc exposure	34
17.	Retention of tenacity and elongation of Nomex Type 433 containing Eastman Inhibitor RMB compared to control after carbon arc exposure	35
18.	Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control sample after xenon arc exposure	36
19.	Retention of tenacity and elongation of Nomex Type 433 xenon containing Uvitex WGS compared to control sample after xenon arc exposure	37
20.	Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after xenon arc exposure	38
21.	Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control sample after xenon arc exposure	39

LIST OF ILLUSTRATIONS (cont'd.)

FIGURE		PAGE
22.	Retention of tenacity and elongation of Nomex Type 433 containing Blanchphor AW compared to control sample after xenon arc exposure	40
23.	Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after xenon arc exposure	41
24.	Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1035 compared to control sample after carbon arc exposure	44
25.	Retention of tenacity and elongation of Nomex Type 433 containing Plastanox 1735 compared to control sample after carbon arc exposure	45
26.	Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1010 compared to control sample after carbon arc exposure	46
27.	Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1098 compared to control sample after carbon arc exposure	47
28.	Retention of tenacity and elongation of Nomex Type 433 containing CGA-316 compared to control after carbon arc exposure	48
29.	Retention of tenacity and elongation of Nomex Type 433 containing AM-105 compared to control after carbon arc exposure	50
30.	Retention of tenacity and elongation of Nomex Type 433 containing IRGASTAB 2002 compared to control after carbon arc exposure	51

LIST OF ILLUSTRATIONS (cont'd.)

FIGURE		PAGE
31.	Retention of tenacity and elongation of Nomex Type 433 containing Zetax compared to control after carbon arc exposure	52
32.	Retention of tenacity and elongation of Nomex Type 433 containing GI-10-460 compared to control after carbon arc exposure	53
33.	Retention of tenacity and elongation of Nomex Type 433 containing NBC compared to control after carbon arc exposure	54
34.	Retention of tenacity and elongation of Nomex Type 433 containing CHA-1056 compared to control after carbon arc exposure	55
35.	Retention of tenacity and elongation of Nomex Type 430 containing urea compared to control after carbon arc exposure	56
36.	Retention of tenacity and elongation of Nomex Type 430 containing urea and thiourea compared to control after carbon arc exposure	57
37.	Retention of tenacity and elongation of Nomex Type 430 containing colloidal sulfur compared to control after carbon arc exposure	58
38.	Retention of tenacity and elongation of Nomex Type 433 with end groups reacted with betaoxynaphthoic acid compared to control after carbon arc exposure	60
39.	Retention of tenacity and elongation of Nomex Type 433 containing oxanilide compared to control after carbon arc exposure	61
40.	Retention of breaking strength and elongation of Nomex fabric exposed in the carbon arc Fade-Ometer	64

LIST OF ILLUSTRATIONS (cont'd.)

FIGURE	PAGE
41. Retention of breaking strength and elongation of Nomex fabric exposed in the xenon arc Fade-Ometer	65
42. The effect of concentration of Blancophor AW on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer	69
43. The effect of concentration of Tinuvin P on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer	70
44. The effect of concentration of oxanilide on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer	71
45. Strength after 40 hours exposure of fabric samples containing Blancophor AW and Tinuvin P	72
46. Strength after 40 hours exposure of fabric samples containing oxanilide and Blancophor AW	73
47. Strength after 40 hours exposure of fabrics samples containing oxanilide and Tinuvin P	74
48. Strength after 100 hours exposure of Nomex fabric containing Blancophor AW and Tinuvin P	75
49. Strength after 100 hours exposure of Nomex fabrics containing oxanilide and Blancophor AW	76
50. Strength after 100 hours exposure of Nomex fabrics containing oxanilide and Tinuvin P	77
51. Retention of breaking strength and elongation of treated (a) and control (D) Nomex fabric after exposure in the carbon arc Fade-Ometer	83

LIST OF ILLUSTRATIONS (cont'd.)

FIGURE	PAGE
52. Retention of breaking strength and elongation of treated (E) and control (A) Nomex fabric after exposure in the carbon arc Fade-Ometer	84
53. Retention of breaking strength and elongation of treated (F) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer	85
54. Retention of breaking strength and elongation of treated (C) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer	86
55. Retention of breaking strength and elongation of treated (B) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer	87

LIST OF TABLES

TABLE	PAGE
1. Potential Stabilizers Screened for Improvement in Nomex UV Stability	10
2. Factorial for Selection of Stabilizer Systems	63
3. Average Strength Measured at Various UV Exposure Levels for all Treatment Combinations	67
4. Breaking Strength and Elongation Before and After UV Exposure	80
5. Tensile Strength Retention (%)	81
6. Elongation Retention (%)	82
7. Properties of Experimentally-Treated Nomex Fabrics	89
8. Results of Vertical Flame Test on Control Treated, and Blank-Dyed Fabrics	91
9. Comparison of Nomex Samples Treated in a Jet and Jig Dyeing Machine	93
10. Strength Retention (%) of Treated Nomex Fabrics After Exposure	94
11. Breaking Strength and Elongation of Untreated and Treated Nomex Specimens Before and After Exposure to Sunshine Arc Light	98
12. Breaking Strength and Elongation of Untreated and Treated Nomex Specimens Before and After Exposure to Xenon Arc Light.	99
13. Breaking Strength and Elongation of Untreated and Treated Nomex Specimens Before and After Exposure to Carbon Arc Light	100

LIST OF TABLES (cont'd.)

TABLE	PAGE
14. Tensile Strength Relation (%) (Sunshine Arc Light)	101
15. Tensile Strength Retention (%) (Xenon Arc Light)	102
16. Tensile Strength Retention (%) (Carbon Arc Light)	103
17. Elongation Retention (%) (Sunshine Arc Light)	104
18. Elongation Retention (%) (Xenon Arc Light)	105
19. Elongation Retention (%) (Carbon Arc Light)	106
20. Tensile Strength of Nomex Webbing Before and After Sunshine Arc Exposure	108

SECTION I

SUMMARY

A. Program Objective and Scope

The objective of this work was the development and evaluation of a treatment system for improvement in the resistance of Nomex fiber and fabrics to UV degradation. Specifically, a system was sought which would yield 75% retention of the tensile strength of Nomex fabrics after 150 hours exposure in the Atlas Sunshine Carbon Arc Fade-Ometer. To achieve this objective, a survey was conducted of all literature and manufacturer's data related to Nomex UV stabilization. Techniques were developed for incorporating stabilizers in Nomex fiber and a number of potential stabilizers (UV absorbers, free radical scavengers, quenching agents) were screened for effectiveness in reducing Nomex UV degradation. Additives which showed promise were tested at various levels and in combination to determine effective concentrations and to develop the best possible stabilizer system. Four fabric samples were treated with the most promising system and evaluated. The most effective system was used to treat 200 yards of Nomex fabric (MIL-C-38351, Type II, Class 1) and 100 yards of Nomex webbing (MIL-W-38283, Type XII). The treated fabric and webbing samples retained greater than 80% of the original tensile strength after exposure for 150 hours in the Atlas Sunshine Carbon Arc Fade-Ometer.

B. Conclusions

Technical literature and manufacturers' data contain little information useful in selecting stabilizers to improve Nomex light stability. Most of the commonly used stabilizers for fibers and plastics are ineffective or even detrimental in degradation of Nomex by UV light. Three compounds (Blancophor AW, Tinuvin P, Oxanilide) were found which reduced the loss in tensile strength and elongation of Nomex fiber during UV exposure.

A modified "dyeing technique" has been developed which permits incorporation of stabilizers in Type 430 continuous filament Nomex. The procedure requires treatment of the fiber at high temperature (265°C) in the presence of large quantities (40 g/l) of a carrier (Tanatex Chemocarrier FPN).

A stabilizer system composed of 33% (owf) Blancophor AW, 33% (owf) Tinuvin P and 5% (owf) Oxanilide proved to be very effective in reducing UV degradation of Nomex. Nomex fabric samples treated with this system showed greater than 80% retention of tensile strength after 150 hours exposure to the Atlas Sunshine Carbon Arc Fade-Ometer compared to less than 50% retention of tensile strength for identical, untreated Nomex fabrics. Similar improvements were observed on exposure of the fabric to the Xenon Arc Fade-Ometer.

C. Recommendation

Attempts should be made to optimized the stabilizer system to achieve more economical treatment. It may be possible to reduce the quantity of stabilizers used significantly with little or no reduction in UV stability.

A "standing bath" solvent treatment technique would probably be preferred to the modified dyeing procedure used in the present work. Such a system could substantially reduce the cost of treating Nomex to improve UV stability.

More extensive outdoor exposure studies should be conducted on treated Nomex samples for comparison with the data obtained by carbon arc and xenon arc exposure.

SECTION II

SELECTION AND EVALUATION OF STABILIZERS

A. Introduction

Heat resistant and nonflammable fibrous materials composed of aromatic or aromatic/heterocyclic polymeric systems are components of a number of Air Force end items including uniforms, flight and protective clothing, life support equipment and decelerator materials. Although these materials show considerable resistance to loss of physical properties when exposed to high temperatures (such as fuel fires), they are generally deficient in resistance to UV degradation. This susceptibility to UV degradation is a major factor in replacement cost and reliability of air force materials. For example, operational experience has shown that degradation due to solar radiation is largely responsible for frequent replacement of parachute pack fabrics [1].

Studies on stabilization of heat resistant fibrous materials to UV degradation have not yielded practical procedures for improvement of the service life of these materials. It was evident that the degradation process was complex and simple single component additives were not likely to give adequate stability. Synergistic stabilizer systems containing a number of carefully selected components were expected to be required to meet target objectives.

An additional problem is encountered in attempting to add stabilizers to Nomex fiber or fabric. After extrusion and drawing aromatic polyamide fibers tend to be intractable and diffusion of materials into the fiber is difficult to achieve. Significant effort was required to develop innovative techniques for addition of stabilizer systems to the fiber and insure their permanency. It was further essential that the selected stabilizer system (and techniques for incorporation in or on the fiber) not adversely affect desirable mechanical or thermal properties of the Nomex fabrics.

-
- [1] May, Donald R., Jr. and Ross, Jack H., Accelerated Weathering of Polyamides, Aromatic Polyamides, and Polybenzimidazole Fabrics, AFML-TR-72-137, October 1972.

B. UV Degradation of Nomex

The susceptibility of aromatic polyamides (aramides) to UV degradation has been well documented [1-4]; however, there is little information available in the literature on the mechanism of UV degradation of these materials. Nomex absorbs UV radiation beginning at approximately 390 nanometers (nm) and extending into the near UV with a peak at approximately 360 nm. This absorption is responsible for both the yellowing of the fiber and the loss in tensile strength [2]. Similar results have been reported on other aromatic polyamides. In this respect the aramides differ significantly from other common polymeric systems. Aliphatic polyamides, for example, are degraded by light in the region near 290 nm [5]. Sunlight is much richer in radiation at 360 nm than at 290 nm and this fact undoubtedly accounts for the much greater susceptibility of aramides to degradation by solar radiation.

Some attempts have been reported to find UV screening agents for improvement of Nomex light stability [3]. These studies have not led to the discovery of viable systems for practical application.

Other information on the fundamental aspects of aramide UV degradation such as -- identity and nature of the absorbing species, structure of the excited state, mechanism of the chemical reactions responsible for loss of

- [2] Ross, Jack H. and Daukays, Mary Ann, Mechanical Properties of Woven Forms of Three Polyaromatic Fibers After Ultraviolet Exposure. AFML-TR-67-415, April 1968.
- [3] Karsny, J.F. and Schwartz, A.M., Nomex Ultraviolet Inhibitors, ASD-TR-72-104, August, 1972.
- [4] Johnson, L.D., Tincher, W.C., and Bash, H.C., "Photodegradation Wavelength Dependence of Thermally Resistant Organic Polymers", J. Applied Polymer Sci., 13, 1825 (1969).
- [5] Taylor, H.A., Tincher and Hamner, W.F., "Photodegradation of Nylon 66. I. Phototendering by TiO_2 ", J. Applied Polymer Sci., 14, 141 (1970).

mechanical properties, possible role of water and/or oxygen in the degradation -- is not available in the literature. These important basic aspects of aramide UV degradation are part of on-going graduate student research at the Georgia Institute of Technology. Some preliminary results of this work are given in Appendix C.

C. Principles of Stabilizer Selection

In the absence of detailed information on aramide photodegradation, guidance for selection of stabilizer systems must be found in the recent advances in knowledge of the nature and behavior of electronic excited states and in understanding of photochemical reactions in polymeric systems. Ultraviolet degradation of these materials can generally be divided into three phases -- absorption of a photon, production of an initial excited species, and subsequent chemical reactions of the excited molecules. Stabilizers which are effective in reducing photochemical degradation must prevent or significantly reduce one or more of these steps.

1. Photon Absorption

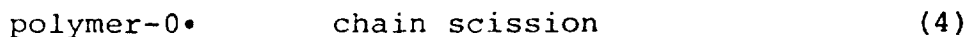
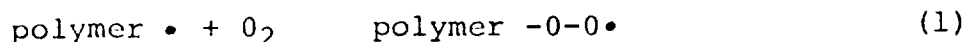
One class of stabilizers compete with the polymer substrate for available photons (screening agents). These materials must have very strong absorption in the same region of the spectrum as the polymeric material. In the case of Nomex these compounds should absorb in the region from 300 to 390 nm. The usual screening agents used for other polymers generally absorb at shorter wavelengths. Quite different materials will be required for Nomex stabilization. In addition the screening agent must not degrade itself on absorption of UV energy.

2. Initial Excited Species

Most polymeric systems degrade by initial production of an excited species (e.g., triplet state, free radical, charge transfer complex, etc.). A second approach to stabilization is the inclusion of a compound capable of reacting with, and therefore deactivating the excited species. Stabilizers for some polymers, particularly aliphatic polyamides (copper and manganese compounds) apparently react in this way.

3. Degradative chemical reactions

Most polymer systems degrade by a free radical-peroxide-hydroperoxide mechanism summarized by the following reactions:



In reaction (1) a free radical (denoted by the dot indicating an unpaired electron) produced in a polymer molecule by the initial excited species reacts with oxygen in the air to give a peroxide radical. The peroxide radical abstracts a hydrogen atom from an adjacent polymer molecule to give a hydroperoxide and a new polymer free radical (reaction 2). The hydroperoxide then cleaves to give an oxy radical and a hydroxyl radical (reaction 3). The oxy radical usually undergoes a polymer chain scission giving a reduction in molecular weight and a loss in mechanical properties (reaction 4). In this series of reactions two new radicals have been produced (polymer $\cdot$ in reaction 2 and $\cdot \text{OH}$ in reaction 3) to continue the free radical chain reaction sequence. Most successful stabilization systems for polymers contain at least one component capable of interrupting this series of chain reactions. These materials either react with free radicals to produce stable products (radical scavenger) or are capable of decomposing peroxides in a nondestructive manner.

Successful systems for polymer stabilization generally contain several components which are capable of intercepting the degradation sequence at several different points. For example, a typical system might include a screening agent to compete with the polymer for photons, a metal ion for preferential reaction with excited species, and a radical scavenger to remove free radicals from the system. Synergistic effects between these types of stabilizers are important in development of a successful stabilizer system.

C. Stabilizers Selected for Screening

1. Literature Survey

A major objective of the literature survey was to identify materials that had been recommended as UV stabilizers for Nomex. A detailed discussion of the literature survey is given in Appendix A. In the important area of UV stabilizers 13 references were discovered. The reported stabilizers were primarily UV screening agents. The literature, therefore, provided little guidance in selection of compounds for Nomex stabilization. Twelve references were found that discussed the mechanism of radiation and UV degradation of Nomex and other aramids. These references were useful in selection of some materials for screening studies.

2. Survey of Manufacturers

a. E. I. duPont de Nemours & Company

Discussions of the Nomex UV stability problems were held with Dr. Calvin J. Cruz, Supervisor Nomex Technical Service and Dr. Bob Thomas, Jackson Laboratory. DuPont's major interest has been in the dye lightfastness of Nomex because this property has limited application of Nomex in commercial aircraft interiors.

At the present time DuPont is adding a UV screening agent to both colorsealed sage green (Type 433) and olive green (Type 432) Nomex. There is little evidence that the additive is effective but they have been reluctant to change the production process by removing it.

The Jackson Laboratory has conducted fundamental studies on the mechanism of degradation of dyes on Nomex. Although the work related more directly to dye lightfastness, the conclusions and results have important implications in selection of UV stabilizers. Some important conclusions were:

- (1) Photodegradation is characteristic of all aromatic polyamides. Extensive structural modifications do not prevent degradation.
- (2) Nomex is a very strong absorber between 350 and 400 nm. The quantum efficiency for degradation is low (10^{-4} to 10^{-5}). The process is a non-chain reaction and it is not autocatalytic.

- (3) Oxygen is necessary for degradation. The uptake of oxygen is linear with time if light intensity is constant. Normal free radical scavengers and antioxidants are not effective stabilizers.
- (4) UV screening agents are partially effective.
- (5) A number of conventional mechanisms have been considered:
 - (a) formation of aminobenzophenone (by Photo-Fries reaction)
 - (b) Photohydrolysis and oxidation
 - (c) Formation of phenazine
 - (d) Tautomeric shift involving cyclization across C=N bonds

None of these mechanisms is completely satisfactory. The possibility of oxygen in the first excited singlet state being important in the mechanism has also been considered. Again the evidence was not conclusive.

The DuPont work suggests that, with the exception of UV screening agents, conventional light stabilizer systems may not be effective on Nomex.

b. Ciba-Geigy

Ciba-Geigy appeared to be aware of the Nomex light stability problem and has conducted some work in the area. Several Ciba-Geigy materials in the Tinuvin series of UV screening agents and the Irganox series of antioxidants were suggested for stabilization of Nomex. An experimental material GI-10-460 (an aromatic diamide of oxalic acid) which is reported to be a light stabilizer for Nomex was also suggested for inclusion in the screening program.

c. Other Manufacturers of Stabilizer Candidates

In addition to DuPont and Ciba-Geigy, conversations were held with representatives of American Cyanamid, Sandoz, Eastman Chemical Products, and Ferro Corporation. The Nomex stability problem was discussed and each company sent samples of materials they manufactured or had under development which might provide UV protection for Nomex. Stabilizer candidates for screening were selected from these materials based on their structures and likely mode of action in interrupting the Nomex degradation mechanism.

3. Stabilizers Screened

The specific stabilizers selected for screening studies are shown in Table 1. The stabilizers fall into four major groups -- UV absorbers, antioxidants, quenchers and/or radical scavengers, and other potential stabilizers which function by mechanisms other than the typical UV stabilizers.

a. UV Absorbers

UV screening agents improve the light stability of fibers and fabrics by competing with the substrate for the photons responsible for degradation. To be effective, screening agents must have two important characteristics. First, they must have strong absorption in the same region of electromagnetic radiation as the substrate. Second, the screening agent must have means of dissipating the excess energy obtained by absorption of electromagnetic radiation without degrading itself or stimulating the degradation of the substrate. These are rather stringent requirements and only a few chemical structures can function as UV screening agents.

The absorption spectrum of Nomex in the near UV and visible region which is responsible for Nomex photodegradation is shown in Figure 1. Compared to most fiber-forming polymers the absorption of Nomex is much nearer the visible region of the spectrum. Sunlight has a significant quantity of energy in this region which may account for the sensitivity of Nomex to UV degradation. Unfortunately, most UV screening agents designed for improving stability of polymeric materials absorb strongly further in the UV than Nomex. The overlap between screener absorption bands and the Nomex degradation band is not as large as desirable for maximum efficiency.

One class of materials which do have strong absorption bands in the same region of the spectrum as Nomex is the fluorescent brightening agents. An absorption spectrum for a typical brightener is shown in Figure 2. A comparison of Figure 2 and Figure 1 indicates that fluorescent brighteners should be able to compete effectively with Nomex for the photons responsible for degradation. In addition, the brightening agents can lose excess energy by fluorescence and can therefore show sufficient stability to be of interest as UV screening agents.

Five optical brighteners were selected for investigation. These materials are given in Table 1. All are

Table 1
POTENTIAL STABILIZERS SCREENED FOR
IMPROVEMENT IN NOMEX UV STABILITY

UV Absorbers

Lencophor EFR
Uvitex NFW
Uvitex WGS
Blancophor AW
Uvitex RBNAD
Tinuvin P
Tinuvin 327
Tinuvin 770
Eastman Inhibitor RMB

Antioxidants

Irganox 1035
Plastinox 1735
Irganox 1010
Irganox 1098
CHI-316

Quenchers

Irgastab 2002
Zetax
GI-10-460
CHA-1058
Nickel dibutyldithiocarbamate
Ferro AM-105

Other

Oxanilide
beta-oxynalplthoic acid
thiourea-urea
colloidal sulfur

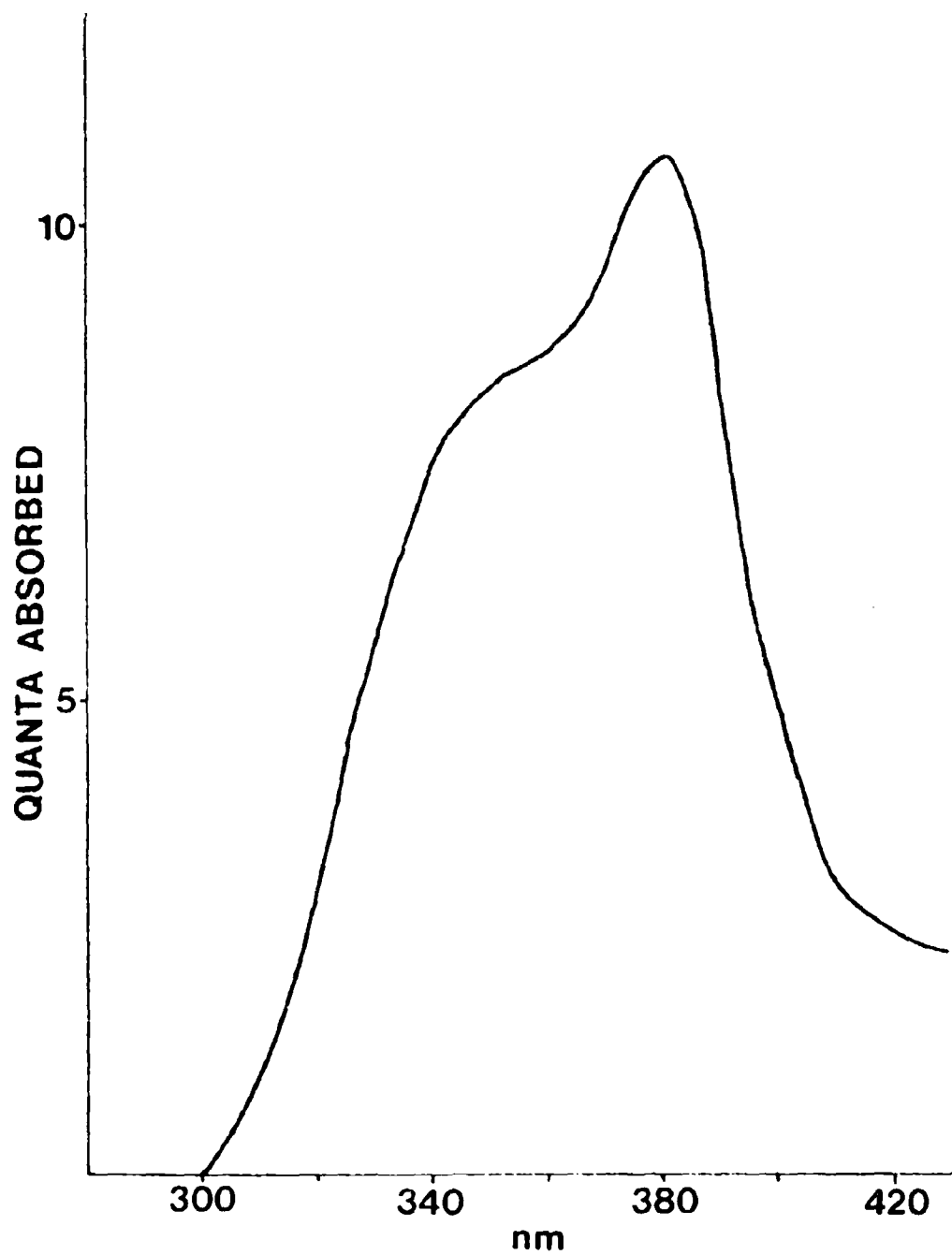


Figure 1. Absorption spectrum of Nomex

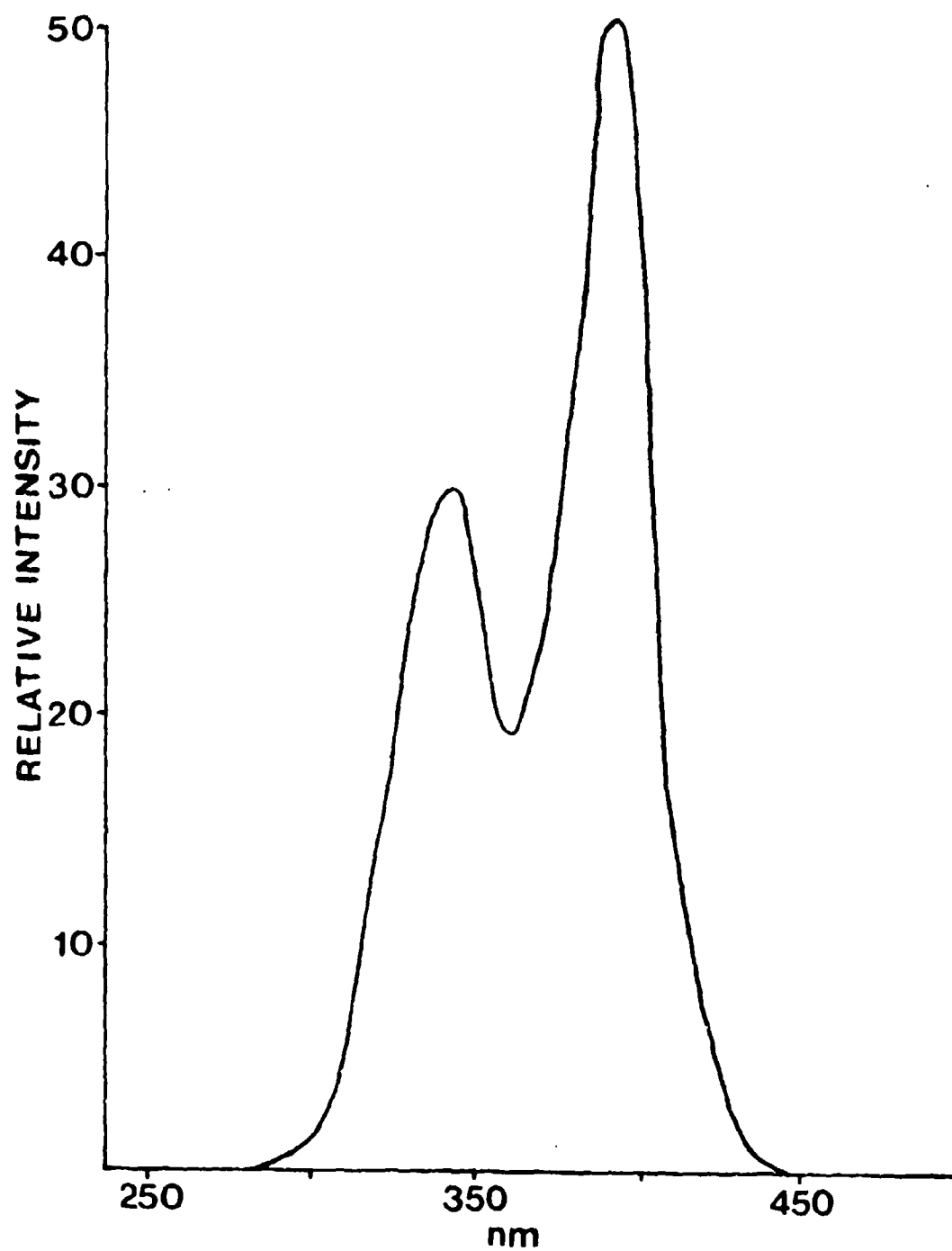


Figure 2. Absorption spectrum of Uvitex RBNAD

optical brighteners recommended for use on polyamides and are reported to be among the more stable optical brighteners recommended for use on polyamides.

In addition to the optical brighteners investigated, studies were also conducted using conventional UV screening agents (absorbers). Because of their excellent performance in a wide range of polymers and reports in the literature on their stabilizing effects in Nomex, The Tinuvin series of screening agents was selected for study. The Tinuvin's are substituted hydroxyphenyl benzotriazoles which have strong absorption in the near UV and have excellent stability to UV degradation. Tinuvin P and Tinuvin 327 were the specific compounds used in this investigation.

In addition one substituted Triazine type UV absorber, Cyasorb UV 800 (American Cyanamid) was also included in the study.

b. Antioxidants

The hindered phenols have been one of the most effective groups of compounds that act as antioxidants. The Irganox compounds are hindered phenols with amide, ester, and thioglyoxal substituent groups.

c. Radical Scavengers/Excited State Quenchers

Organometallic compounds and metallic salts have been effective in stabilizing aliphatic amides, probably by reaction with either free radicals or with excited species produced by the absorption of light. The compounds of this type shown in Table 1 have been effective in stabilizing other polymers against UV degradation.

A number of commercial quenching agents as well as several experimental materials were included in the screening studies.

d. Other Potential Stabilizers

A number of other compounds were investigated which do not fall in the usual categories of UV stabilizers. It has been reported that sulfur dyes have a light stabilizing action on aromatic polyamides and thiourea has been suggested as a light stabilizer for dyes. An attempt has been made to incorporate this material in Nomex by a padding-thermofixation process (200°C).

Oxidation of thiourea results in the formation of compounds possessing the disulfide link and also elemental sulfur, both of which may act to stabilize the fibers.

During the course of the screening studies, some results were obtained which suggested that amine end groups might be related to the degradation of Nomex. Beta-oxy-napthoic acid was added in an attempt to remove amine end groups by chemical reaction.

One reference in the patent literature [6] suggested that oxanilide is a good stabilizer against UV degradation. Since this material is structurally similar to Nomex, oxanilide was included in the materials screened for effectiveness in Nomex stabilization.

D. Techniques for Addition of Stabilizers to Nomex

In order for a stabilizer to be effective, it must be incorporated in the fiber or in a resin used in finishing. Little is known concerning the incorporation of various materials in Nomex except what is available in the published dyeing technology. This information is confined to recommended procedures for the application of cationic dyes. Since the types of materials being considered as stabilizers include both ionic and non-ionic materials, initial studies included the application of selected dyes from several classes of dyes by techniques and under conditions recommended for cationic dyes to learn more concerning the relationship between structural features of dyes and their substantivity to and diffusion in the fiber. These experiments were carried out both in the presence and absence of a suitable plasticizer for the fiber to promote diffusion in the fiber. Based on the results obtained, stabilizers (UV screens, antioxidants, UV stabilizers, fluorescent brighteners) were applied to the fiber using conditions for their application which would be predicted to promote reasonable sorption and degree of fiber penetration.

In all of the literature concerning the dyeing of Nomex, high concentrations of dye carriers are required at dyeing temperatures higher than 212°F. Many carriers have been evaluated for the application of cationic

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- [6] Luethi, C.; Biland, H. R.; Duennenberger, M.; "Bis(oxalic acid aromatic diamides) useful as ultraviolet stabilizers for polymers;" South African Patent 68:2,135; September 1968.

dyes [7]. Those recommended include benzaldehyde [8] for Nomex E8 (a fiber chemically modified for dyeing with cationic dyes) and acetophenone [9]. Recommendations for dyeing Nomex type 450 include the use of acetophenone (40 g/l) at a dyeing temperature of 250 F. Conversations with Dr. P. G. Noble and Richard Hunt of Tootal Limited, Manchester, England, revealed that they had successfully dyed Nomex with cationic dyes using benzyl alcohol. A British patent [10] which describes this process has been issued to Tootal. In their work it was discovered that important factors in the light stability of cationic dyes on Nomex were the purity of the dyes, and the type and purity of surfactants used for emulsification of the carrier.

DuPont makes no recommendation for the dyeing of Nomex type 430; however, they report that it has been dyed successfully following the teachings of U.S. Patent 3,771,949 [11]. This dyeing process is very complicated requiring pretreatments of the fiber with high boiling liquids such as ethylene glycol, propylene glycol, tetraethylene glycol, and their alkyl derivatives at temperatures of approximately 190°C followed by application of cationic dyes in solvent mixtures consisting typically of such solvents as dimethylacetamide, dimethylformamide, and dimethylsulfoxide.

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- [7] Schumm, R.W. and Cruz, C.J.; "Dyeing and Finishing Nomex Nylon"; Textile Chemist and Colorists, 1, 388 (1969).
 - [8] Evans, B.A. and Schumm, R.W.; "Dyeing Nomex Type 450 Nylon"; Textile Chemists and Colorist, 2, 262 (1970).
 - [9] duPont Technical Information Bulletin N-249, June 1971.
 - [10] Easthope, E. and Noble, P.G.; "Improvements in the Dyeing of Textile Materials (Aromatic Polyamides)"; British Patent 1,277,434; June 1972.
 - [11] Hermes, J.; "Pretreatment and Dyeing of Shaped Articles Derived from Wholly Aromatic Polyamides"; U.S. Patent 3,771,949; November 1974.

Fabrics made from Nomex type 430 dyed using procedures recommended for Nomex type 450 are unsatisfactory due to streakiness and lack of penetration of the dye into the fiber. The following types of dyes have been applied to Nomex type 430 at 250°F using the carrier, benzyl alcohol, at concentrations up to 100 g/l:

Leveling acid
Neutral dyeing acid
Disperse
Cationic

In all cases, 5.0% dye based on fiber weight was used. Medium depths of shade were obtained with disperse, cationic, and neutral dyeing acid dyes when the concentration of carrier was 100 g/l. Propylene carbonate was ineffective as a carrier under the same dyeing conditions. The dyeing results with benzyl alcohol were convincing evidence that anionic, cationic, and non-ionic materials can be incorporated in the fiber.

Acetophenone is recommended by duPont as a carrier for dyeing Nomex 450. It was discovered that Chemo-carrier FPN, a compounded carrier composition reported to be based on acetophenone (Tanatex Corporation), was effective in applying cationic and disperse dyes to Nomex. The concentration of the carrier required was 40 g/l at a dyeing temperature of 250-260°F.

Other materials which were investigated included salicylic acid and o-benzoic sulfimide. They were chosen because it was thought that they may be effective carriers due to the fact that they are both small molecules possessing high dipole moments. In addition, they are also capable of forming complexes with metal ions which could serve as stabilizers for Nomex. Dyeing studies using these materials showed that both materials provide some carrier action, salicylic acid being more effective than o-benzoic sulfimide.

Of all carriers investigated in the dyeing experiments, Chemocarrier FPN proved to be most effective for incorporation of dyes in Nomex. This carrier was used in all subsequent experiments in which stabilizer were incorporated in Nomex.

Potential stabilizers were applied to Nomex Type 433 Sage Green 200 denier, 100 filament yarn samples by procedures similar to those used for dyeing of Nomex fiber.

The fiber (2.5 grams) was wound loosely on a stainless steel wire frame and placed in stainless steel cans containing the treatment solution. Composition of the treatment bath was

2.5 grams stabilizer candidate
5.0 ml Chemocarrier FPN (Tanatex)
125 ml total volume of bath (50:1 liquor ratio)

The cans were sealed and placed in an Atlas High Temperature Launder-Ometer at room temperature. The temperature was raised to the treatment temperature (250°F for optical brighteners and 260°F for the UV absorbers) at 3 F per minute. The temperature was held at 250°F (or 260°F) for two hours followed by a 15 minute cooling cycle. The fiber samples were then removed and scoured in a bath containing

5.0% Merpul HC (o.w.f.)
6.0% $\text{Na}_4\text{P}_2\text{O}_7 \cdot 3 \text{H}_2\text{O}$ (o.w.f.)
125 ml total value of scouring bath
(50:1 liquor ratio)

The scouring was carried out at 180°F for 15 minutes followed by a thorough rinse.

A control sample (blank dyed sample) was prepared using the same procedure described above except that the optical brightener, UV absorber, or other stabilizers were omitted.

As noted earlier sulfur containing compounds and in particular sulfur dyes (containing disulfide bonds -S-S) have been reported to stabilize aromatic polyamides against UV degradation. Two techniques for in-situ production of sulfur containing compounds were employed - reaction between urea and thiourea and acid decomposition of sodium thiosulfate.

The treatments of Nomex with aqueous solutions of urea and thiourea were as follows:

1. Urea 100 g/l
2. Thiourea 100 g/l
3. Urea and thiourea, 50 g/l each

Skeins (2.5 g) of Nomex yarn, Type 430, were treated in 125 ml of these solutions at 250°F for two (2) hours followed by rinsing to remove superficially held urea and

thiourea. The treated yarns were then subjected to Fade-Ometer exposure.

An attempt was made to produce colloidal sulfur in Nomex by first treating the yarn in a solution of formic acid (40 g/l) at 250°F for 2 hrs. followed by a treatment with an aqueous solution of sodium thiosulfate (10 g/l) at 212°F for 15 minutes. It is known that this reaction produces colloidal sulfur.

For these preliminary screening studies, no attempt was made to obtain quantitative data on the quantity of stabilizers actually picked-up from the bath by the Nomex fiber. Fibers were examined under a UV light following the treatment with optical brighteners and it was apparent that substantial quantities of the brighteners had been incorporated in the fiber.

E. Exposure and Testing

Control samples, samples which had been blank dyed and samples containing UV screening agents were exposed to light from either a xenon-arc or carbon-arc in Atlas Fade-Ometers. Xenon-arc exposures were carried out in a Model F Fade-Ometer equipped with a preaged 2500 watt arc with IR absorbing inner and quartz outer filters. The Fade-Ometer was equipped with a humidity control unit and was operated at a black panel temperature of 150°F and a relative humidity of 50%. Samples were exposed up to 100 hours with specimens removed from the Fade-Ometer at 20 hour intervals.

Carbon-arc exposures were conducted in a Type W Weather-Ometer with twin enclosed carbon-arcs. Relative humidity was maintained at 50% and the black panel temperature at 150°F.

In each series of exposures, both control and "blank dyed" samples were exposed simultaneously with the treated specimens.

Breaking strength and elongation of yarns were tested with an Instron constant-rate-of-extension tester, following procedures described in ASTM method D 2256. Tests on control and irradiated yarns were made with a 5 inch gage length and an extension rate of 100 percent per minute. The time required to break is a function of gage length, extension rate, and breaking elongation. Since breaking elongation was expected to vary with level of irradiation,

time-to-break was not used as a criterion of testing as specified in the ASTM method. The 5-inch gage length was chosen to accommodate the relatively short yarn lengths exposed to the UV light source.

Because of the difficulty of securing the same tension in all the filaments and because of slippage in the clamps, erratic results are frequently obtained with zero-twist multifilament yarns unless a small amount of twist is inserted before testing. A twist of $(110 \pm 10 \text{ tpi})/\sqrt{D}$, where D is the multifilament yarn denier, was used to overcome these problems.

Twenty tests were made on each sample. This level of testing was selected to provide a maximum error of ± 3 percent for strength and ± 5 percent for elongation of the control yarns. Variation in observed results of both of these properties was expected to increase with increased levels of irradiation. Consequently, the error in estimation of these properties measured on the exposed yarns was somewhat higher.

F. Results of Screening Studies

1. Exposure Studies on Untreated Nomex Samples

Samples of Nomex type 430 (white) were exposed to the carbon arc and xenon arc lamps in the Fade-Ometer for 100 hours. Tensile strength and elongation were determined at 20 hour intervals for the exposed samples. Results of these experiments are shown in Figures 3 and 4. It is apparent from these data that exposure to the carbon arc gives much more rapid deterioration in the properties of Nomex. The carbon arc has very intense bands of radiation between 350 and 425 nm. This intense output corresponds directly with the wavelengths of energy responsible for Nomex degradation. The carbon arc exposure is therefore probably more severe than outdoor exposure in degradation of Nomex. Xenon arc exposure probably compares more favorable with outdoor exposure. The results also clearly indicate that the fiber elongation is more severely affected than the tenacity on exposure to UV radiation.

Similar exposure studies were conducted on Nomex type 433 (sage green) yarns and the results are shown in Figures 5 and 6. It is apparent from these results that the rate of degradation of the type 430 (white) Nomex is much greater than rate for type 433 (sage green) for both exposure sources.

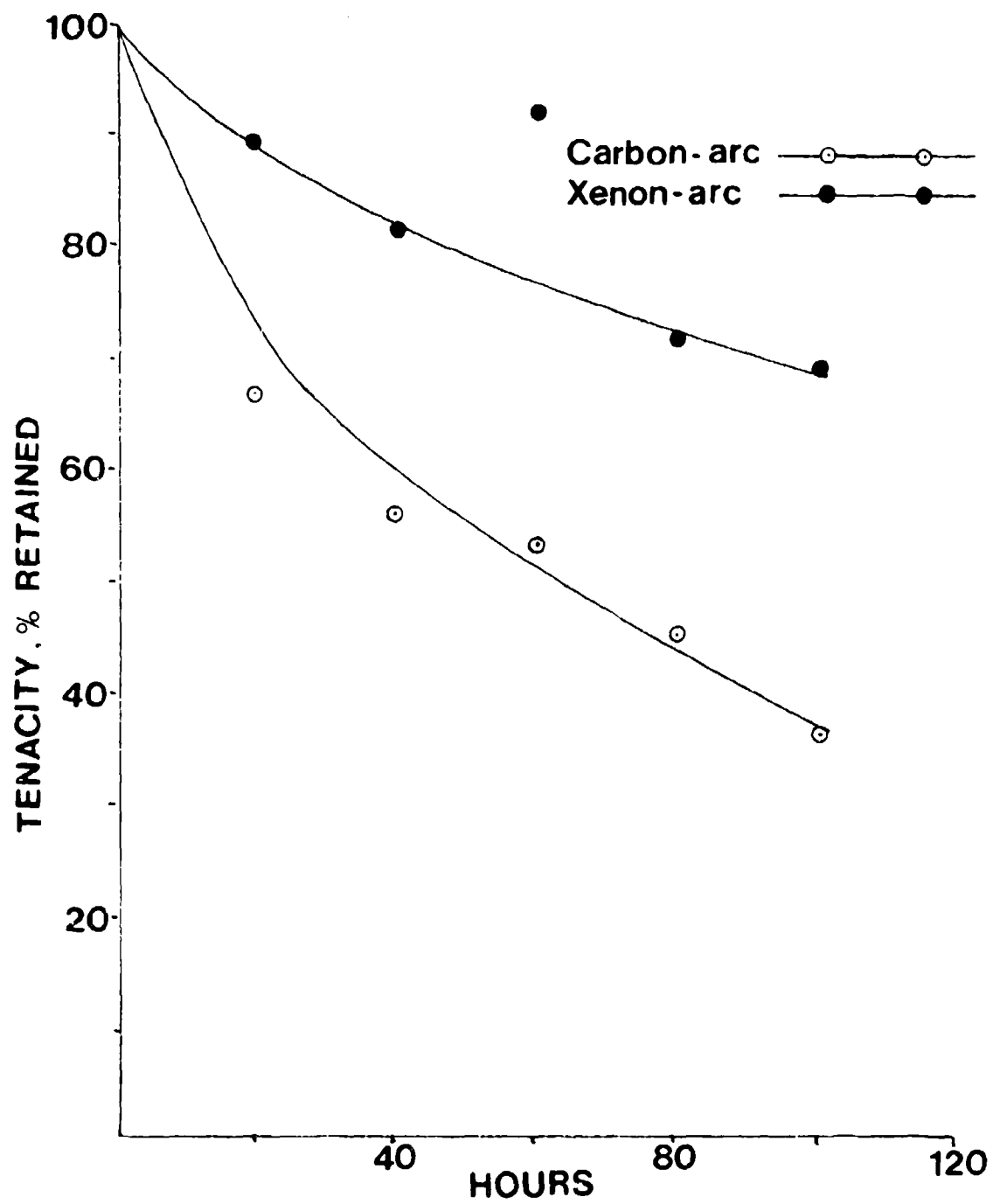


Figure 3. Effect of UV exposure on Nomex yarn tenacity

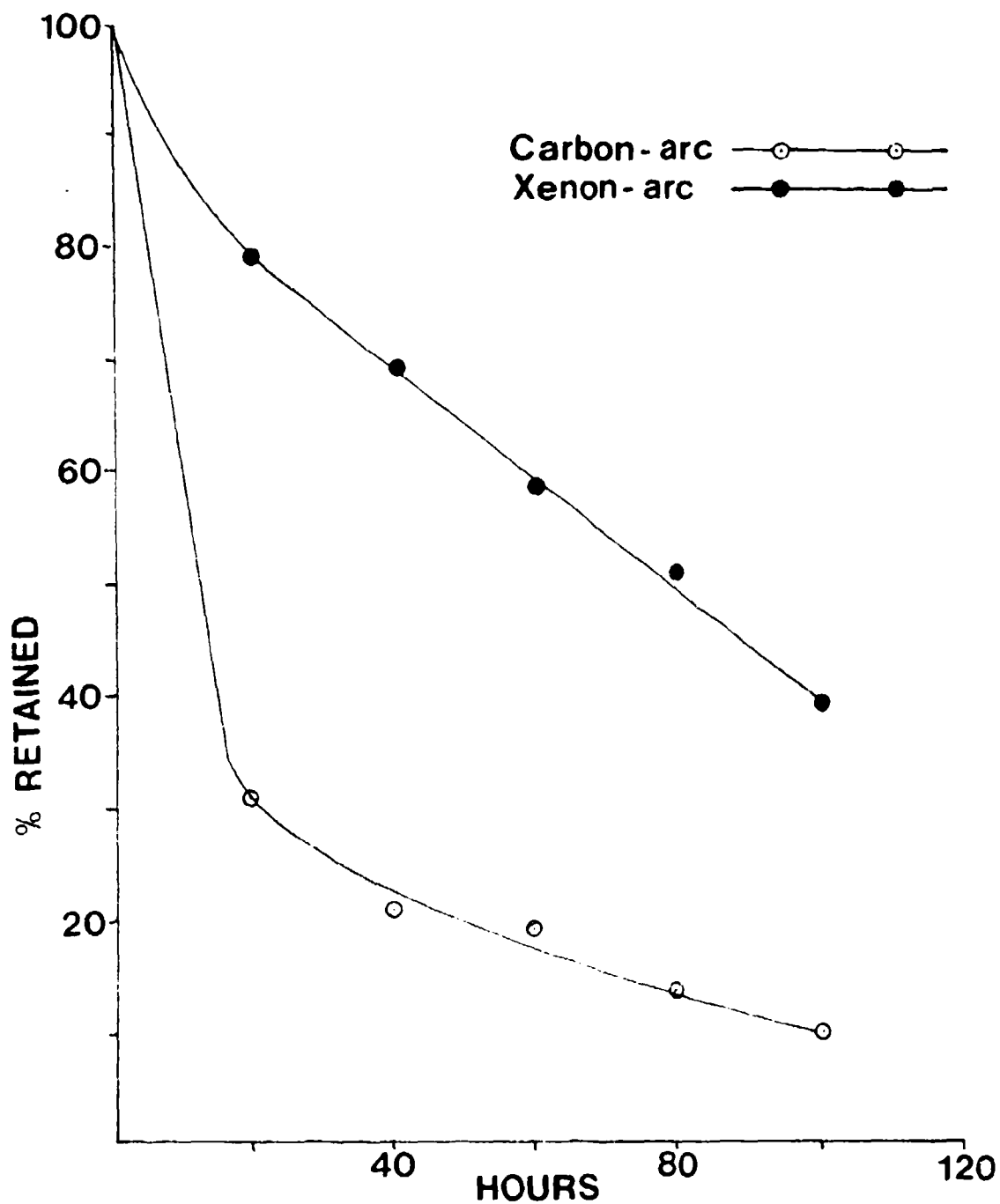


Figure 4. Effect of UV exposure on Nomex yarn elongation

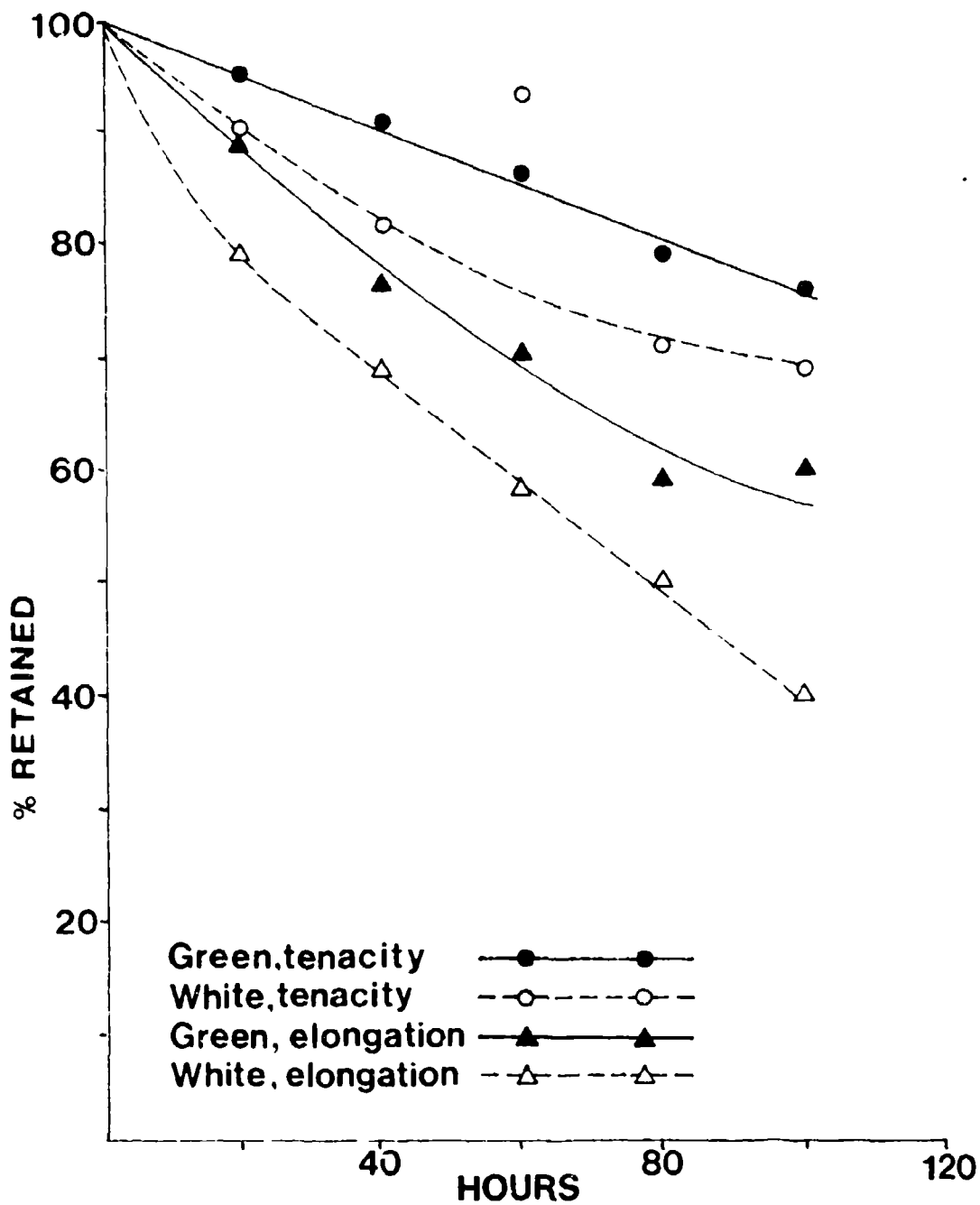


Figure 5. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after xenon arc exposure.

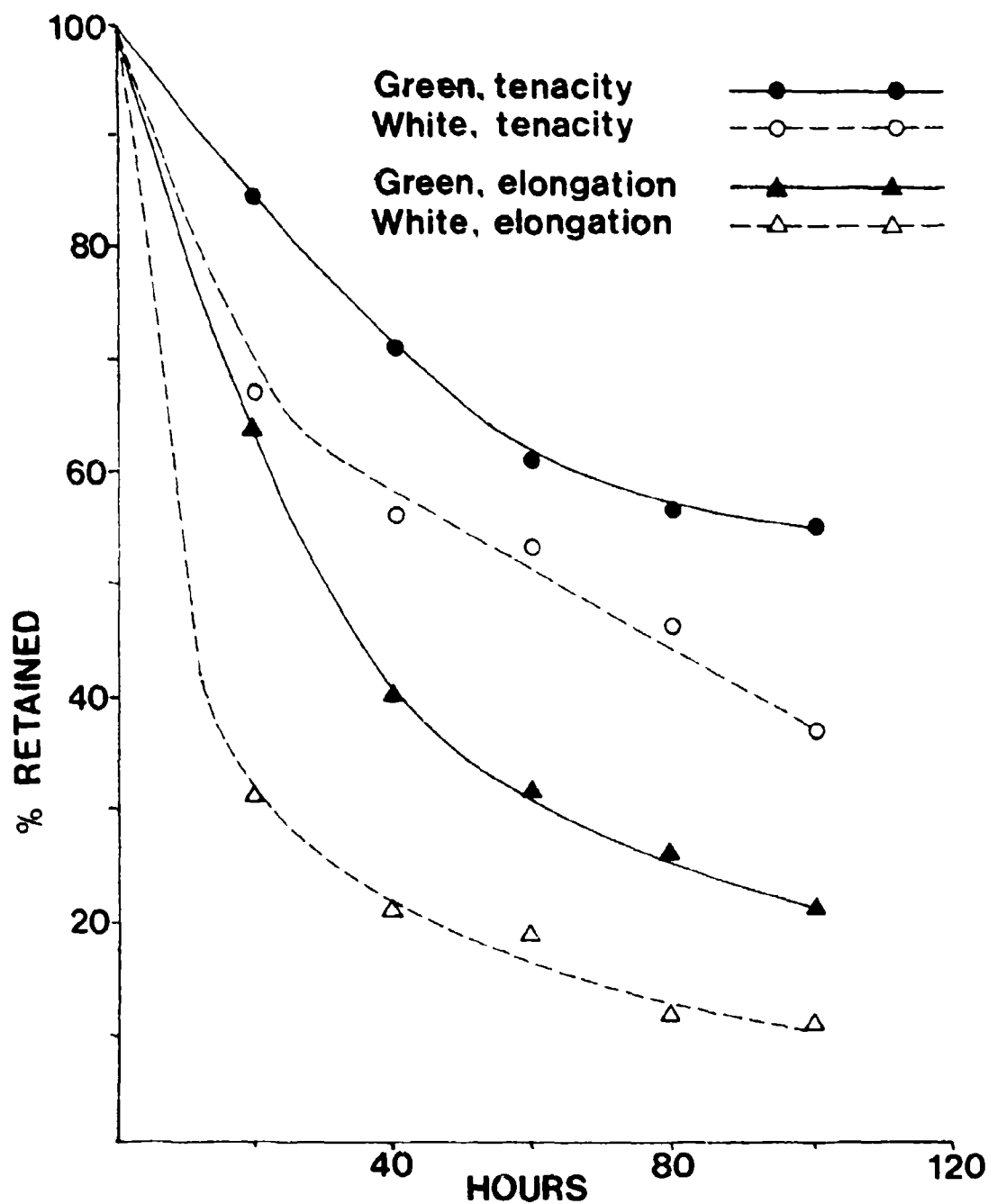


Figure 6. Retention of tenacity and elongation of Nomex Type 430 (white) and Type 433 (sage green) after carbon arc exposure.

It is probable that duPont is adding a UV stabilizer to type 433 Nomex. This stabilizer may be contributing to the improved property retention for this type Nomex. The green pigment in type 433 may also be contributing to the improved UV resistance.

The effect of the treatment process for addition of stabilizer to Nomex type 433 (sage green) yarn samples is shown in Figure 7. Some slight improvement in retention of elongation and in some cases retention of tenacity are observed from the "blank dyeing" alone. This is undoubtedly due to retention of small quantities of residual swelling agent (carrier) in the fiber which acts as a plasticizer in reducing the brittleness resulting from UV degradation. In a few cases, some loss in tenacity is observed for "blank dyed" samples. This probably results from mechanical damage to the yarn during the dyeing operations. The changes observed due to the treatment process were small enough not to adversely affect the conclusions derived from the stabilizer screening studies. All subsequent screening studies on the effects of stabilizers on UV stability of Nomex were conducted on Nomex type 433 (sage green) yarn. The carbon-arc Fade-Ometer was the principal exposure source used since it gives more rapid degradation and was likely, therefore, to more clearly identify useful stabilizers. Xenon arc exposures were carried out on samples containing a number of potential stabilizers for comparison with the carbon-arc data.

2. Exposure Studies on Nomex Treated with UV Absorbers

Retention of tenacity and elongation of Nomex samples containing UV absorbers compared to control samples after exposure for 20,40,60,80, and 100 hours in the carbon arc Fade-Ometer are shown in Figures 8-17. Similar results for xenon arc exposures are shown in Figures 18-23.

Nomex yarn containing Leucophor EFR showed a significant reduction in both tenacity and elongation in all exposure experiments (Figures 8 and 18). This material is clearly capable of phototendering Nomex. Samples containing Uvitex WGS (Figures 9 and 19) indicate that this optical brightener has little or no effect on property retention on UV exposure. A similar conclusion is indicated by results on samples containing Uvitex RBNAD (Figure 10 and 20). Results are less clear for Uvitex NFW containing samples (Figure 11 and 21). This bright-

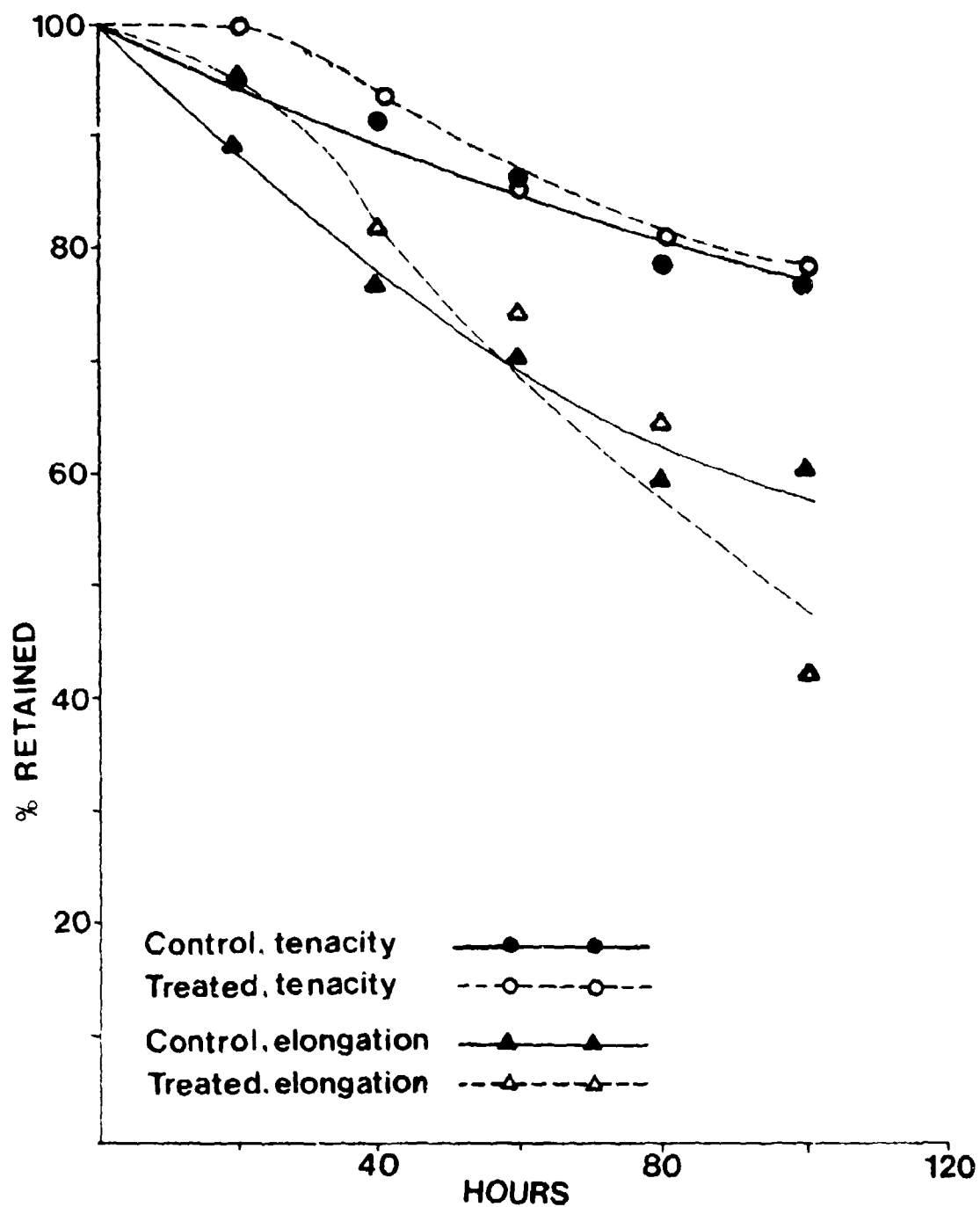


Figure 7. Retention of tenacity and elongation of Norex Type 433 control and blank dyed after xenon arc exposure.

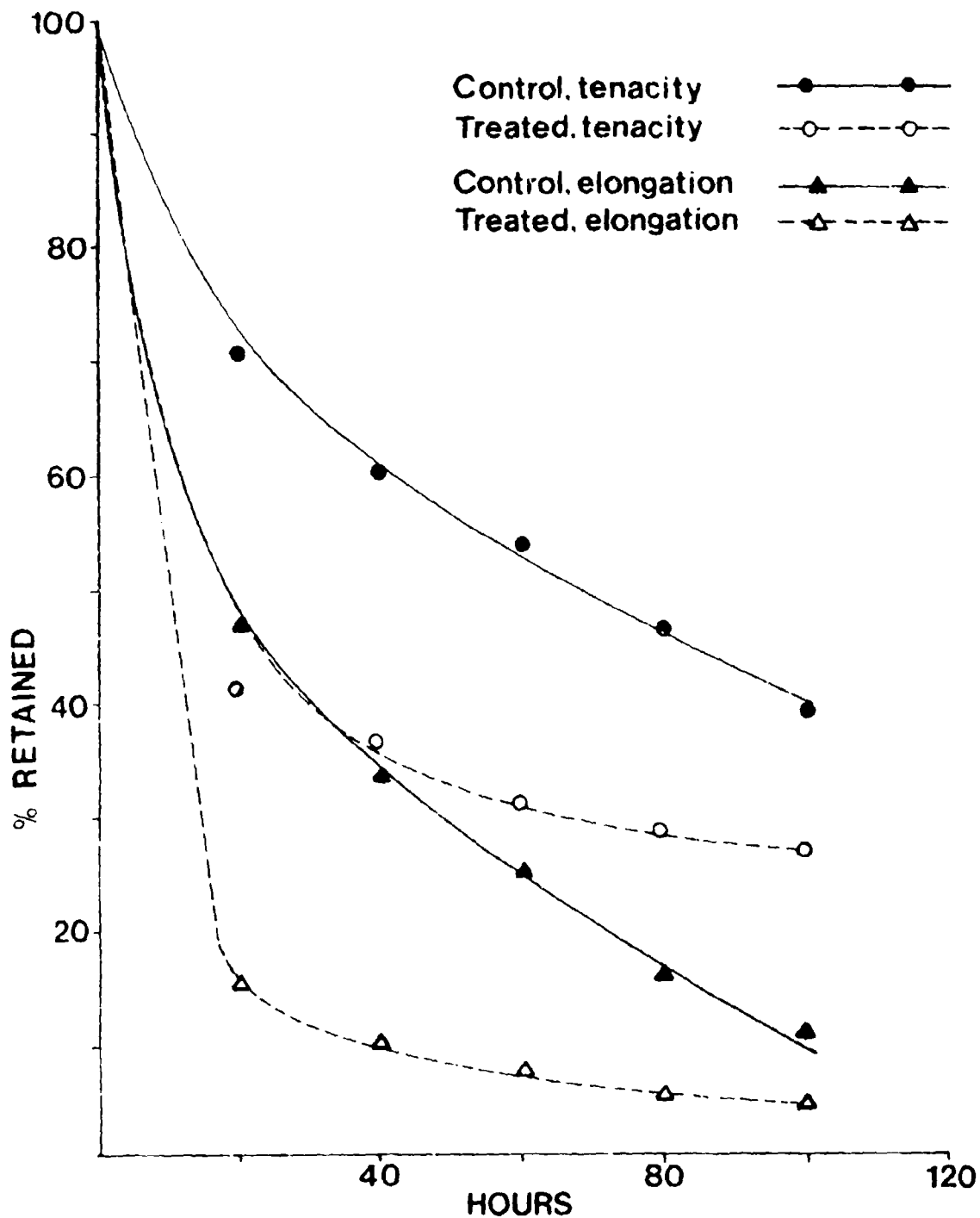


Figure 8 - Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control after carbon arc exposure.

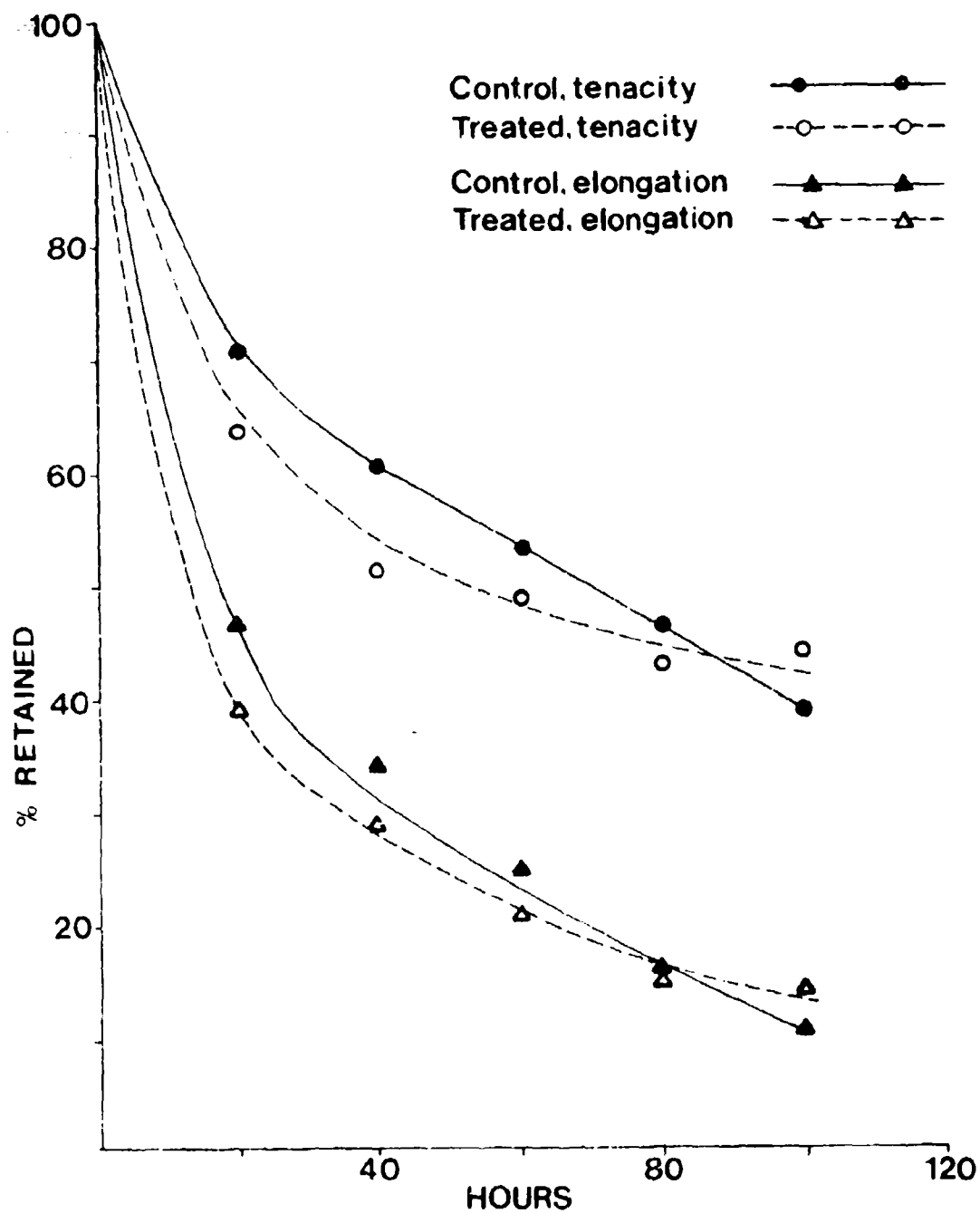


Figure 9. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex WGS compared to control after carbon arc exposure.

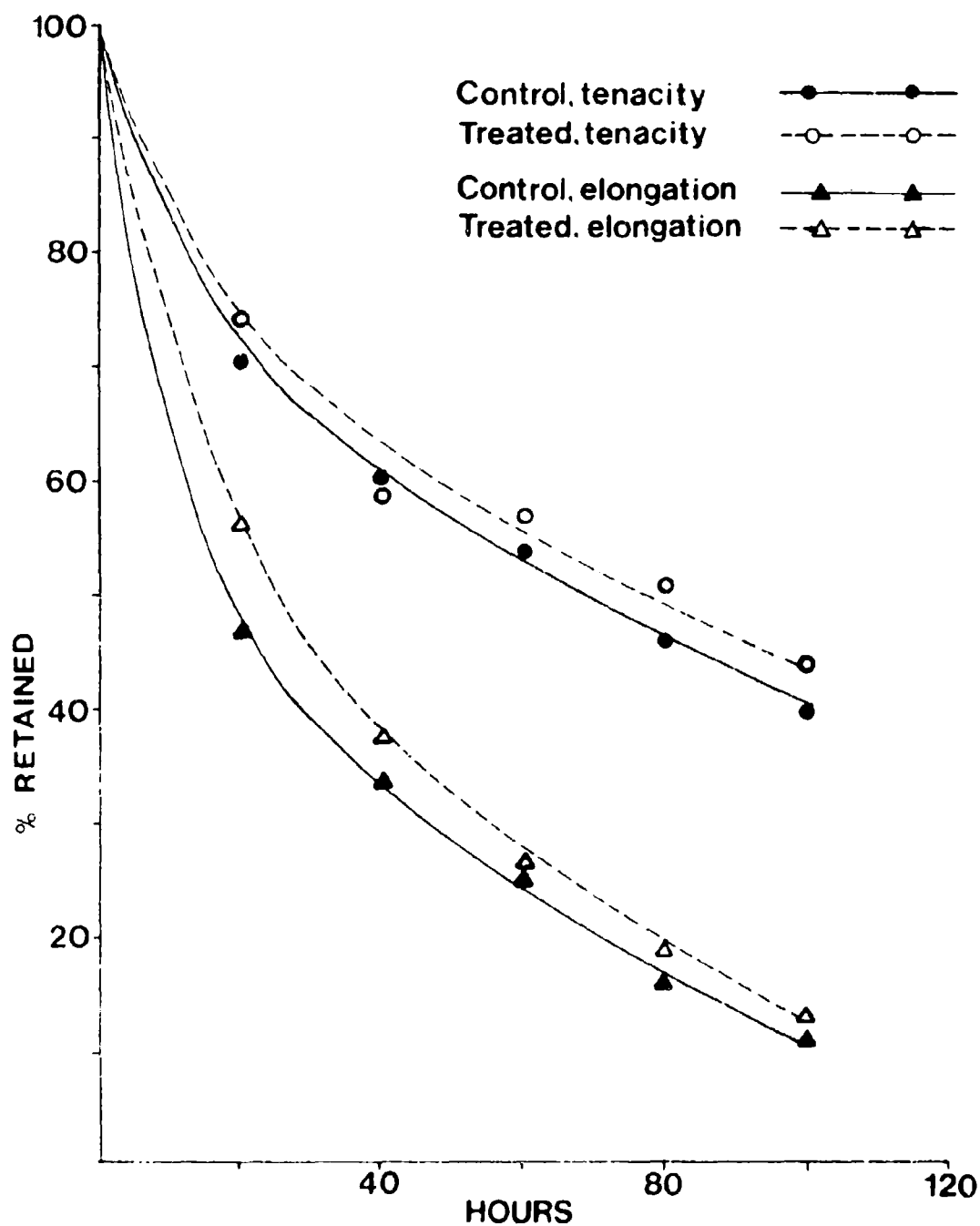


Figure 10. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after carbon arc exposure.

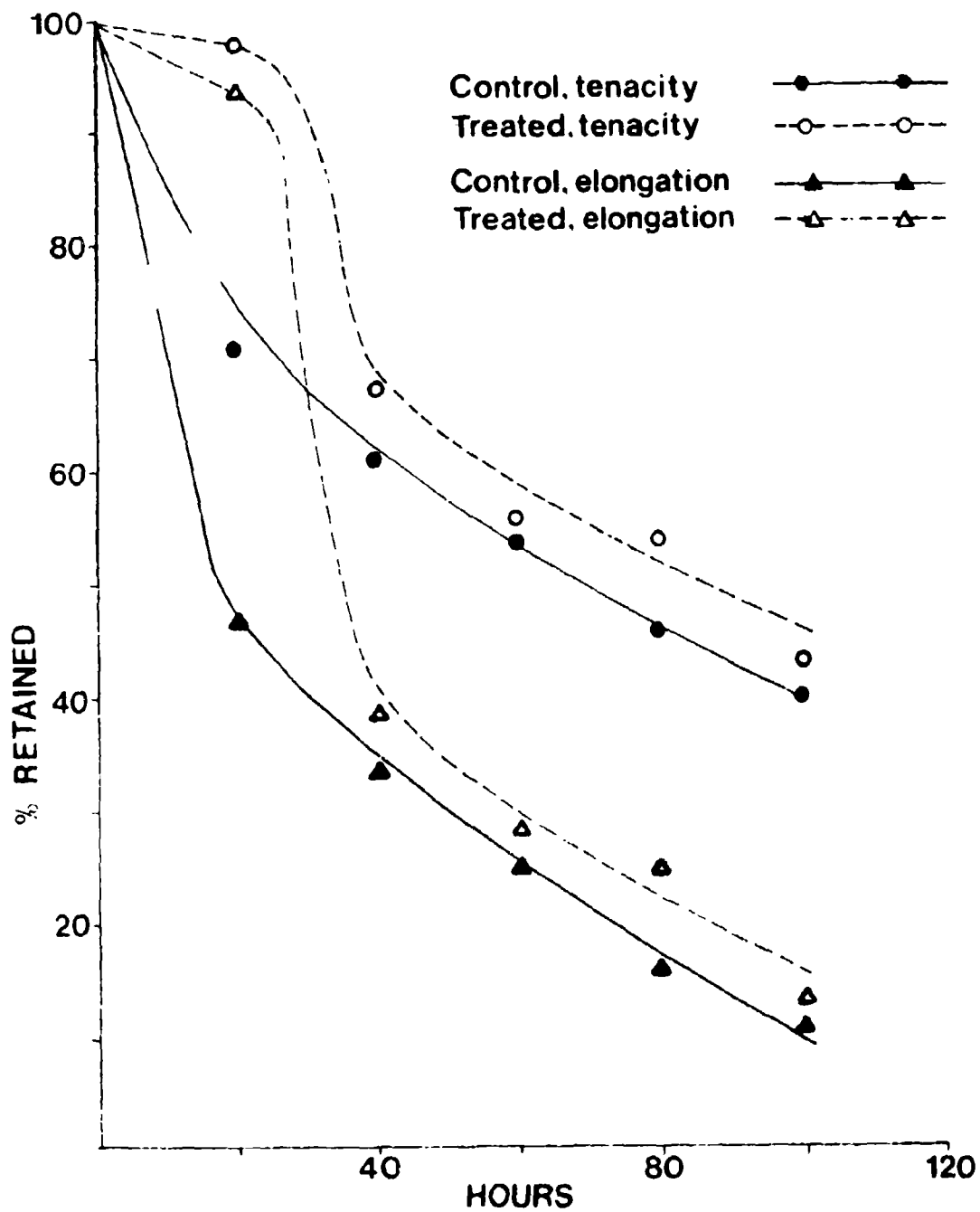


Figure 11. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control after carbon arc exposure.

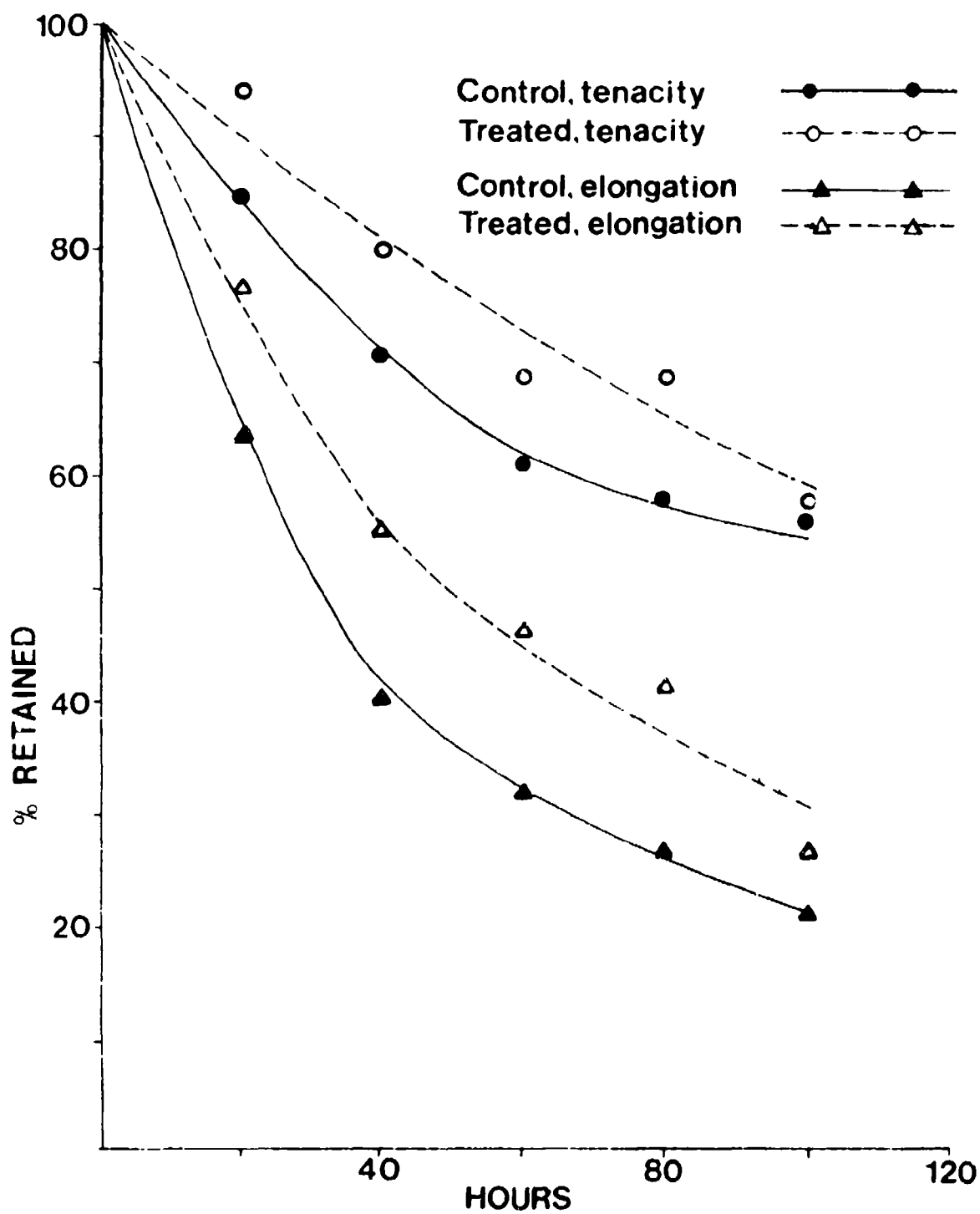


Figure 12. Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after carbon arc exposure.

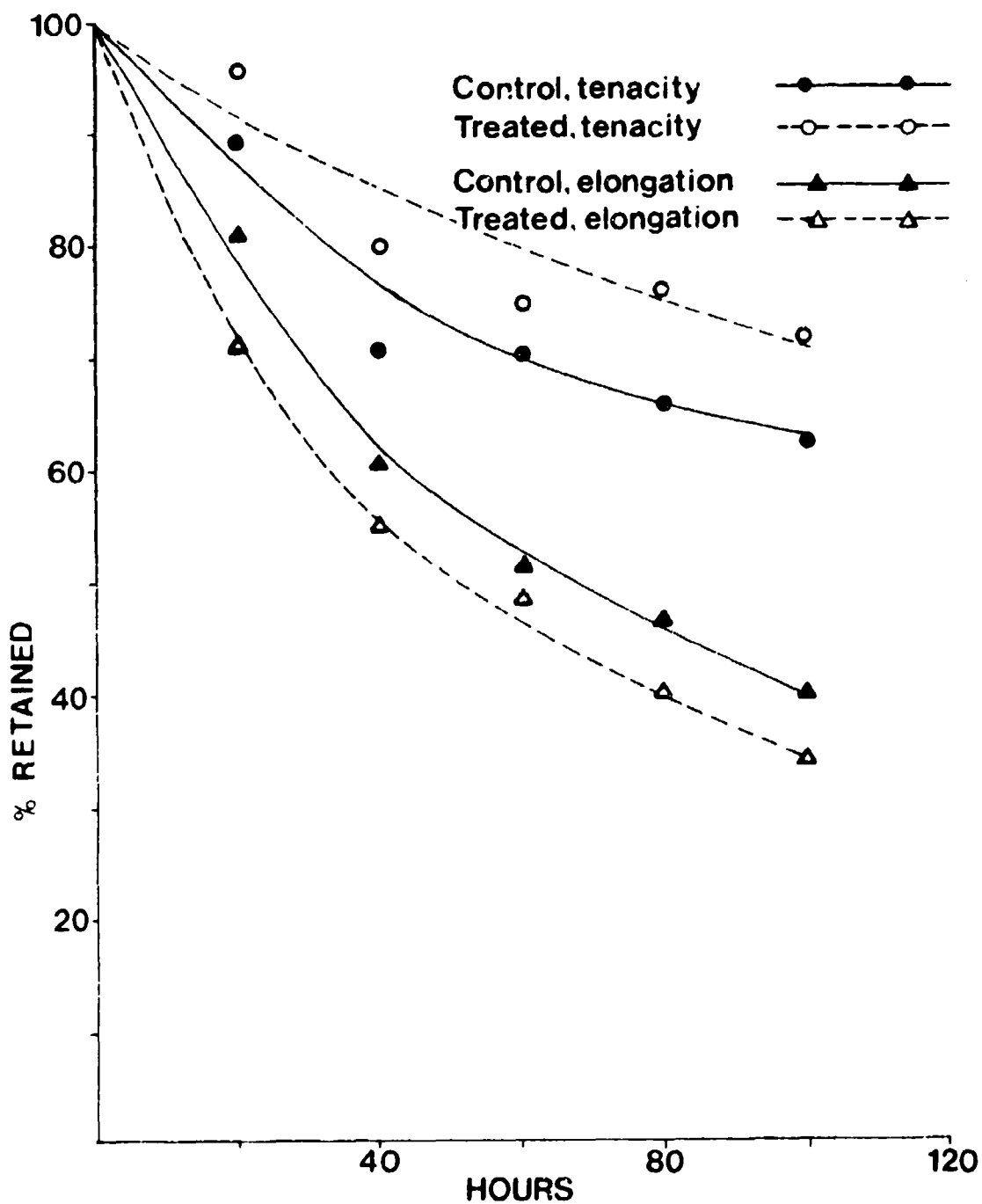


Figure 13. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after carbon arc exposure.

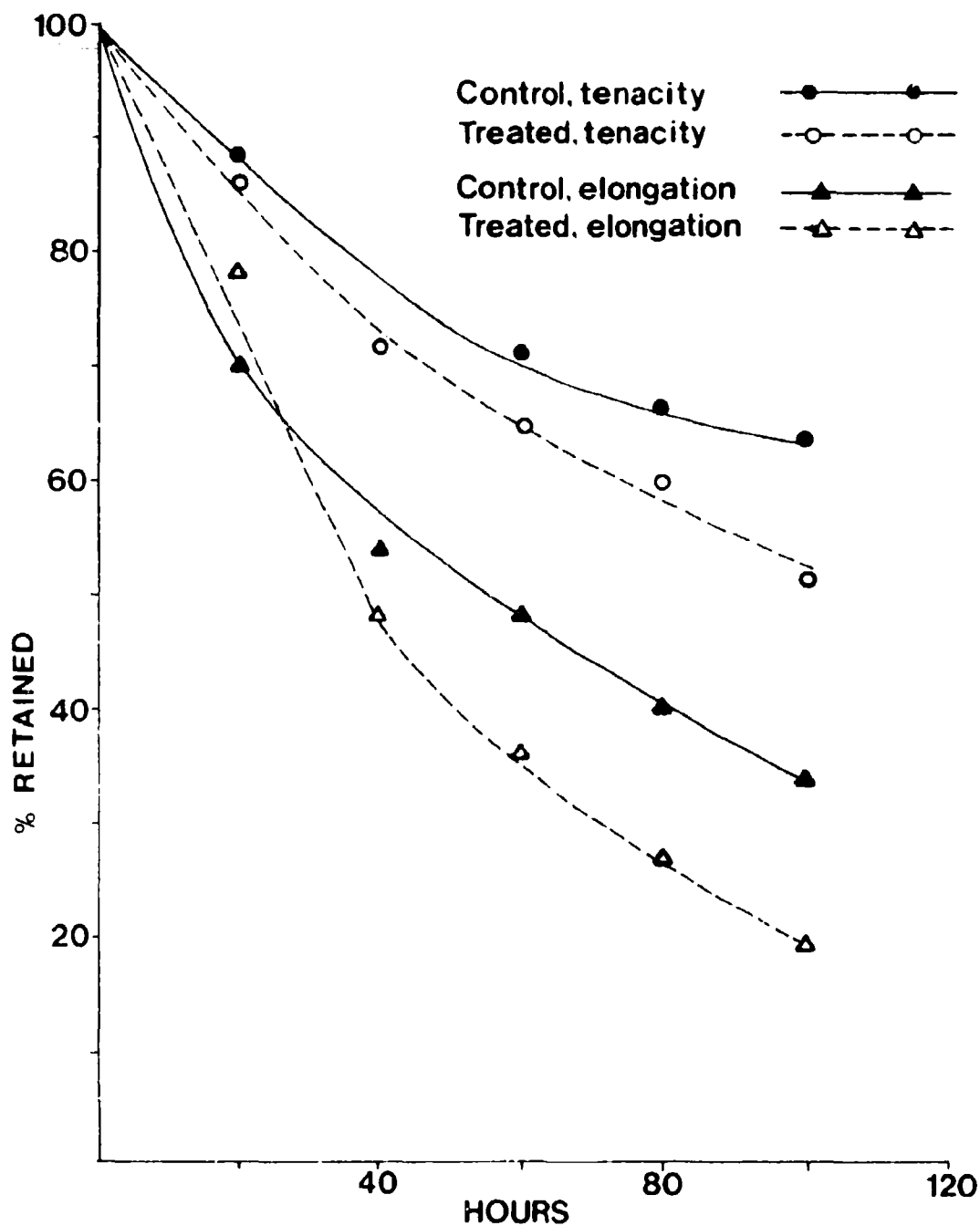


Figure 14. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 327 compared to control after carbon arc exposure.

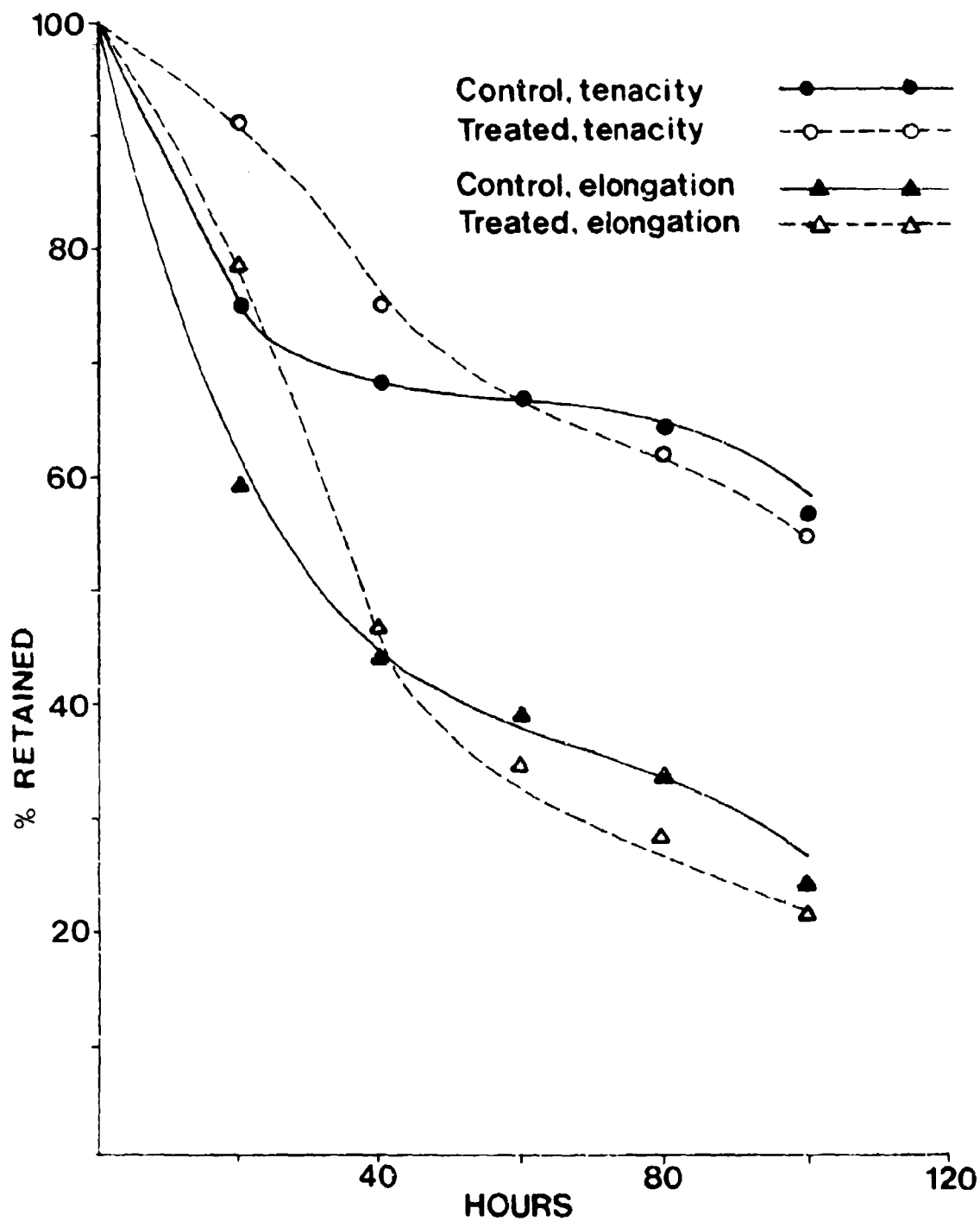


Figure 15. Retention of tenacity and elongation of Nomex Type 433 containing Cyasorb UV-800 compared to control after carbon arc exposure.

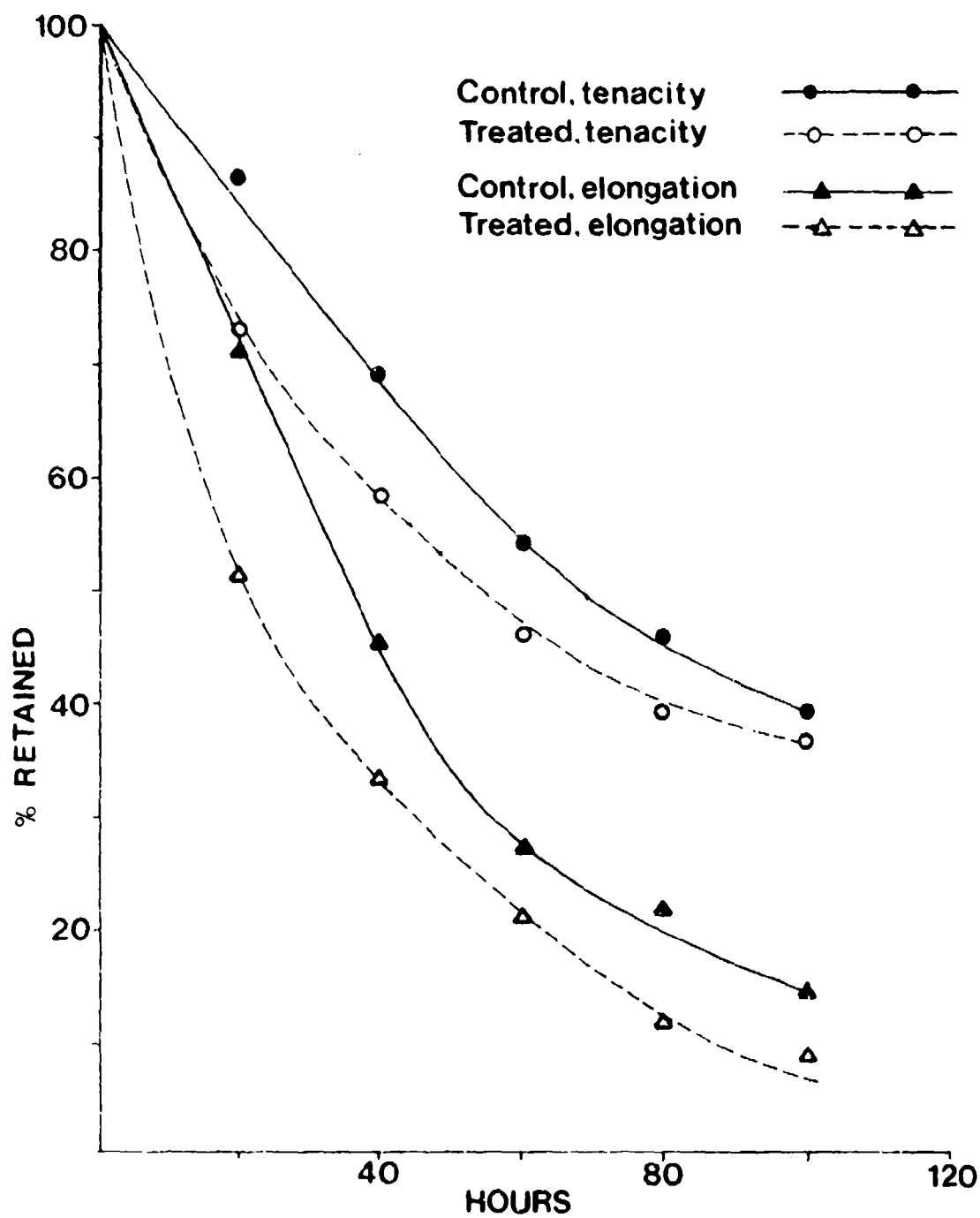


Figure 16. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin 770 compared to control after carbon arc exposure.

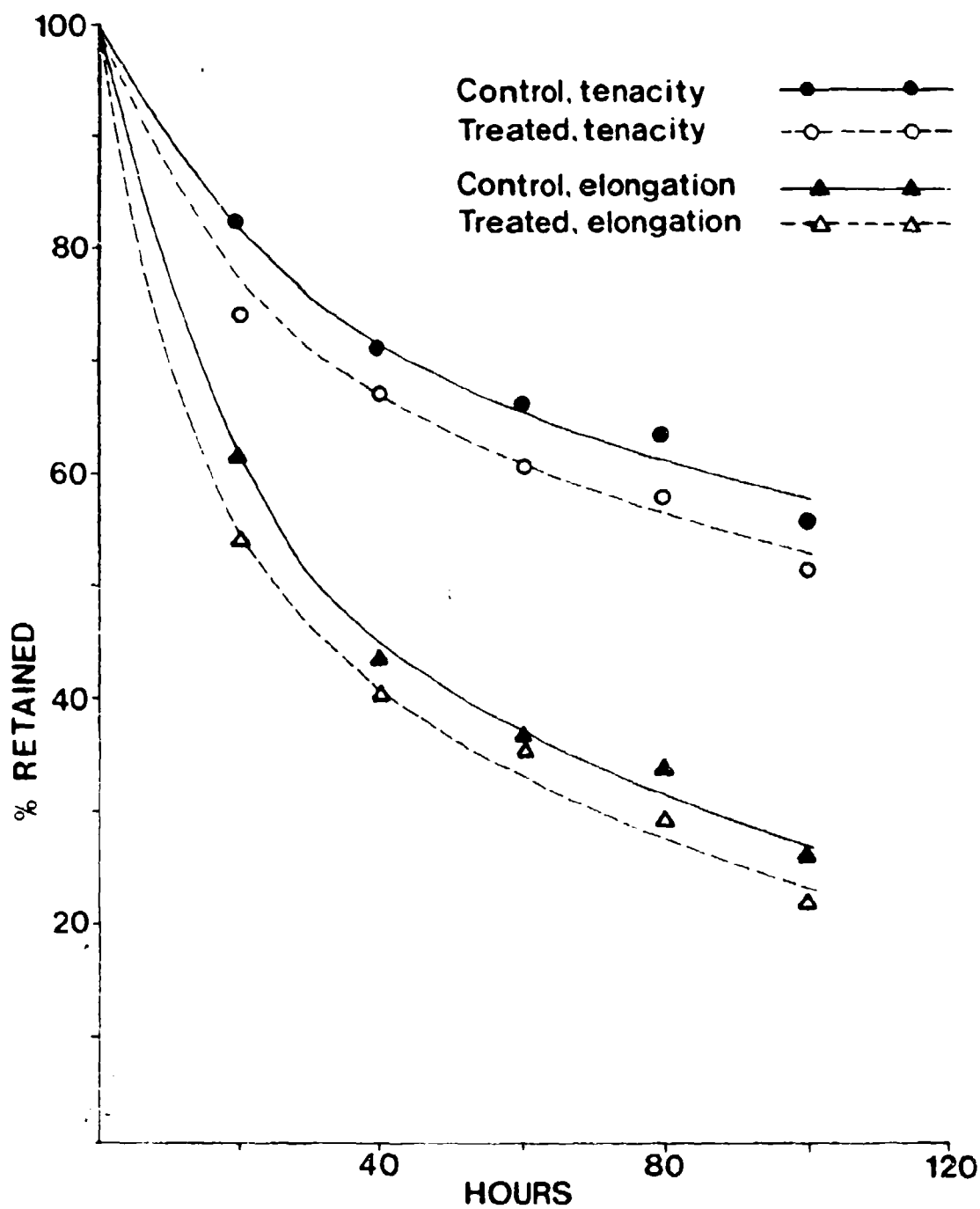


Figure 17. Retention of tenacity and elongation of Nomex Type 433 containing Eastman Inhibitor RMB compared to control after carbon arc exposure.

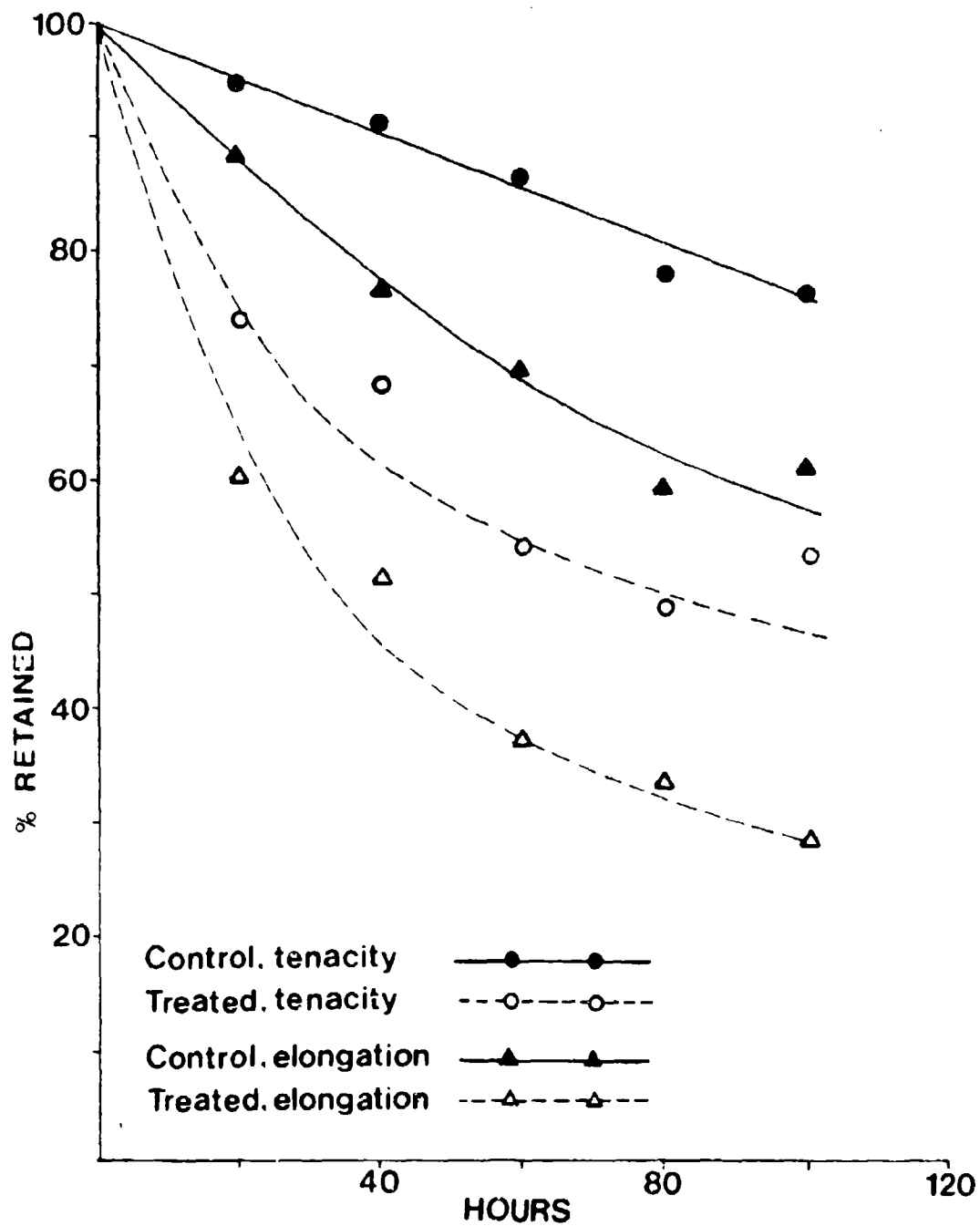


Figure 18. Retention of tenacity and elongation of Nomex Type 433 containing Leucophor EFR compared to control sample after xenon arc exposure.

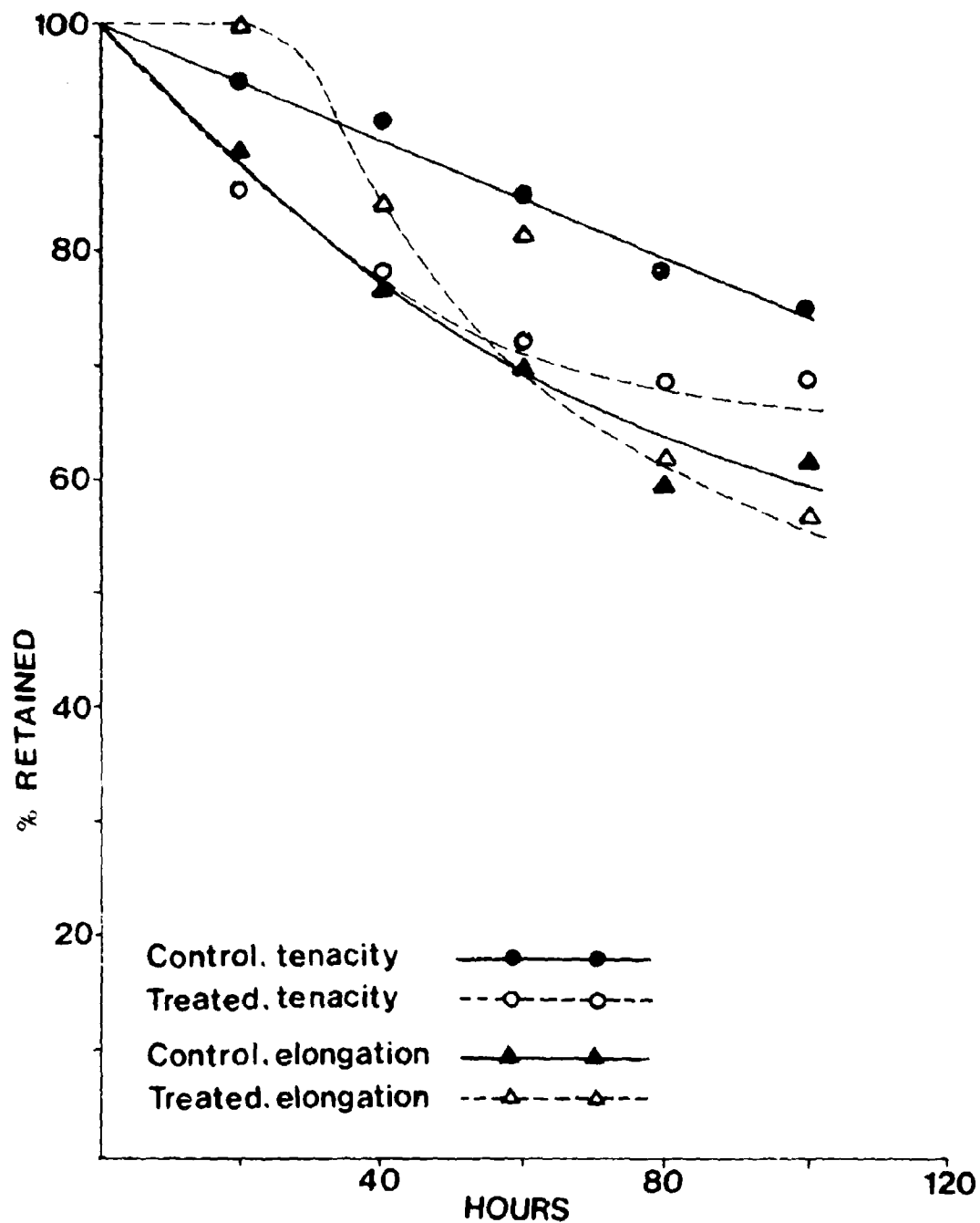


Figure 19. Retention of tenacity and elongation of Nomex Type 433 xenon containing Uvitex WGS compared to control sample after xenon arc exposure.

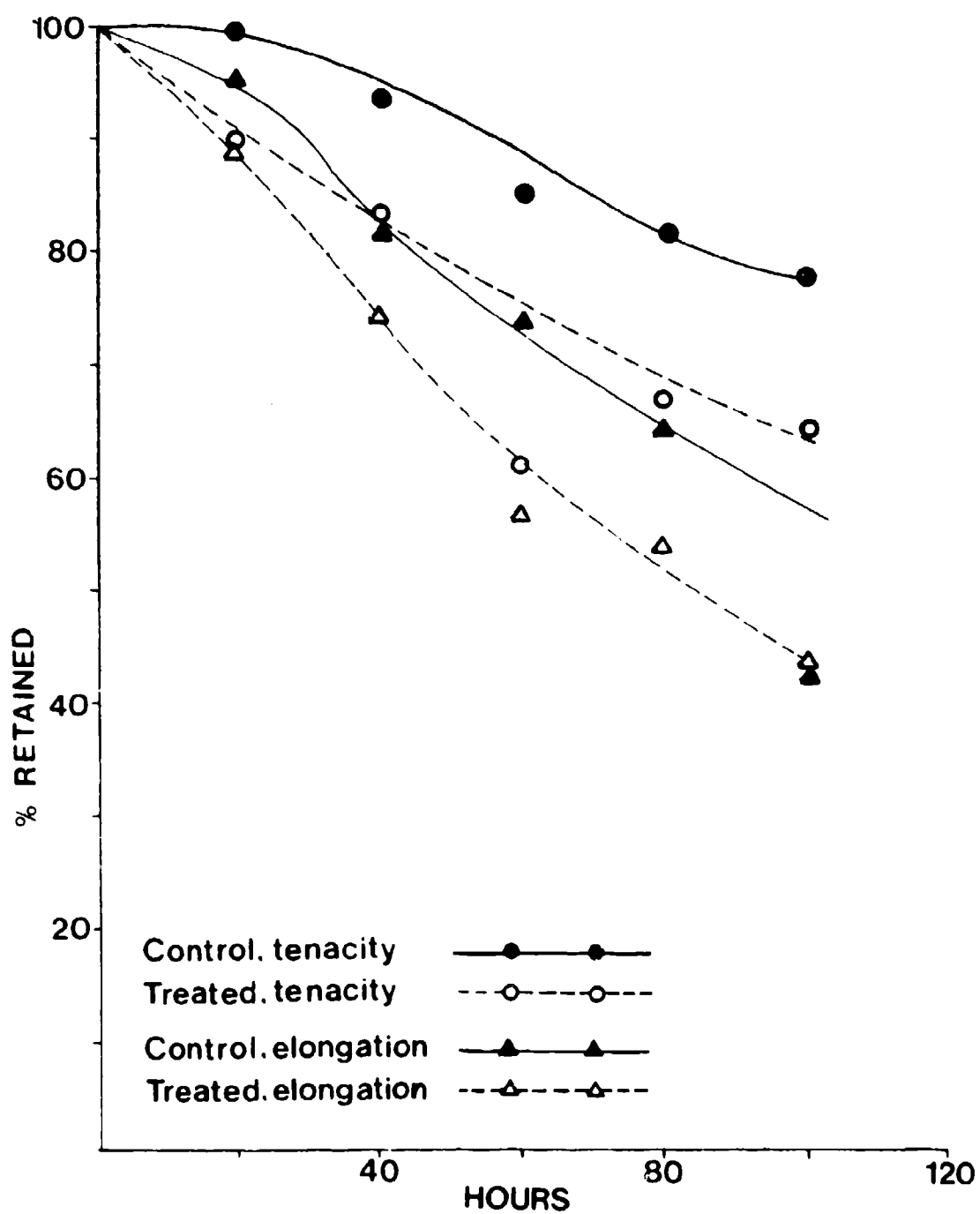


Figure 20. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex RBNAD compared to control after xenon arc exposure.

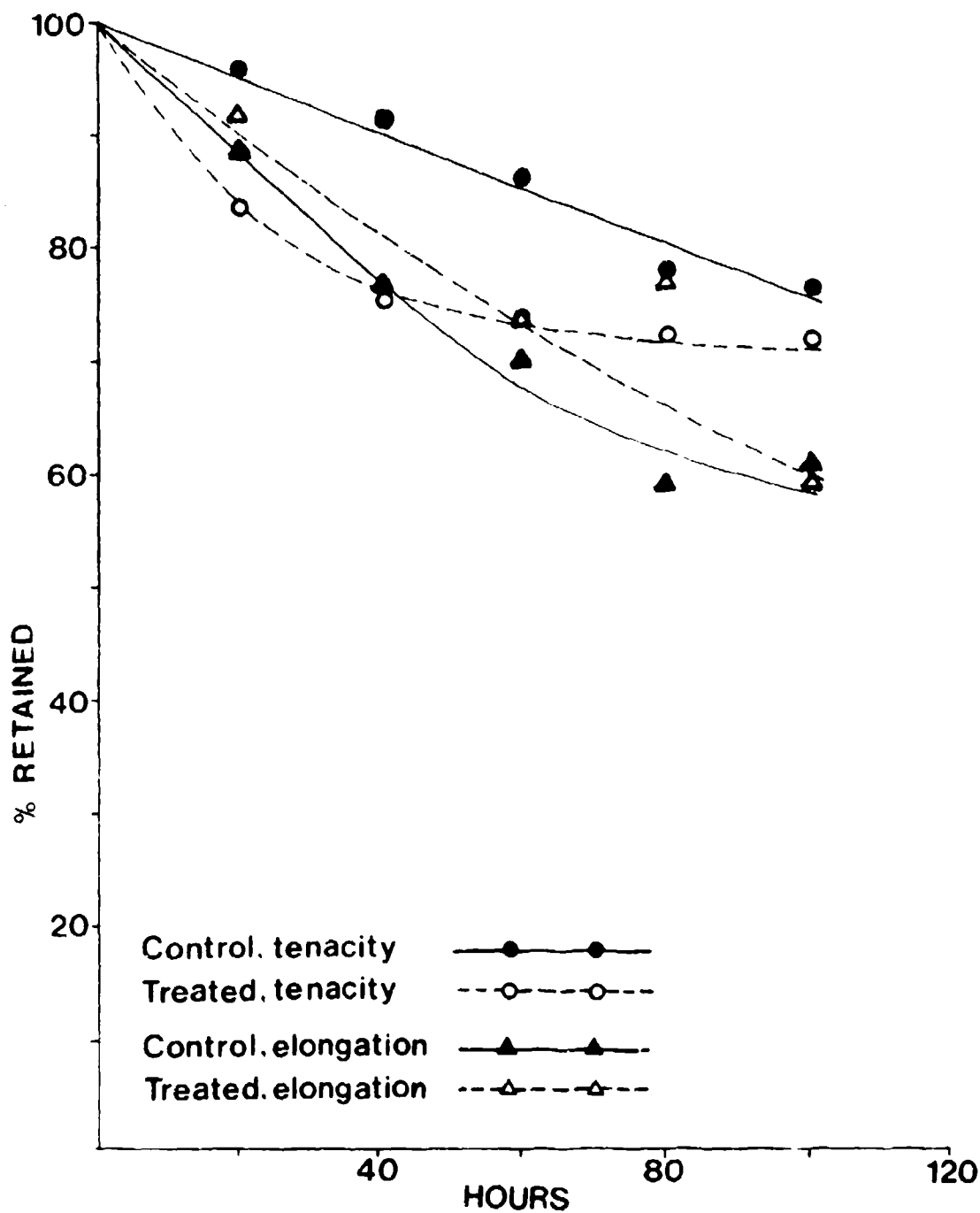


Figure 21. Retention of tenacity and elongation of Nomex Type 433 containing Uvitex NFW compared to control sample after xenon arc exposure.

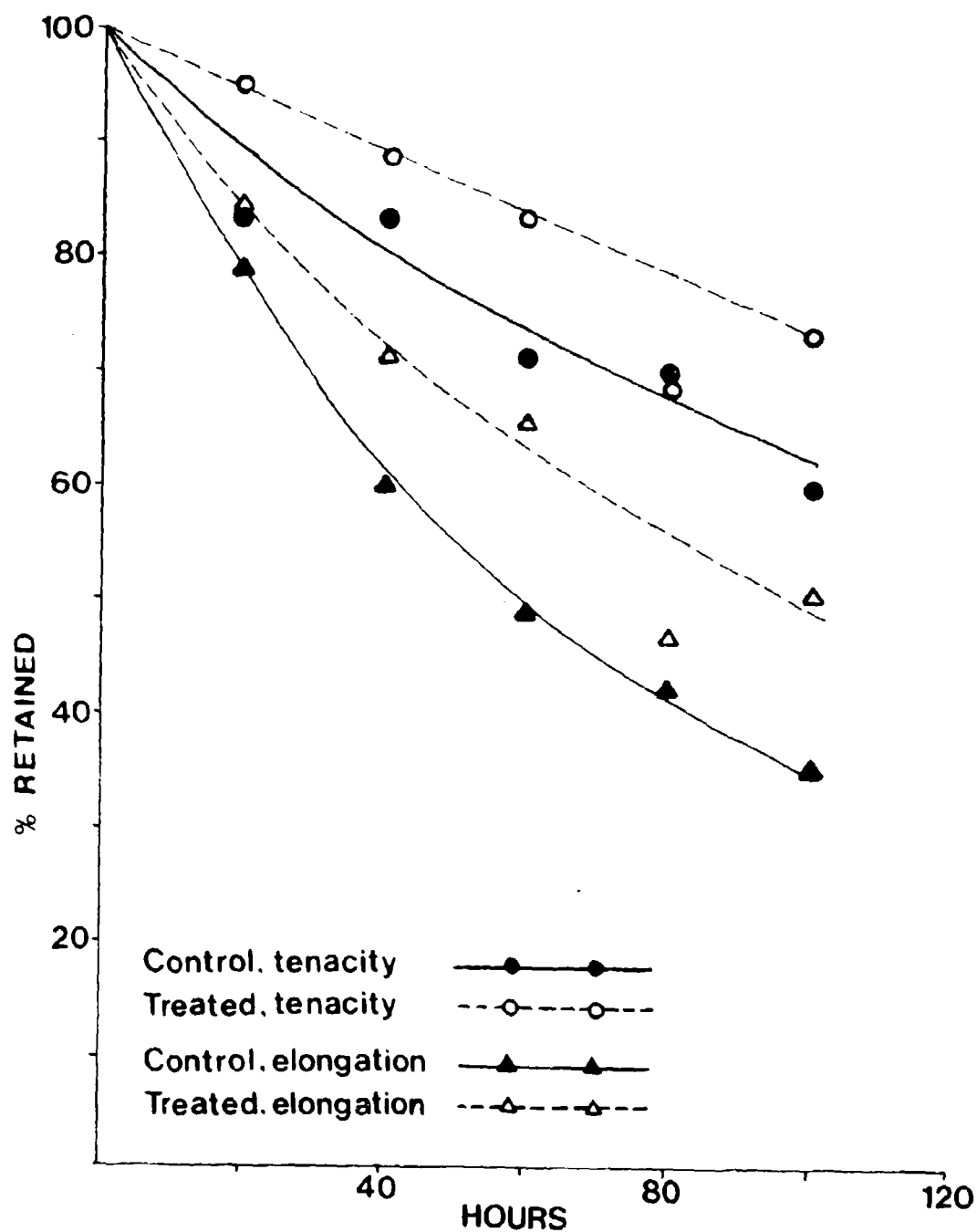


Figure 22. Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after xenon arc exposure.

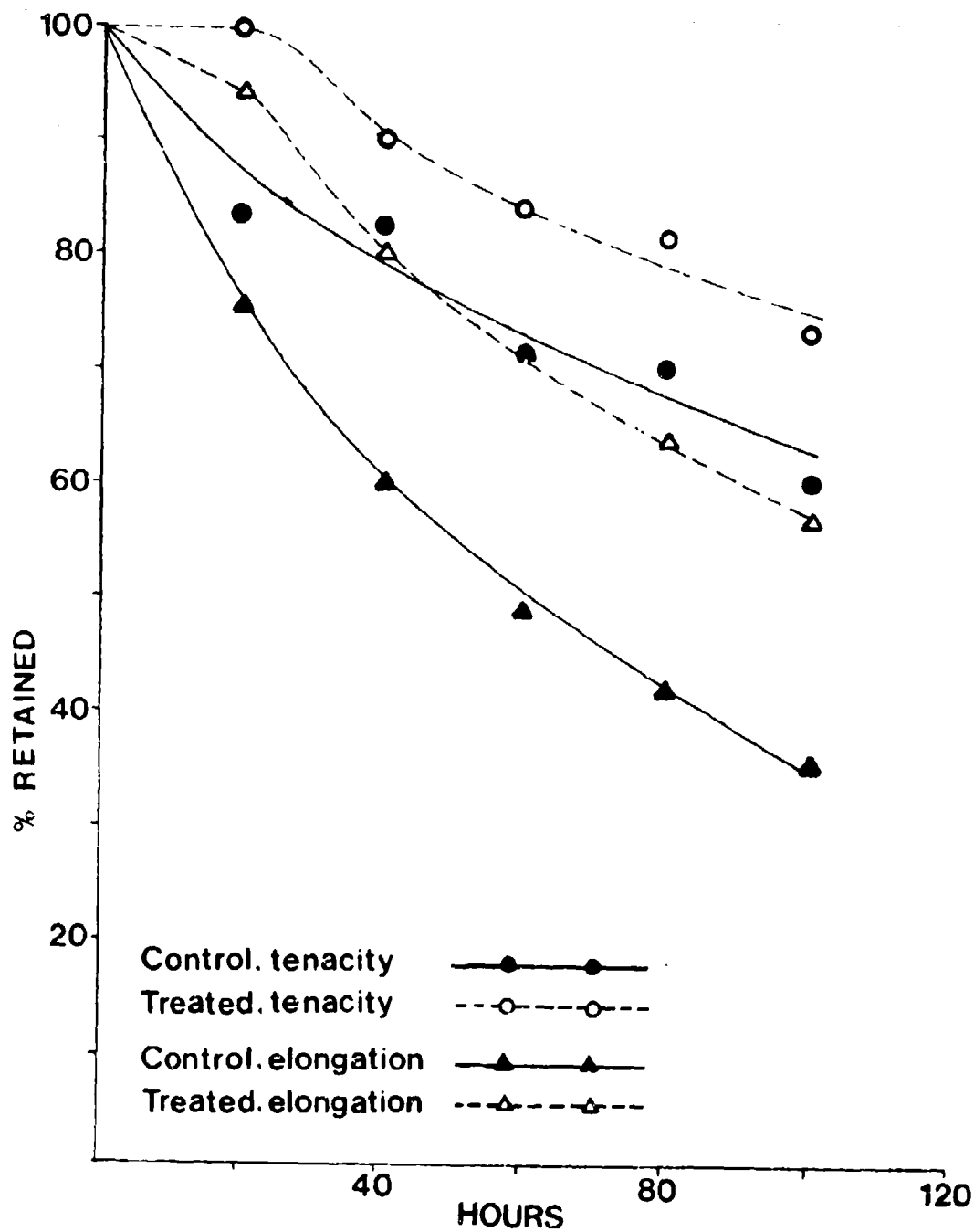


Figure 23. Retention of tenacity and elongation of Nomex Type 433 containing Tinuvin P compared to control after xenon arc exposure.

ener appears to have some protective effect in the first 20 hours of carbon-arc exposure. The stabilizing effect is rapidly lost however, probably due to degradation of the optical brightener itself. A similar stabilization is not observed for xenon arc exposure. The higher output of the xenon arc in the UV region may give a more rapid degradation of the Uvitex NFW. It should be noted that results for xenon exposure of the Uvitex NFW containing sample appear to be somewhat erratic. It does, however, apparently provide some small stabilizing effect on Nomex degradation.

The most promising of the optical brighteners for Nomex stabilization appears to be Blancophor AW (Figures 12 and 22). This material gave a clear stabilizing effect at all exposure times. A statistical analysis of the data confirmed that Blancophor AW containing Nomex has significantly greater retention of tenacity and elongation than the blank dyed sample.

Results for samples containing standard UV absorbers indicate that of the absorbers tested only Tinuvin P gave long term improvement in retention of tensile strength and elongation. Cyasorb UV-800 was effective during the first 40 hours of exposure (Figure 15) but gave tensile strength retention no better than the control after 100 hours. Degradation of the absorber itself may be responsible for this result. Tinuvin 327 (Figure 14) and Tinuvin 770 (Figure 16) both appear to reduce the stability of Nomex. This result was surprising in view of the beneficial effect exhibited by Tinuvin P. One other UV screening agent of a different chemical structure than the benzotriazoles was also studied. Eastman Inhibitor RMB (Resorcinol Monobenzoate) which rearranges to give 2,4 - dihydroxybenzophenone was added to Nomex and the samples exposed to the carbon arc Fade-Ometer. Results are shown in Figure 17. These results suggest that benzophenone type stabilizers do not appear to be effective on Nomex.

The retention of tenacity and elongation of Nomex samples containing Tinuvin P is shown in Figures 13 and 23. These data clearly indicate that a stabilizing effect is observed at all exposure times.

This study of UV screening agents for stabilization of Nomex suggests that some optical brighteners and UV absorbers can have a beneficial effect on Nomex degradation. In both cases the effect is small. Both Blan-

cophor AW and Tinuvin P were selected for further study is subsequent phases of the project.

3. Exposure Studies on Nomex Treated With Antioxidants

The antioxidants investigated in this study are listed in Table 1. These materials were added to Nomex yarn Type 433 by the dyeing procedures described previously. The antioxidants selected are of the hindered phenol type with other structural features designed to enhance the antioxidant characteristics.

Samples of yarn containing the antioxidants were exposed to the carbon arc Fade-Ometer for periods up to 100 hours. Tenacity and elongation of the yarn samples were determined before and after exposure.

The percent retention of tenacity and elongation for samples containing Irganox 1035 is shown in Figure 24. This antioxidant gives no perceptible difference in the stability of Nomex.

Similar results for samples containing Plastanox 1735, Irganox 1010, Irganox 1098 and CSA-316 are shown in Figures 25, 26 and 27, and 28. All of these antioxidants reduce the stability of Nomex slightly. The reasons for this effect are not known at the present time.

The results of these studies suggest that antioxidants as a class show little promise as stabilizers for Nomex. Since these materials are primarily effective in free radical oxidative degradation reactions, the results at least indicate that such reaction mechanisms are not involved in Nomex UV degradation.

4. Exposure Studies on Nomex Treated With Quenchers

Six compounds reported to stabilize polymeric systems by a quenching mechanism have been added to Nomex. The compounds investigated are given in Table 1. All were added to Nomex type 433 yarn by the modified dyeing procedure described previously.

Samples containing quenchers were exposed in the carbon arc Fade-Ometer for up to 100 hours and exposed and control (blank dyed) samples tested on the Instron.

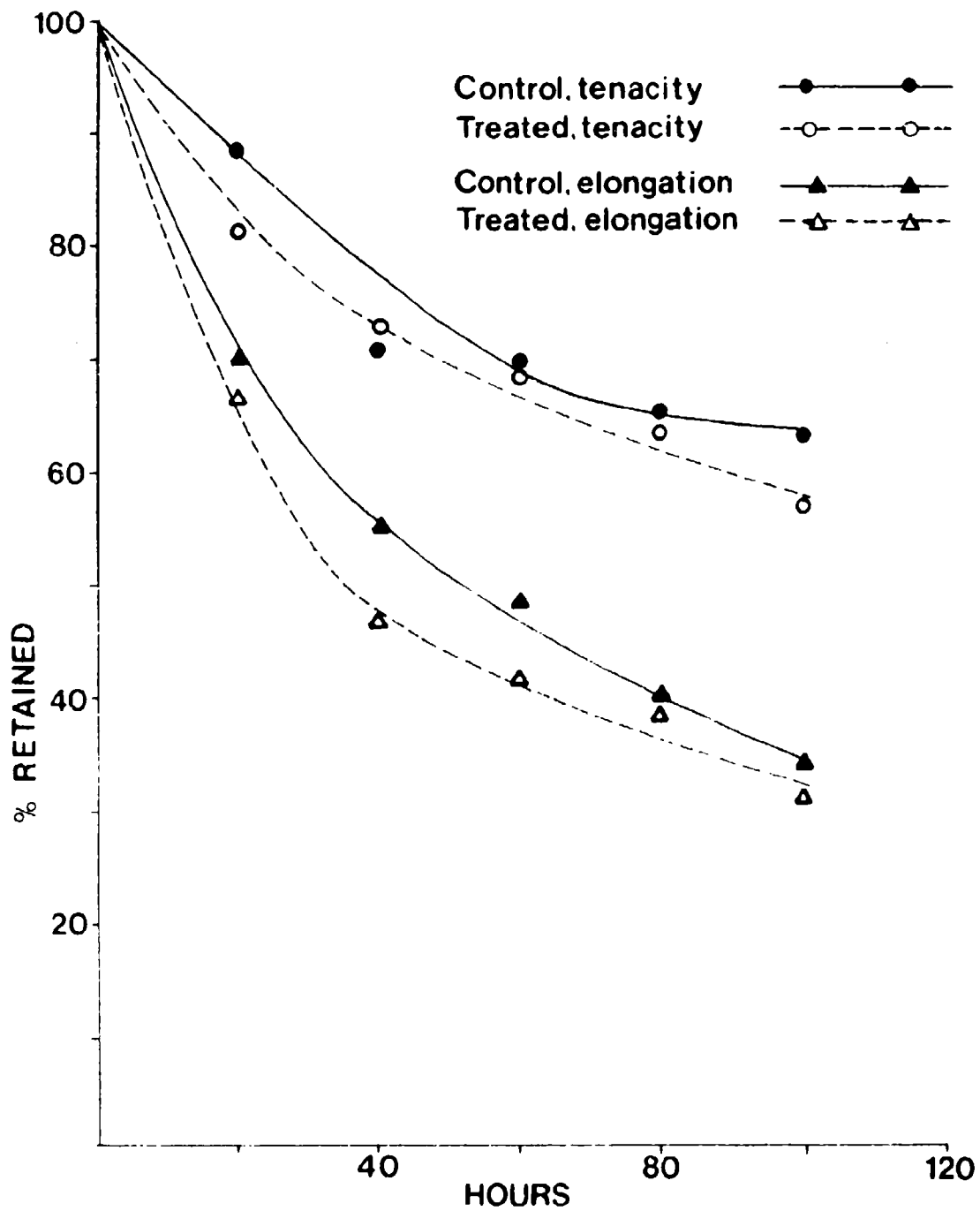


Figure 24. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1035 compared to control sample after carbon arc exposure.

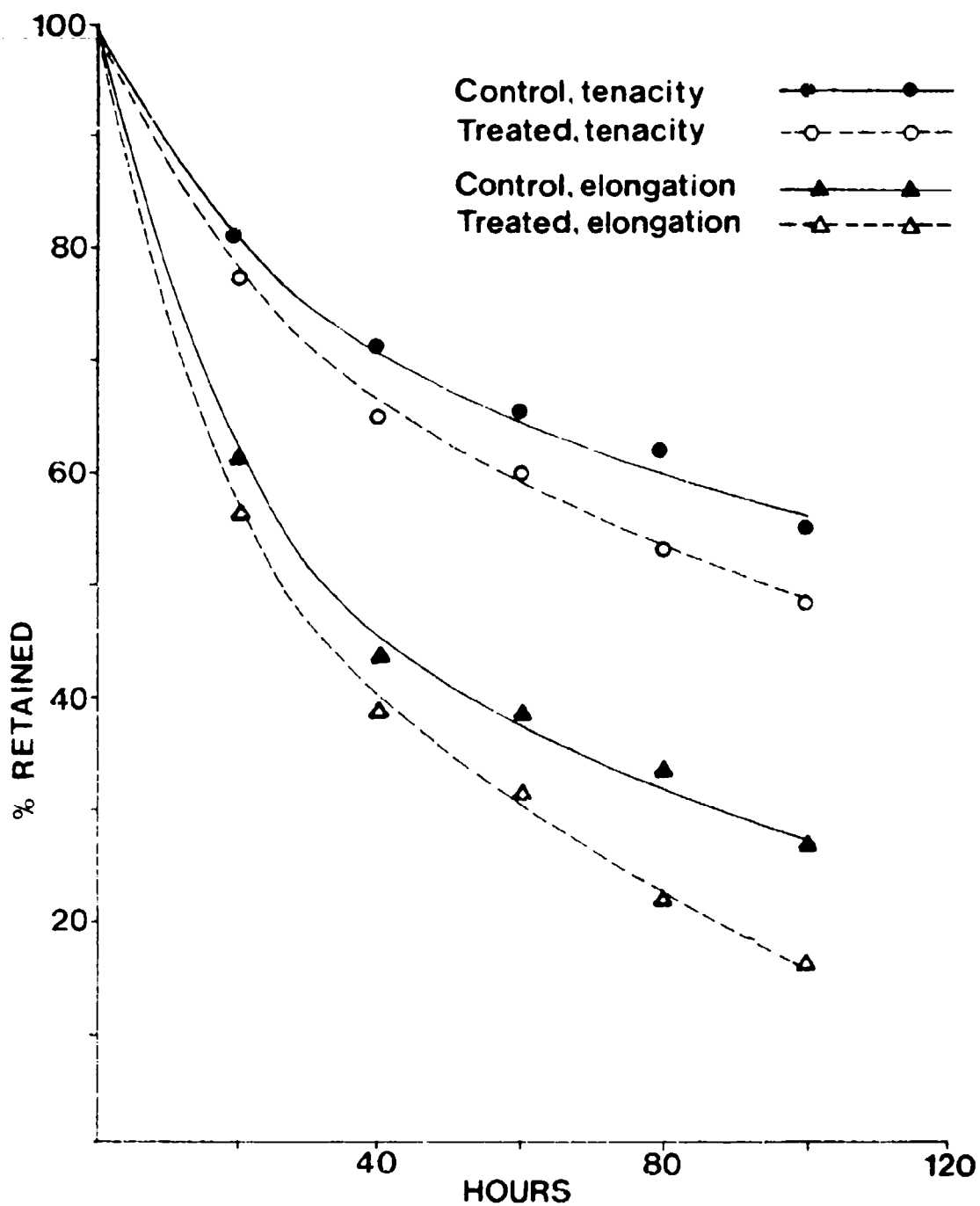


Figure 25. Retention of tenacity and elongation of Nomex Type 433 containing Piastanox 1735 compared to control sample after carbon arc exposure.

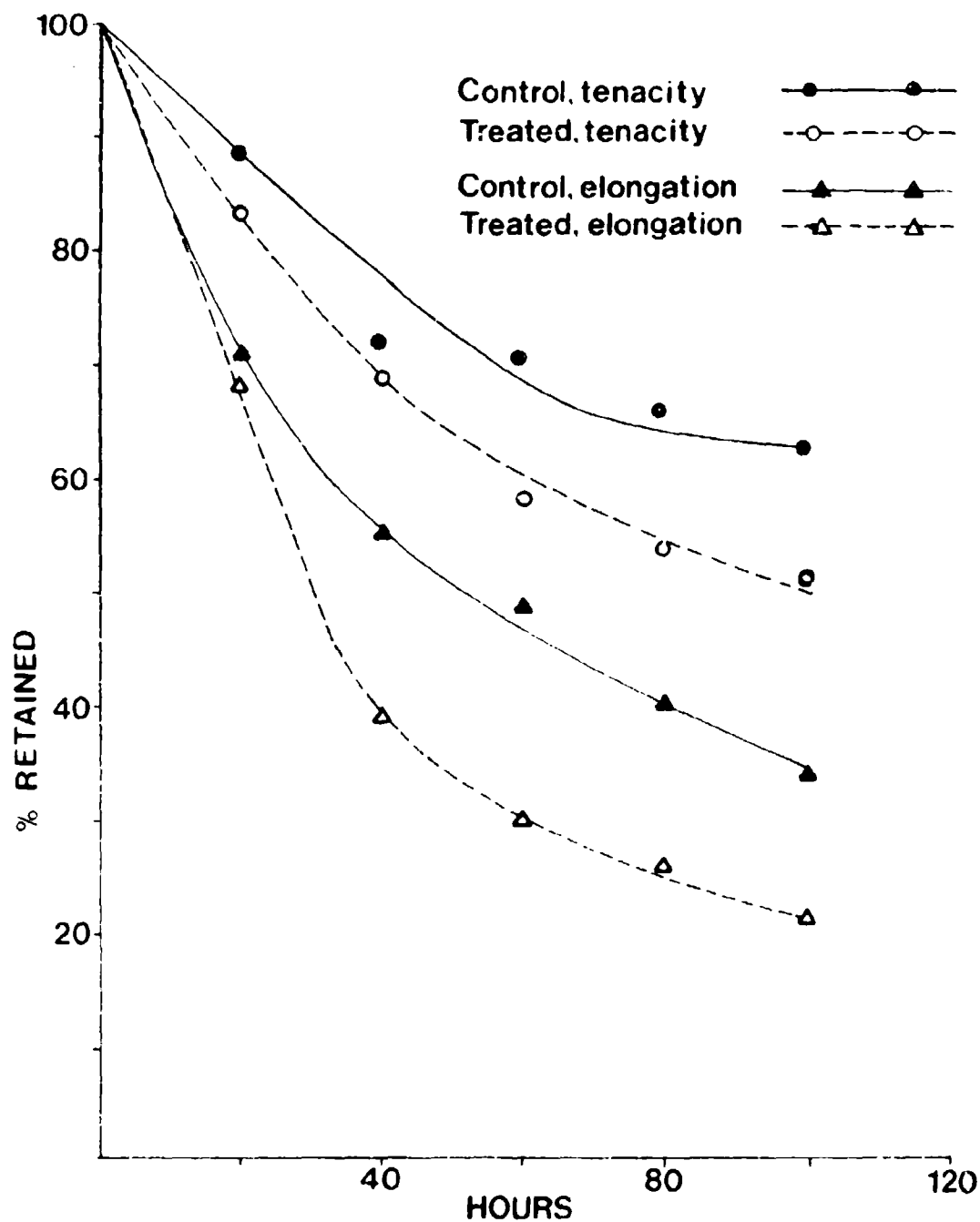


Figure 26. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1010 compared to control sample after carbon arc exposure.

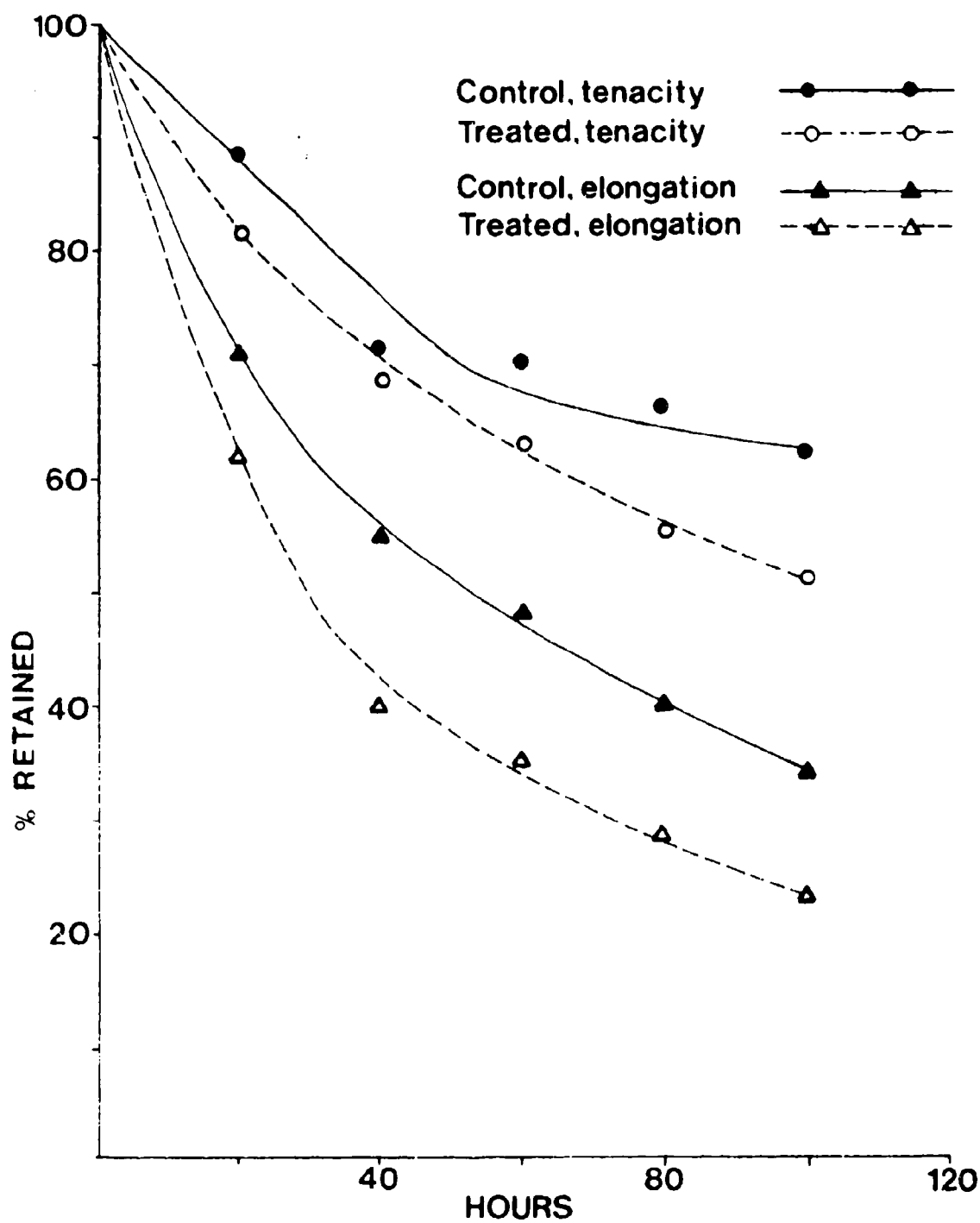


Figure 27. Retention of tenacity and elongation of Nomex Type 433 containing Irganox 1098 compared to control sample after carbon arc exposure.

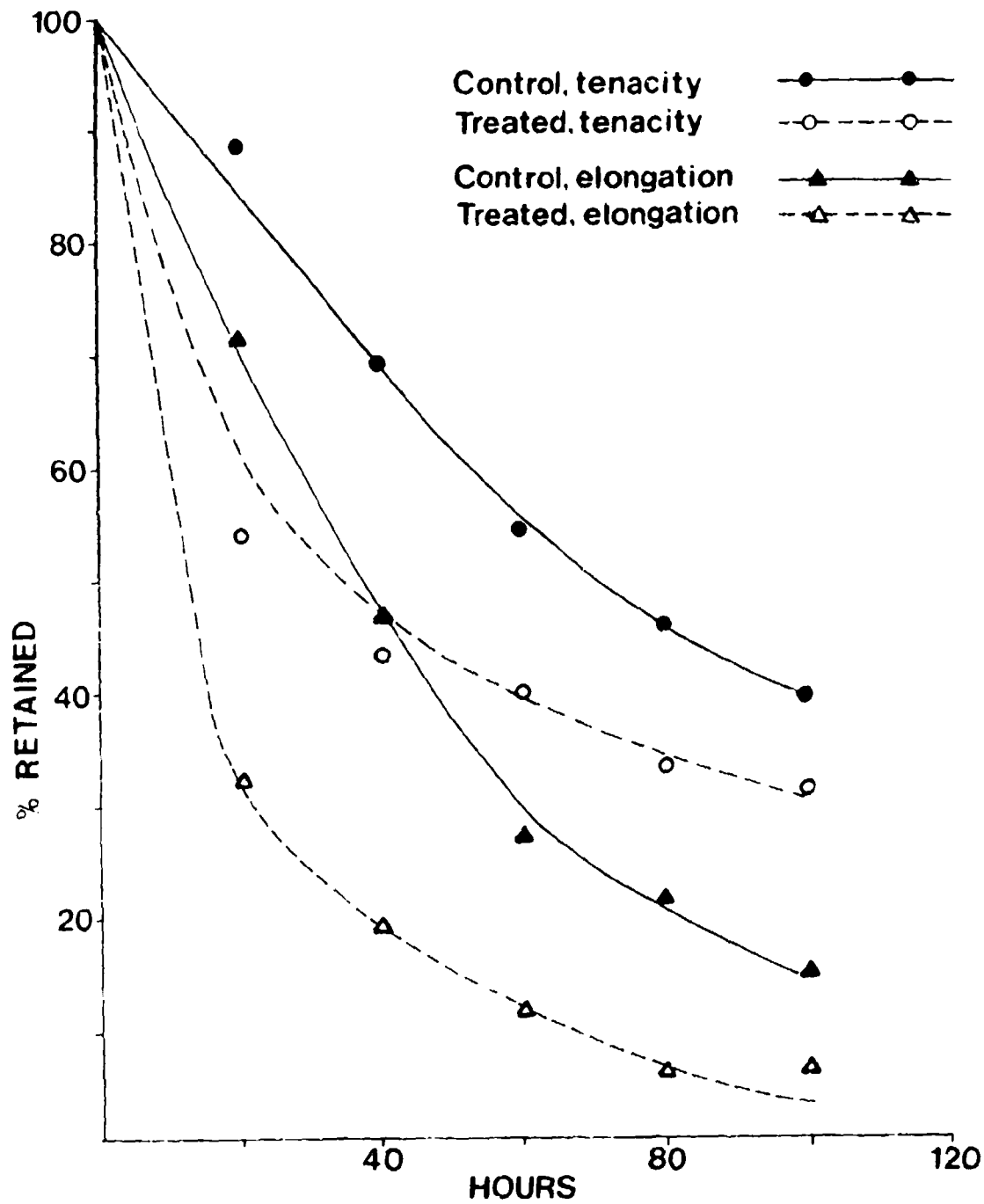


Figure 28. Retention of tenacity and elongation of Nomex Type 433 containing CGA-316 compared to control after carbon arc exposure.

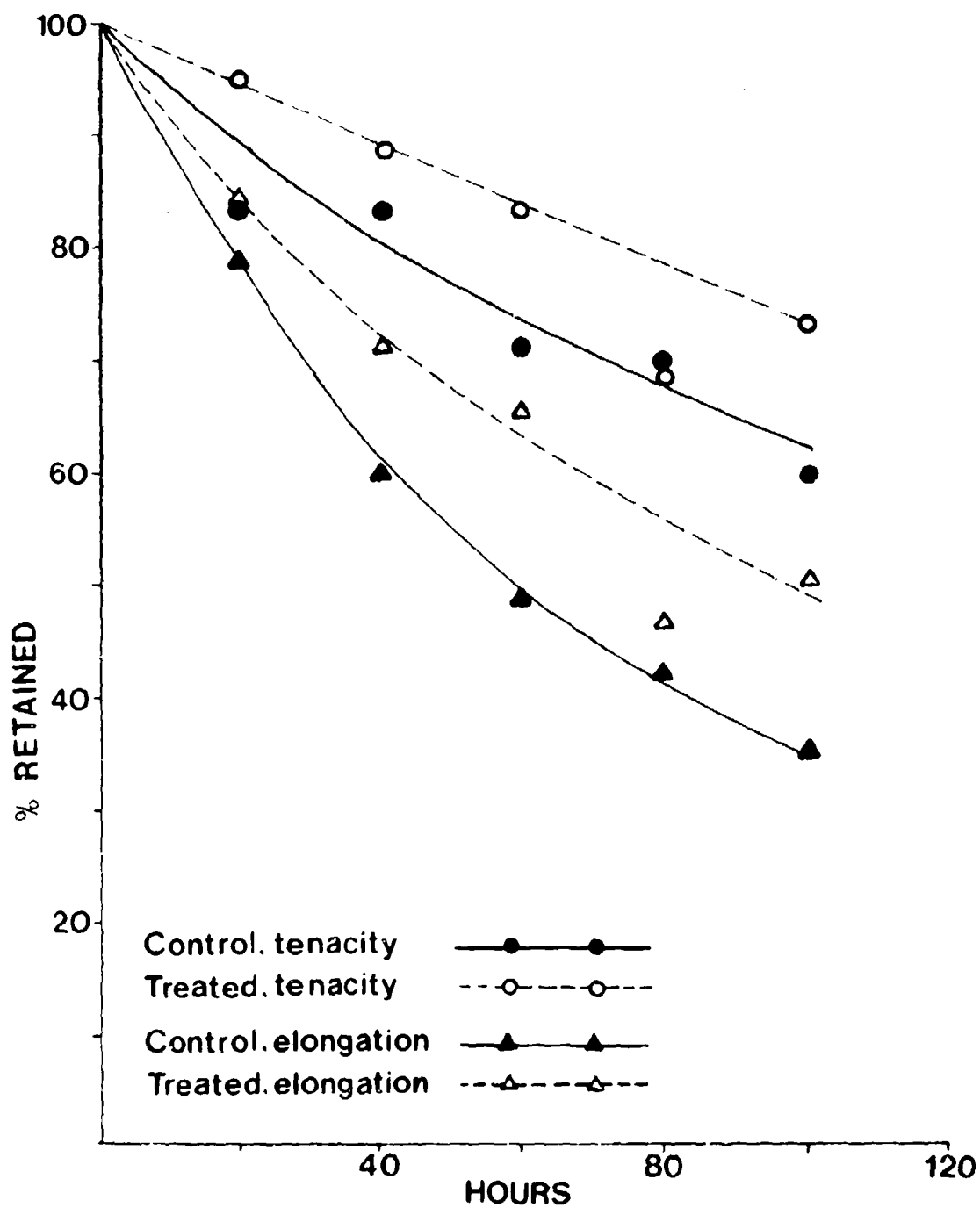


Figure 22. Retention of tenacity and elongation of Nomex Type 433 containing Blancophor AW compared to control sample after xenon arc exposure.

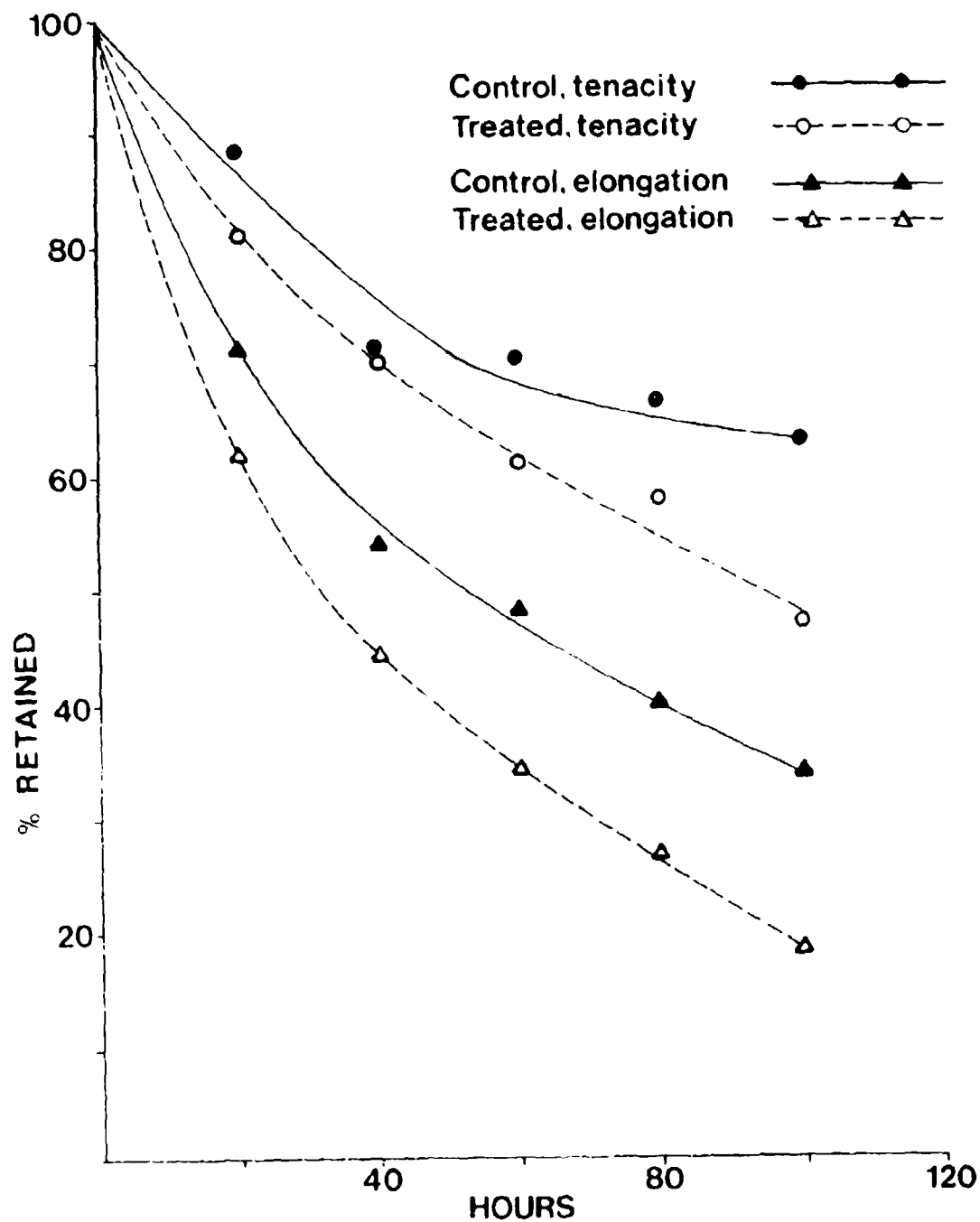


Figure 29. Retention of tenacity and elongation of Nomex Type 433 containing AM-105 compared to control after carbon arc exposure.

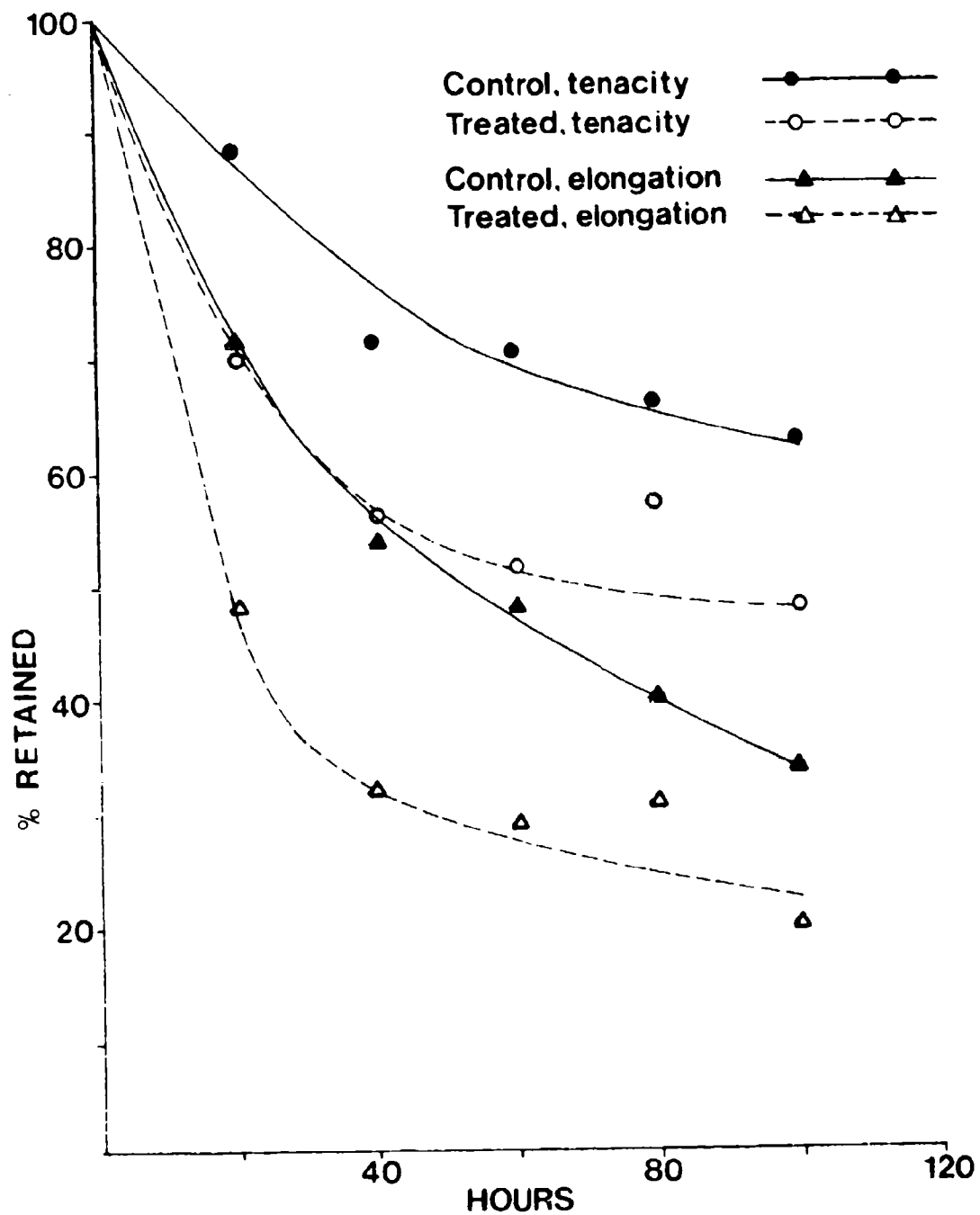


Figure 30. Retention of tenacity and elongation of Nomex Type 433 containing IRCASTAB 2002 compared to control after carbon arc exposure.

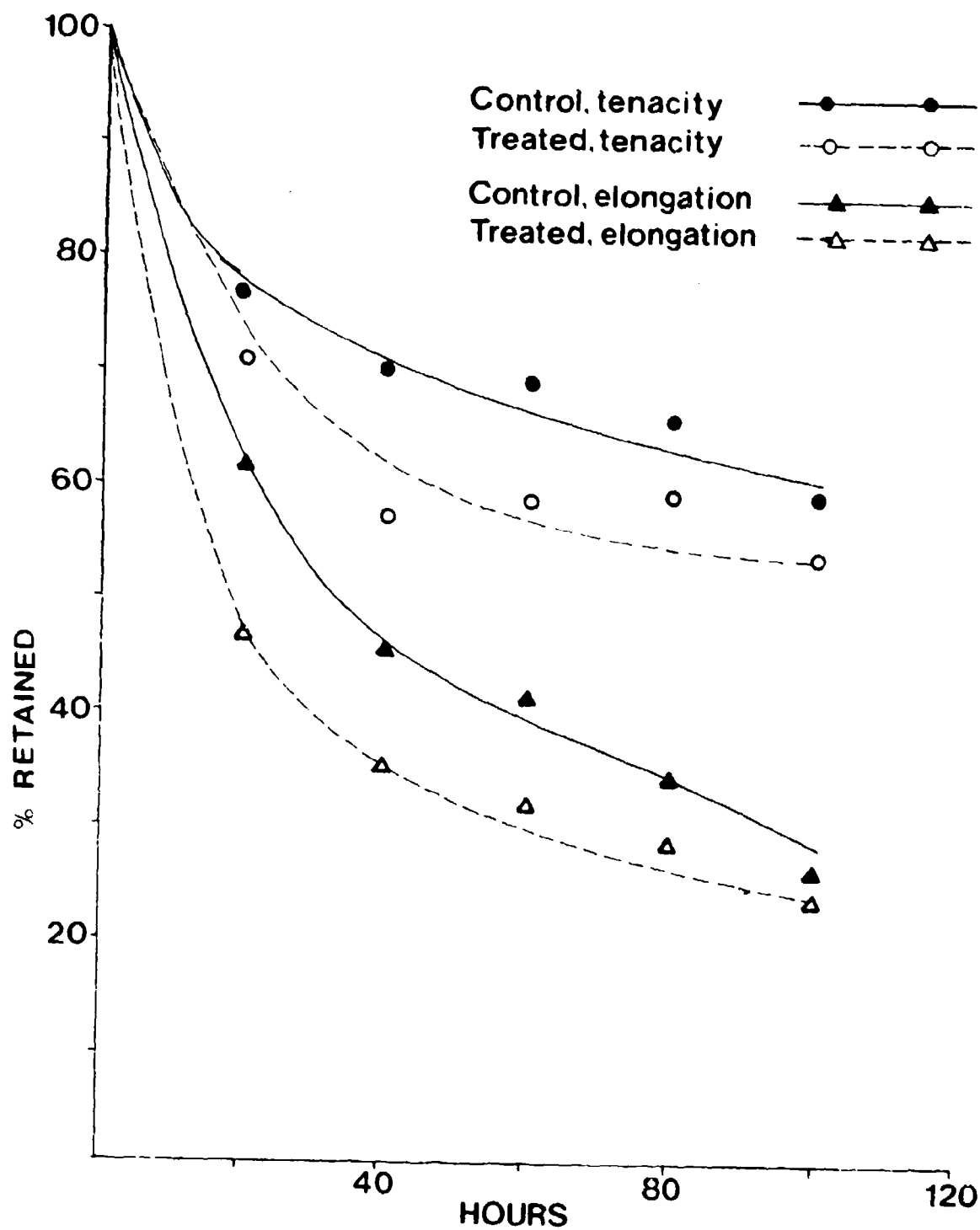


Figure 31. Retention of tenacity and elongation of Nomex Type 433 containing Zetax compared to control after carbon arc exposure.

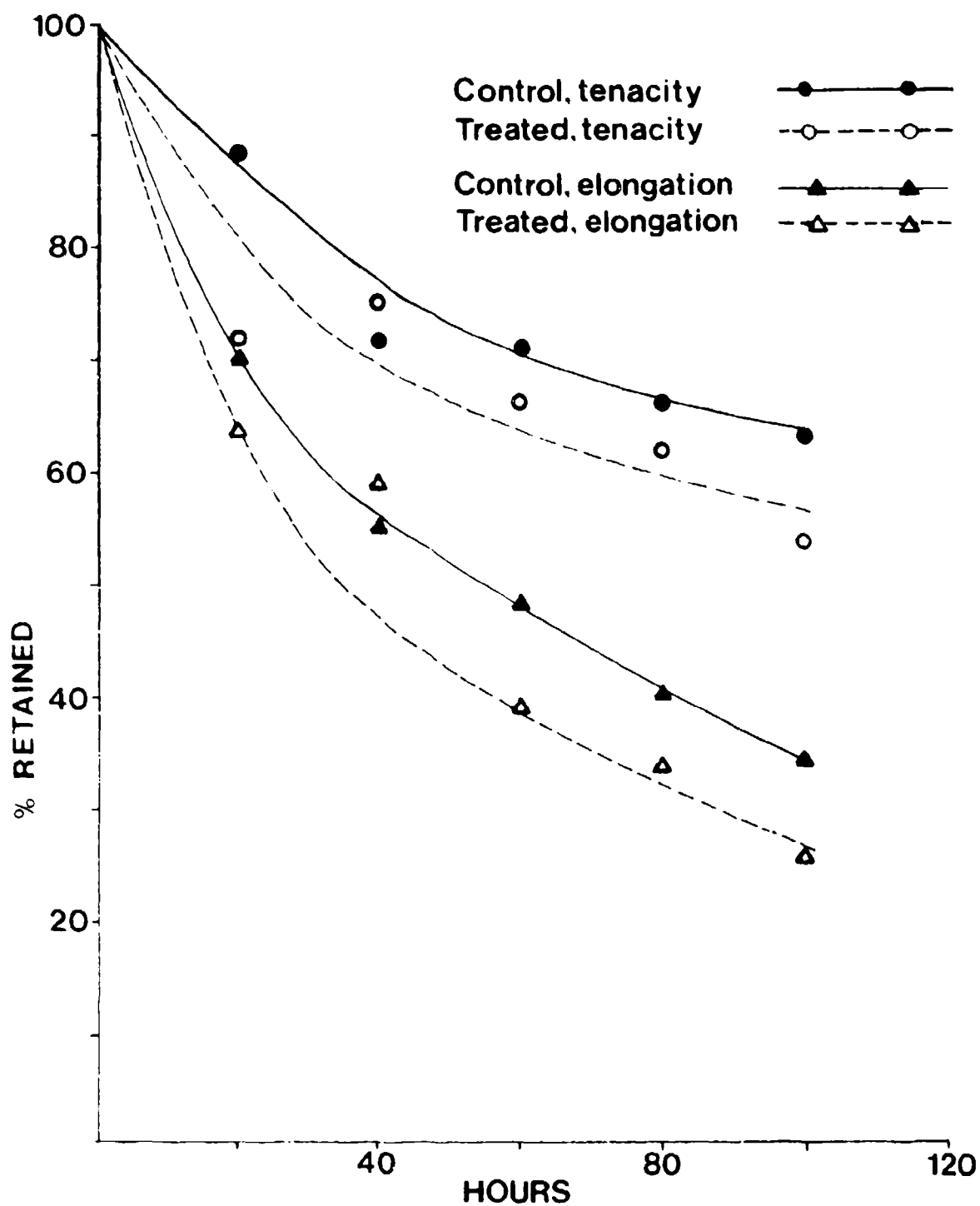


Figure 32. Retention of tenacity and elongation of Nomex Type 433 containing GI-10-460 compared to control after carbon arc exposure.

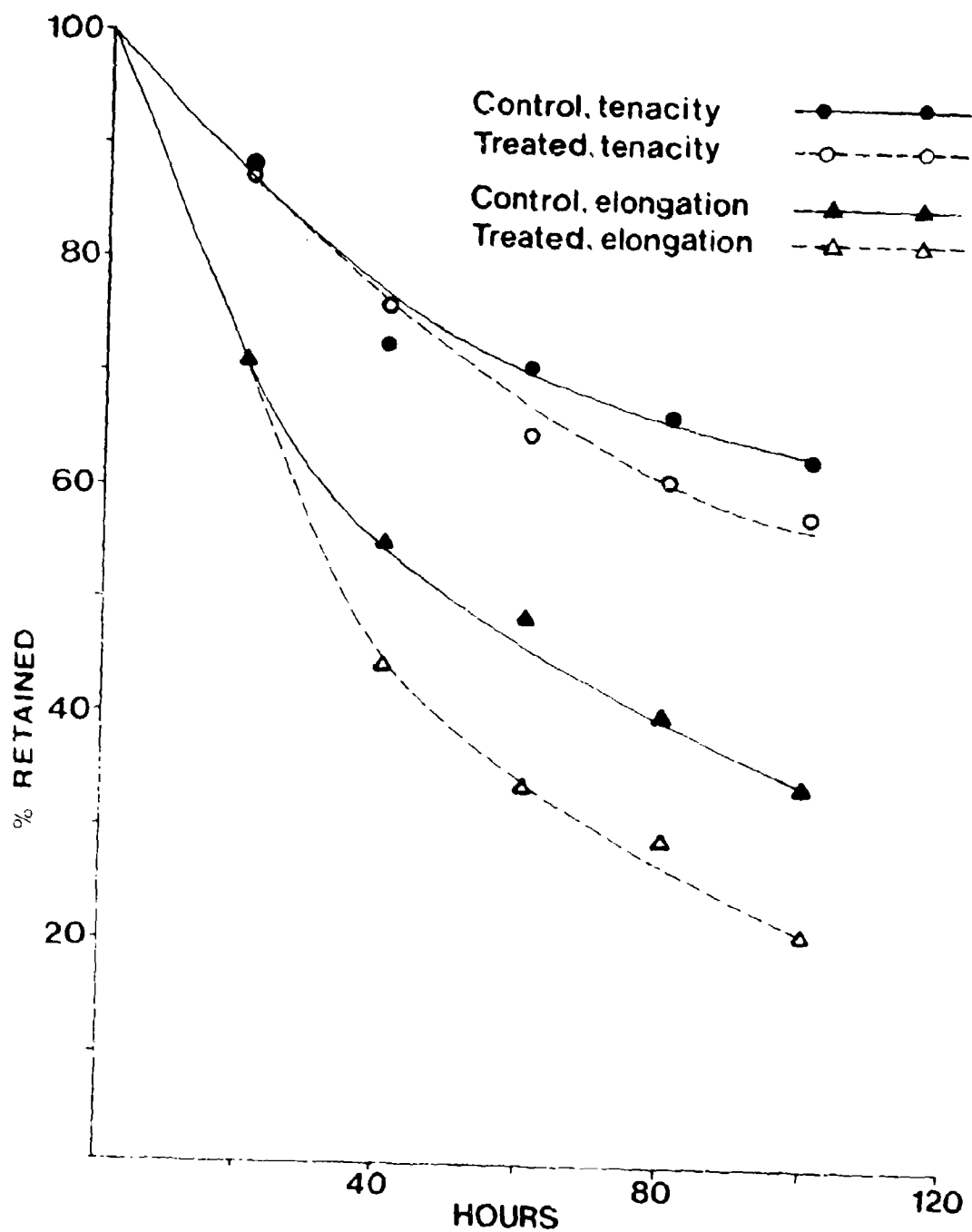


Figure 33. Retention of tenacity and elongation of Nomex Type 433 containing NBC compared to control after carbon arc exposure.

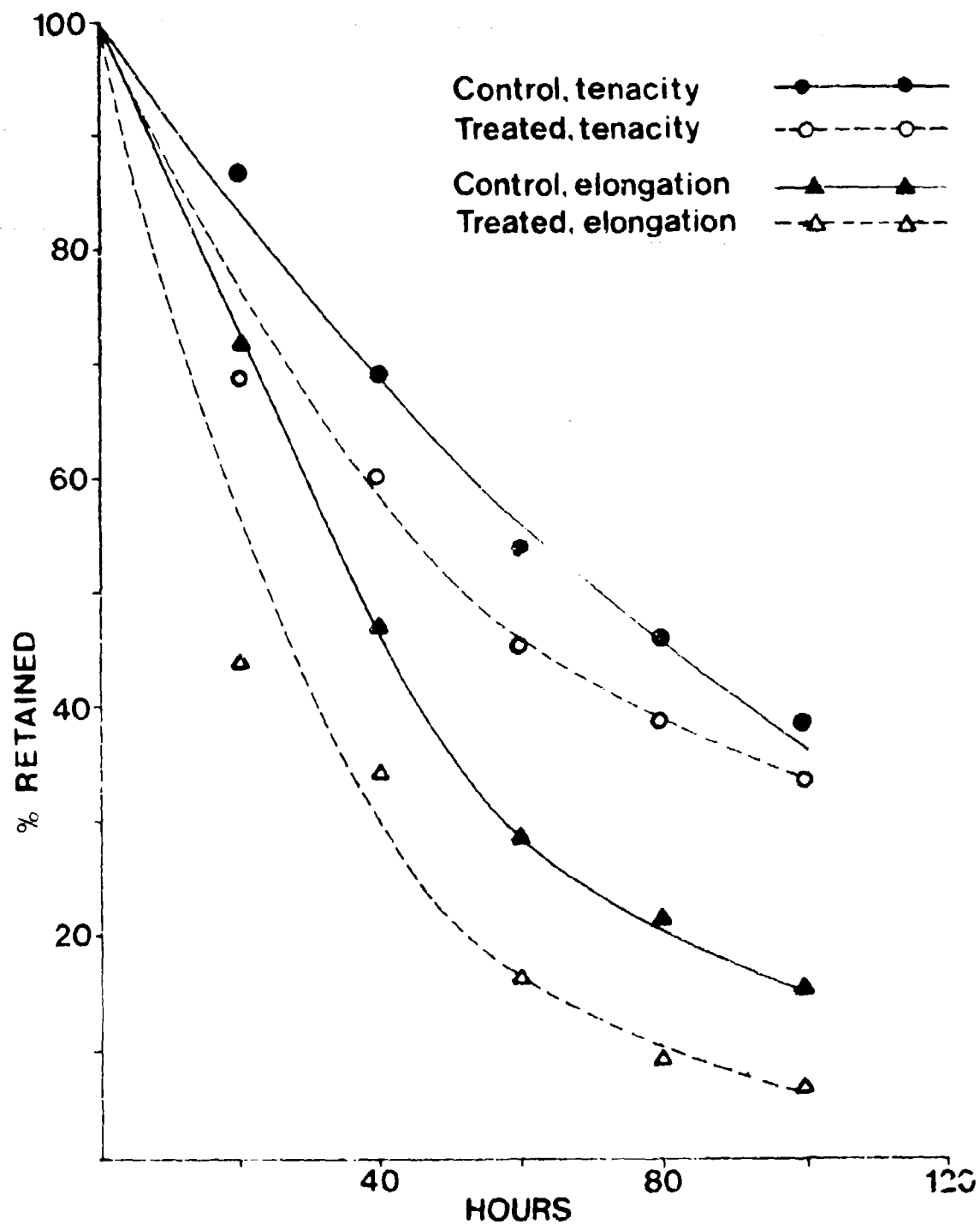


Figure 34. Retention of tenacity and elongation of Nomex Type 433 containing CIA-1056 compared to control after carbon arc exposure.

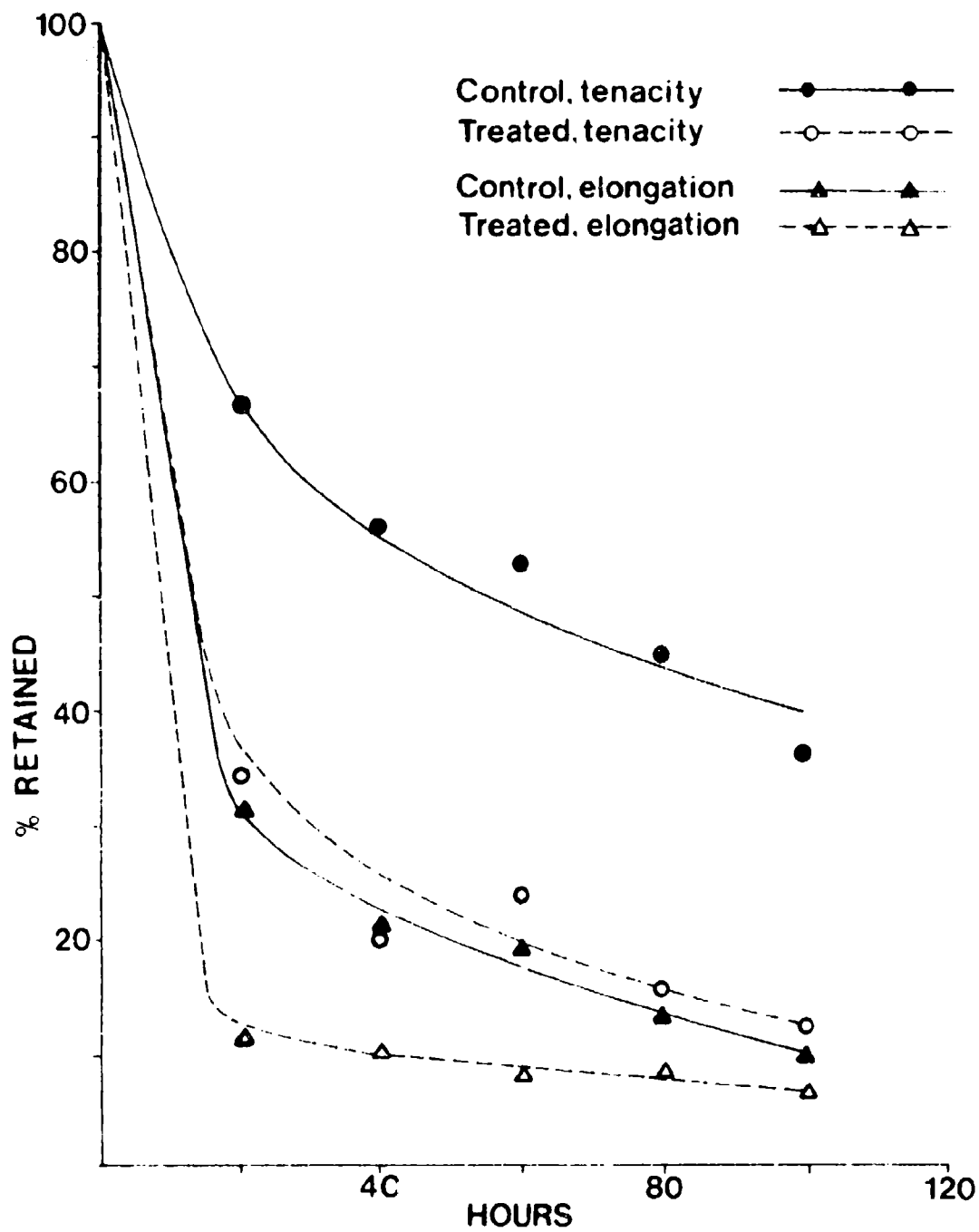


Figure 35. Retention of tenacity and elongation of Nomex Type 430 containing urea compared to control after carbon arc exposure.

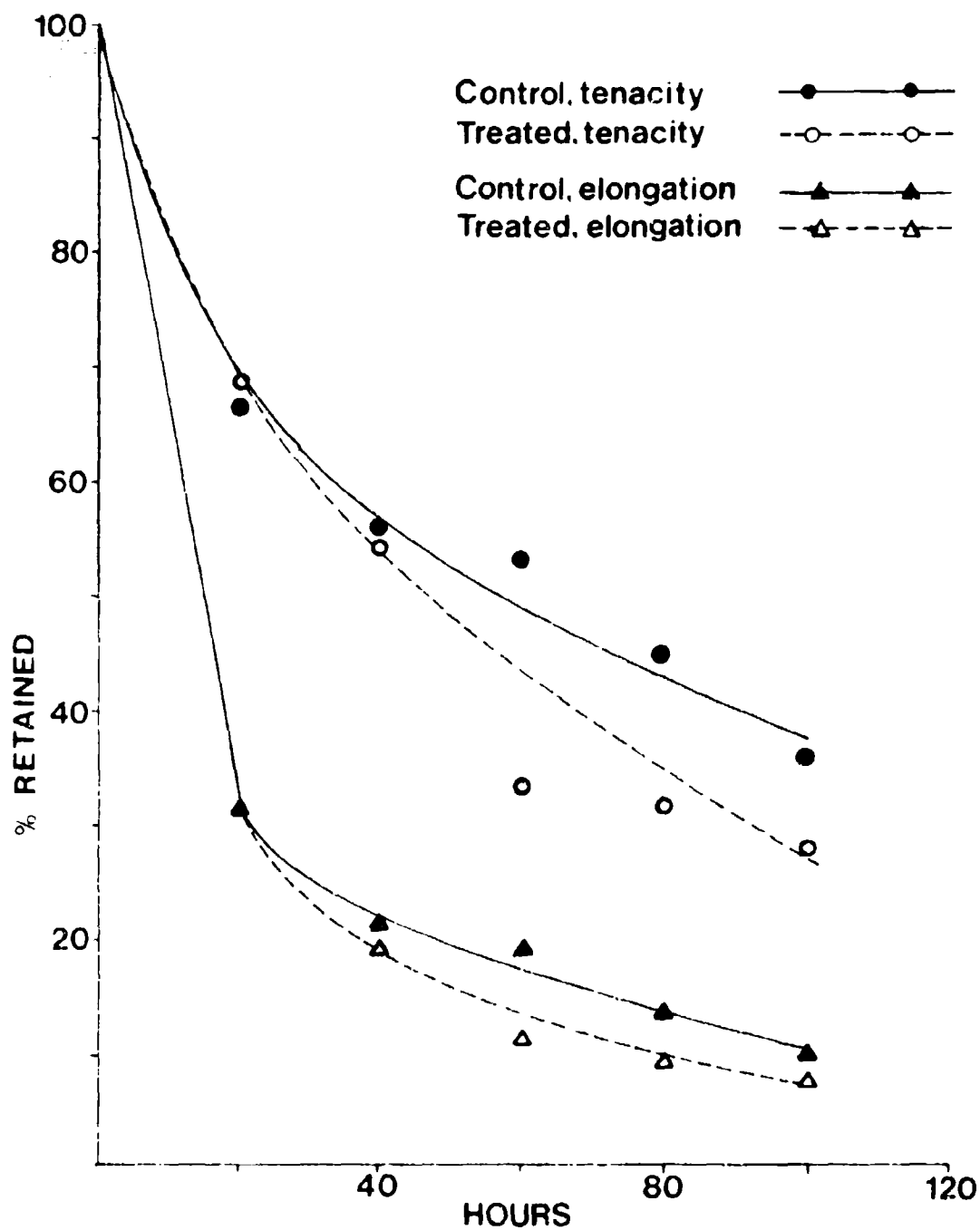


Figure 36. Retention of tenacity and elongation of Nomex Type 430 containing urea and thiourea compared to control after carbon arc exposure.

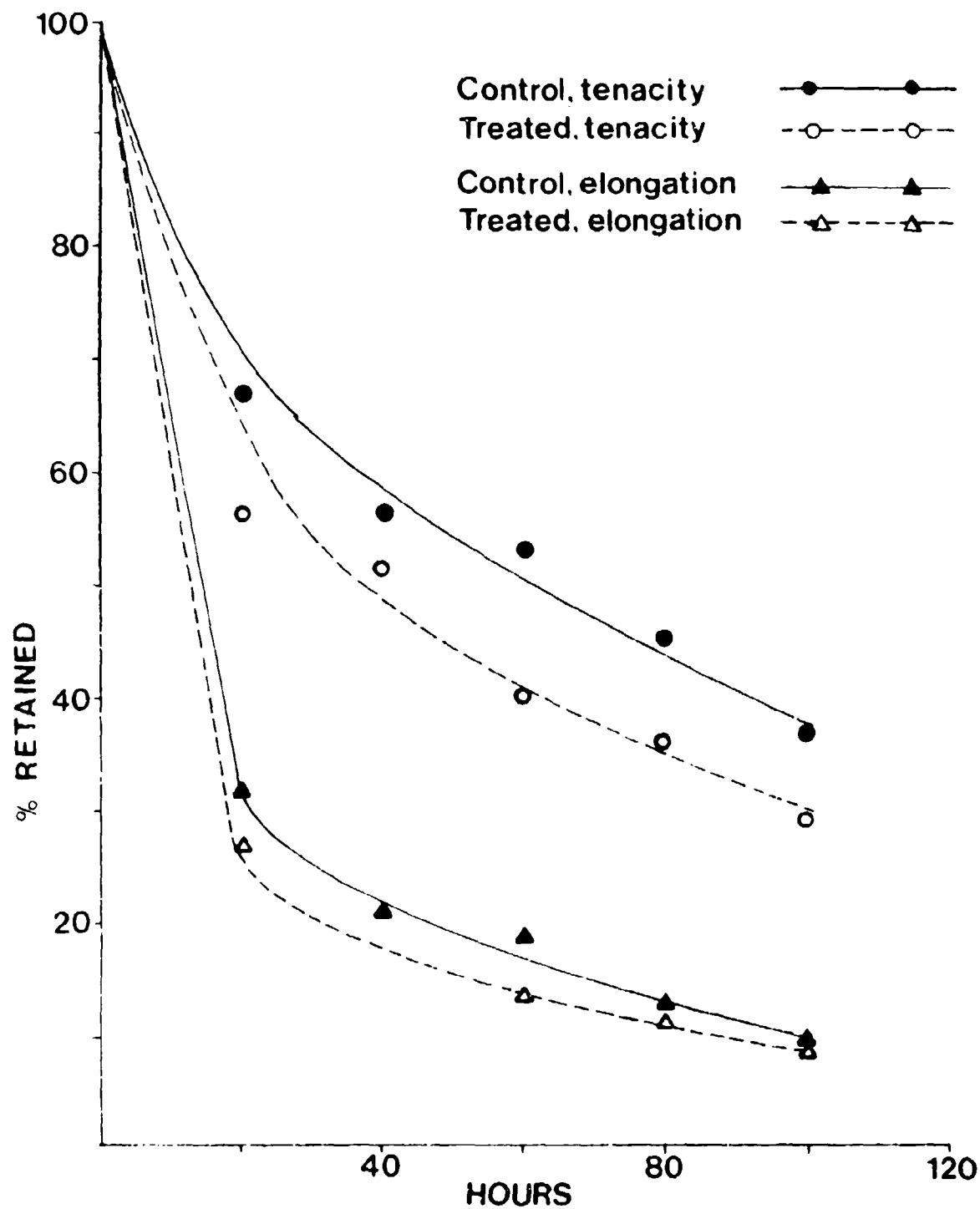


Figure 37. Retention of tenacity and elongation of Nomex Type 430 containing colloidal sulfur compared to control after carbon arc exposure.

Aromatic amines in the presence of nitrous acid react to form diazonium salts which readily react with phenols to produce diazo compounds. These reactions are used extensively in preparation of the diazo class of dyestuffs and were used to reduce the number of amine end groups in a sample of Nomex yarn.

The yarn samples were first treated with nitrous acid in the presence of a carrier. They were then treated with beta-oxynaphthoic acid. Formation of the colored diazo compound gave evidence that the aromatic amine end groups were undergoing reaction.

Samples with reacted amine end groups were exposed to the carbon arc Fade-Ometer and compared with control samples. Results are shown in Figure 38. These results suggest that reduction in amine end group content does not provide greater stability to Nomex yarn.

The only other potential stabilizer giving evidence of stabilizing Nomex against UV degradation was oxanilide. Retention of tenacity and elongation after 100 hour exposure to the carbon arc is shown in Figure 39. Oxanilide appears to give significant improvement in tenacity. Retention of elongation is not appreciably affected. Oxanilide was selected for further study.

G. Studies on DuPont E-11 Fabrics

Two of the effective stabilizers, Tinuvin P and Blancophor AW, were also applied to a new experimental thermally stable fabric designated E-11. Results of these studies are presented in Appendix B.

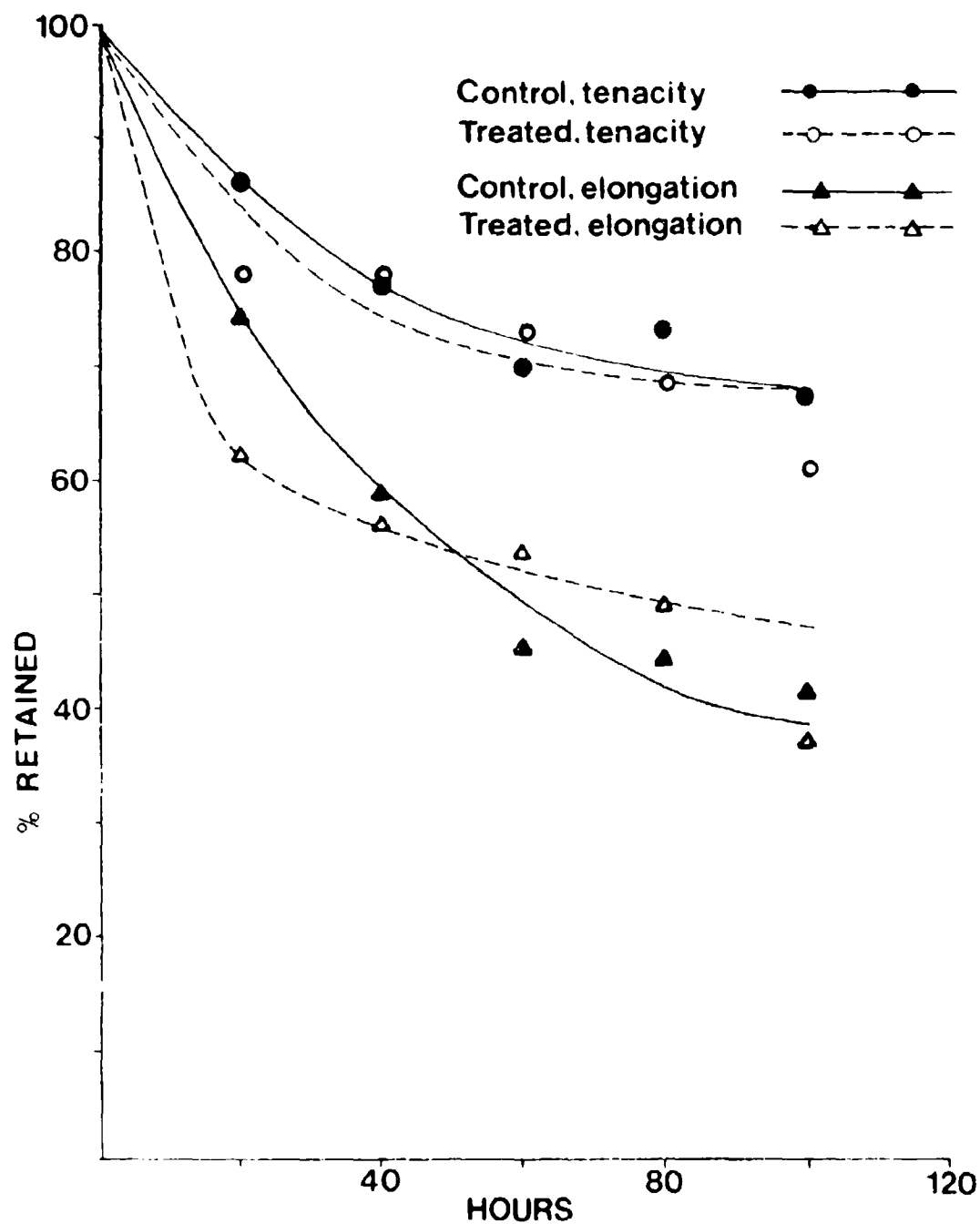


Figure 38. Retention of tenacity and elongation of Nomex Type 433 with end groups reacted with beta-oxynaphthoic acid compared to control after carbon arc exposure.

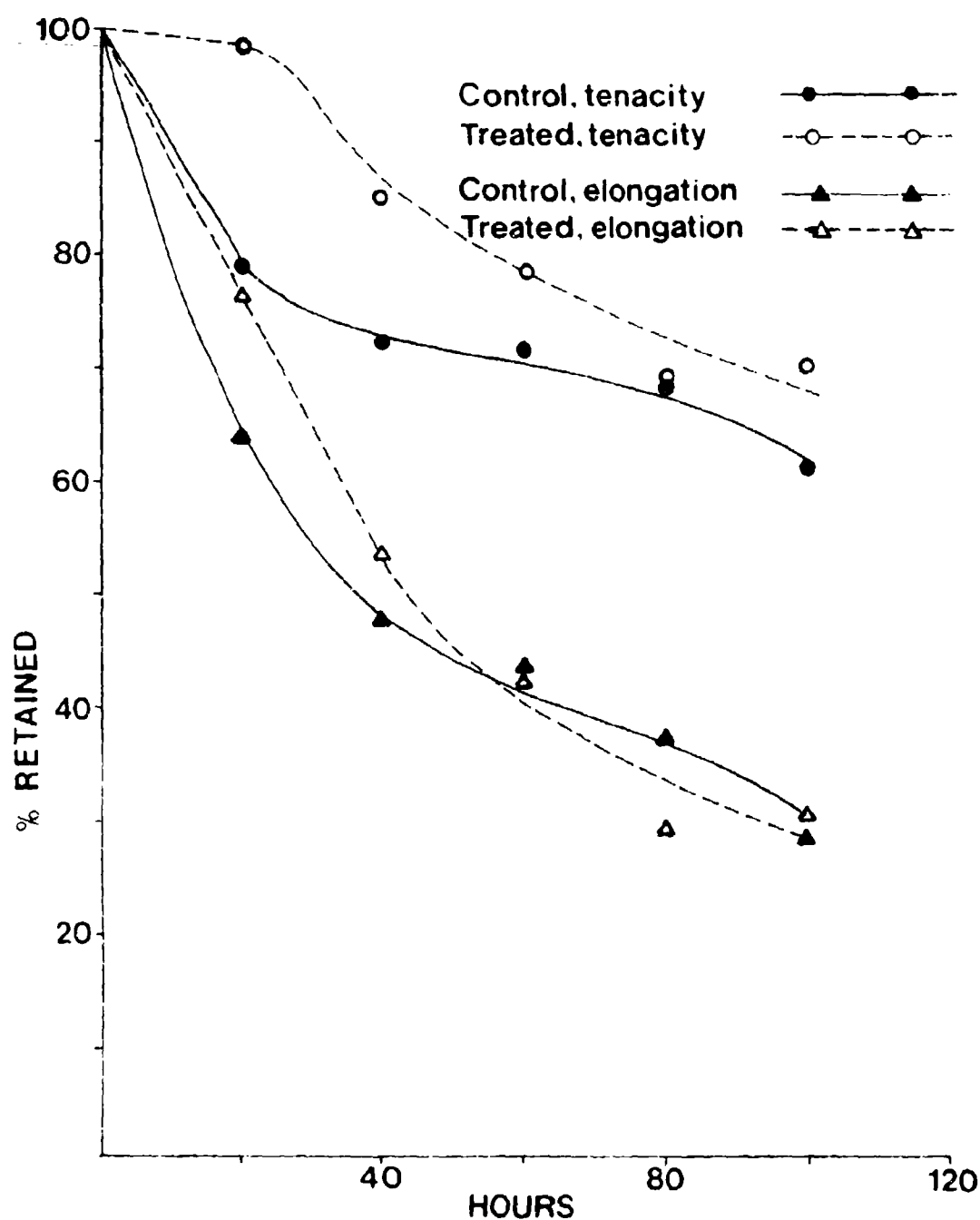


Figure 39. Retention of tenacity and elongation of Nomex Type 433 containing oxanilide compared to control after carbon arc exposure.

SECTION III

DEVELOPMENT OF STABILIZER SYSTEMS

A. Factorial Experiment

Based on the stabilizer screening studies, three compounds were selected for further study -- Blancophor AW, Tinuvin P, and oxanilide.

Blancophor AW is a commercially available optical brightener of the aminocoumarin type produced by GAF. Of the three compounds, Blancophor AW appeared to have the most beneficial effect on Nomex light stability. In all experiments conducted Blancophor AW increased retention of both tenacity and elongation of Nomex yarn.

Tinuvin P is a UV screening agent of the benzotriazole type produced by the Ciba-Geigy Company. It has been reported to be a stabilizer for Nomex but the results have not been consistent. In addition to being a strong UV absorber, it has been suggested that Tinuvin P may also act as a quencher of excited states.

Oxanilide is the diamide produced by reaction of oxalic acid with aniline. It is sometimes used as a "copper inhibitor" in stabilizer formulations for polymers. A variety of mechanisms have been suggested to explain the stabilizing action of oxanilide including the quenching of excited states and UV absorption. The mechanism by which oxanilide stabilizes Nomex is not known at the present time.

A factorial experiment was carried out to investigate the three selected stabilizers at 4 concentration levels (0, 33, 66, and 100% o.w.f.) on Nomex sage green fabric (Mil-C-38351, Type II, Class 1) to establish optimum concentrations for stabilization and to determine if synergistic effects are present. The experimental plan and the order in which the experiments were conducted as given in Table 2.

Results of initial exposure experiments on the Nomex fabric are shown in Figures 40 and 41. Samples of fabric were exposed for 0, 20, 40, 60, 80 and 100 hours and strength and elongation determined in the warp and fill orientation by the 1" ravel strip test. In both carbon arc and xenon arc exposure the loss in breaking strength and elongation

TABLE 2
 FACTORIAL FOR SELECTION OF
 STABILIZER SYSTEMS

<u>Experiment No.</u>	<u>Sample*</u>
1	A ₃ B ₁ C ₁
2	A ₃ B ₁ C ₃
3	A ₂ B ₂ C ₂
4	A ₂ B ₂ C ₂
5	A ₁ B ₃ C ₁
6	A ₁ B ₁ C ₁
7	A ₃ B ₃ C ₁
8	A ₁ B ₃ C ₃
9	A ₃ B ₃ C ₃
10	A ₁ B ₁ C ₃
11	A ₀ B ₀ C ₀

* A = Blancophor AW
 B = Tinuvin P
 C = Oxanilide
 0 = 0 % OWF
 1 = 33 % OWF
 2 = 66 % OWF
 3 = 100% OWF

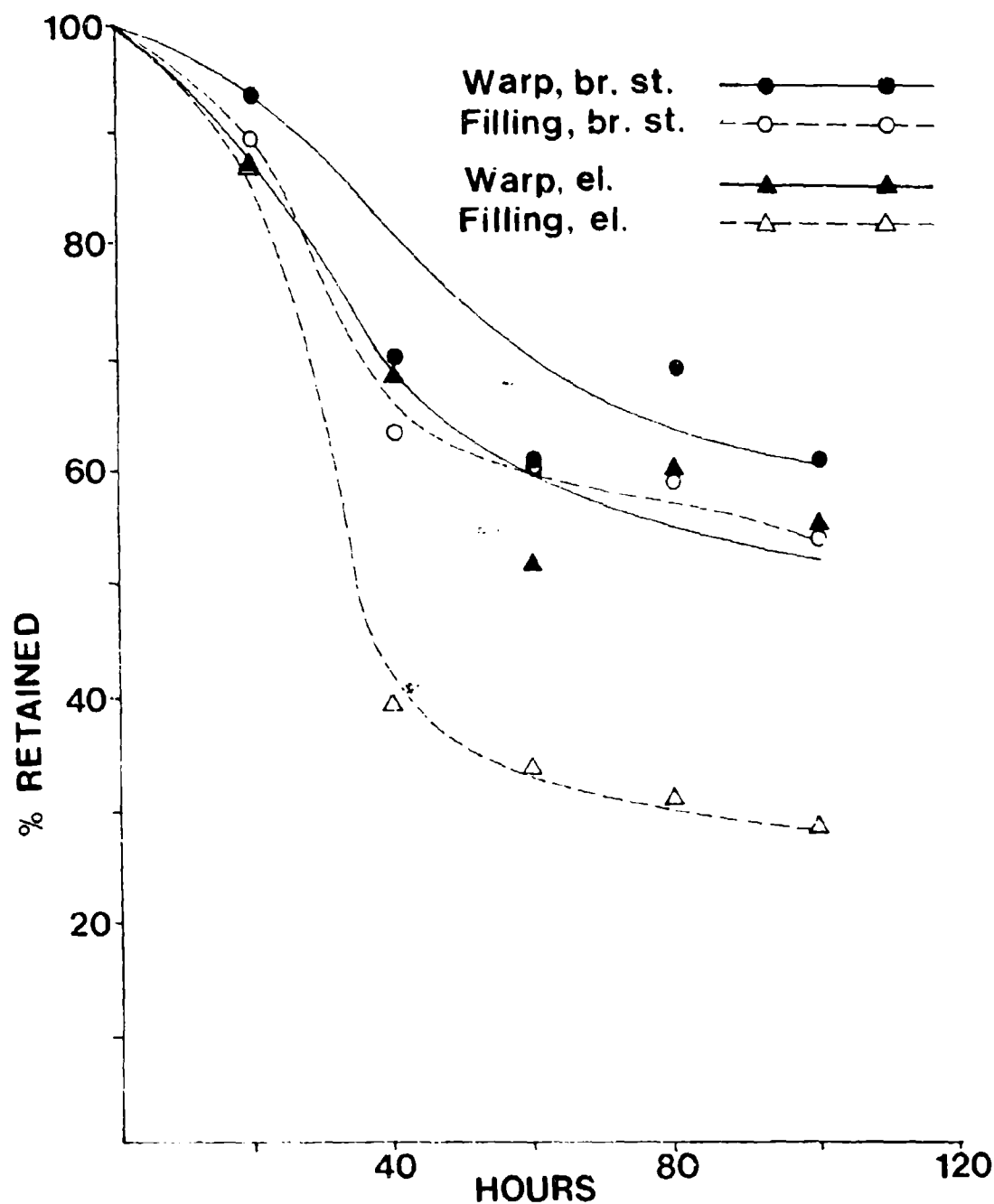


Figure 40. Retention of breaking strength and elongation of Nomex fabric exposed in the carbon arc Fade-Ometer.

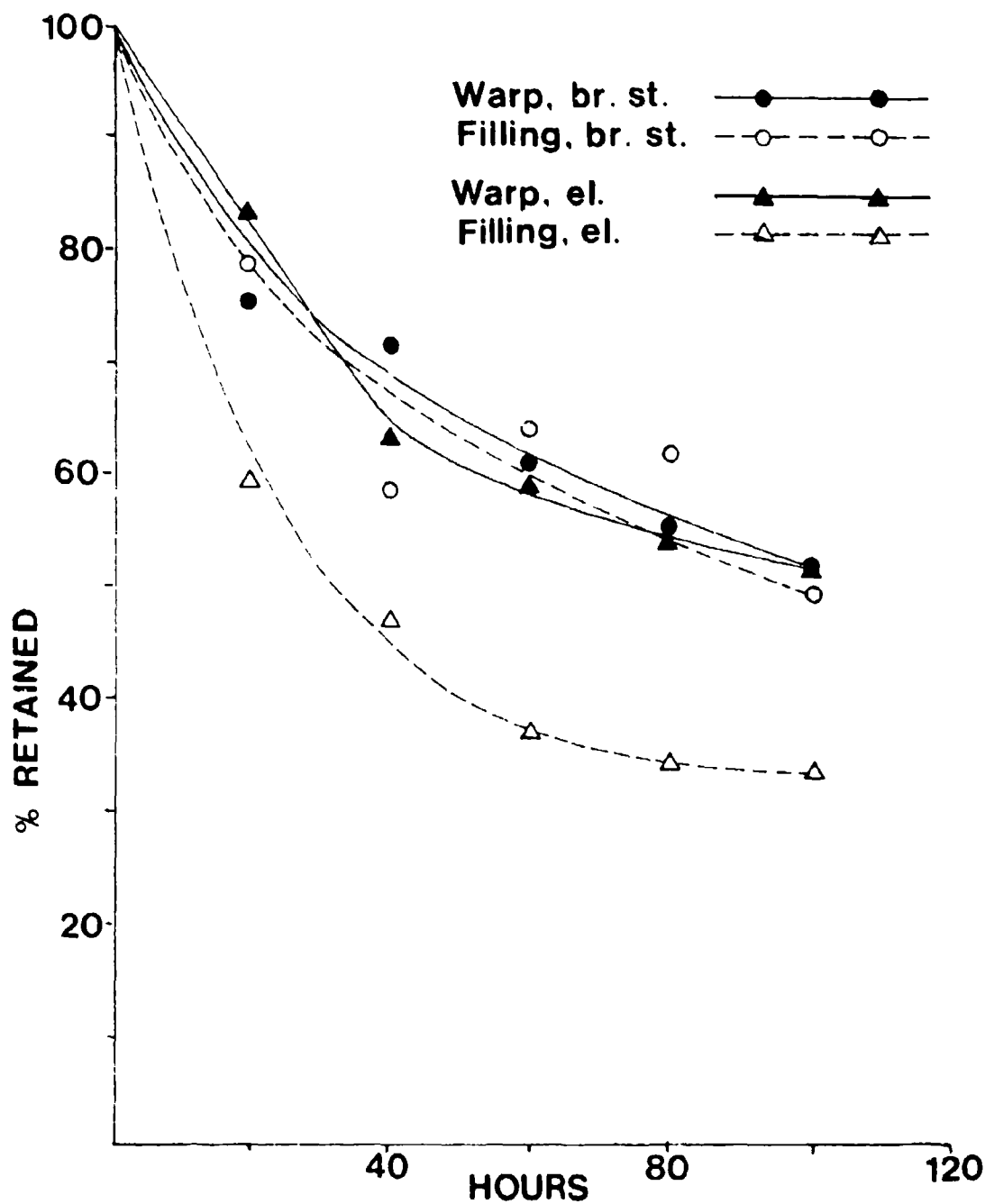


Figure 41. Retention of breaking strength and elongation of Nomex fabric exposed in the xenon arc Fade-Ometer.

in the warp direction and the loss of breaking strength in the filling direction follow very similar curves. The elongation in the filling direction decreases more sharply on exposure. In subsequent experiments changes in properties in the warp direction on exposure were determined as this is the direction subjected to greatest stress in end-use applications of Nomex fabric.

Results of the central composite design experiment for testing three stabilizers (Blancophor AW, Tinuvin P, and Oxanilide) at four concentration levels (0%, 33%, 66% and 100%) are shown in Table 3. Results are reasonably consistent with a few exceptions. Several samples at the 60 hour exposure time ($A_3B_1C_1$, $A_3B_1C_3$) show unusually low strengths. Data at 80 and 100 hours for these samples suggest that some problem of undetermined origin is responsible for the low values at the 60 hour exposure time. Sample $A_1B_3C_1$ shows extremely high values for the strength both initially and after all exposure times. The reason for these unusually high values is not apparent.

TABLE 3

AVERAGE STRENGTH MEASURED AT VARIOUS UV EXPOSURE
LEVELS FOR ALL TREATMENT COMBINATIONS

Treat. Comb.	Average Strength (Pounds) After Exposure					
	<u>0</u>	<u>20</u>	<u>40</u>	<u>60</u>	<u>80</u>	<u>100</u>
A ₀ B ₀ C ₀	224	198	170	160	159	146
A ₁ B ₁ C ₁	244	219	213	199	199	197
A ₁ B ₁ C ₃	234	192	182	186	205	213
A ₁ B ₃ C ₃	221	240	224	212	201	198
A ₃ B ₁ C ₁	212	184	203	127	162	218
A ₃ B ₁ C ₃	215	205	178	117	180	191
A ₃ B ₃ C ₃	229	230	215	183	207	207
A ₁ B ₃ C ₁	270	260	230	233	227	229
A ₃ B ₃ C ₁	222	229	205	202	217	193
A ₂ B ₂ C ₂	203	217	218	219	220	221

95% Confidence Limit = $\pm$ 14 lbs.

A₀B₀C₀ - UV inhibitors not present

A₁B₁C₁ - UV inhibitors present in lowest
concentrations

A₃B₃C₃ - UV inhibitors present in highest
concentrations

The effects of concentration of the three stabilizers on UV stability of Nomex fabrics are shown in Figures 42, 43 and 44. The strength after both 40 and 100 hours exposure for samples containing Blancophor AW (Figure 42) suggest that little improvement in strength retention occurs above 33%. In fact there is some indication that higher levels may actually give less strength retention than the 33% level. Similar results were obtained for Oxanilide as shown in Figure 44. The drop in strength at higher concentration was somewhat more pronounced in this case.

Tinuvin P does not reach maximum effectiveness until approximately 50% OWF is present in the dyebath. There is little difference in strength at the 67 and 100% level (see Figure 43).

The lack of data between 0 and 33% for all additives at least suggested the possibility that lower levels might be as effective as 33%. A sample was prepared, therefore, with 10% of each of the additives in the dyebath. The results for this sample is shown as the dotted circle and circled x in Figures 42 - 44.

Interactive effects between the stabilizer candidates are shown in Figure 45 - 50. No pronounced effects are observed between the various components. In general, high levels of B in combination with low levels of A and C gave somewhat higher strengths.

Another important observation made during the factorial experiment was that the Blancophor AW reduced the dye lightfastness of the sage green fabric. The color change was somewhat more pronounced than the change observed for the sage green fabric with no additions.

Based on the results of the factorial experiment, four stabilizer systems were selected for in-depth investigation. From Figures 42 and 44, it appears reasonable that levels of Blancophor AW and Oxanilide above 33% (owf) do not contribute appreciably to the retention of tensile strength on UV exposure. Similarly, levels of Tinuvin P above 50% (owf) are probably not beneficial.

A number of criteria were used in selection of the stabilizer systems. First, the lowest levels expected to be effective were selected to reduce treatment costs and give lower add-on of chemicals which may adversely affect other properties of the fabric. Second, at least two

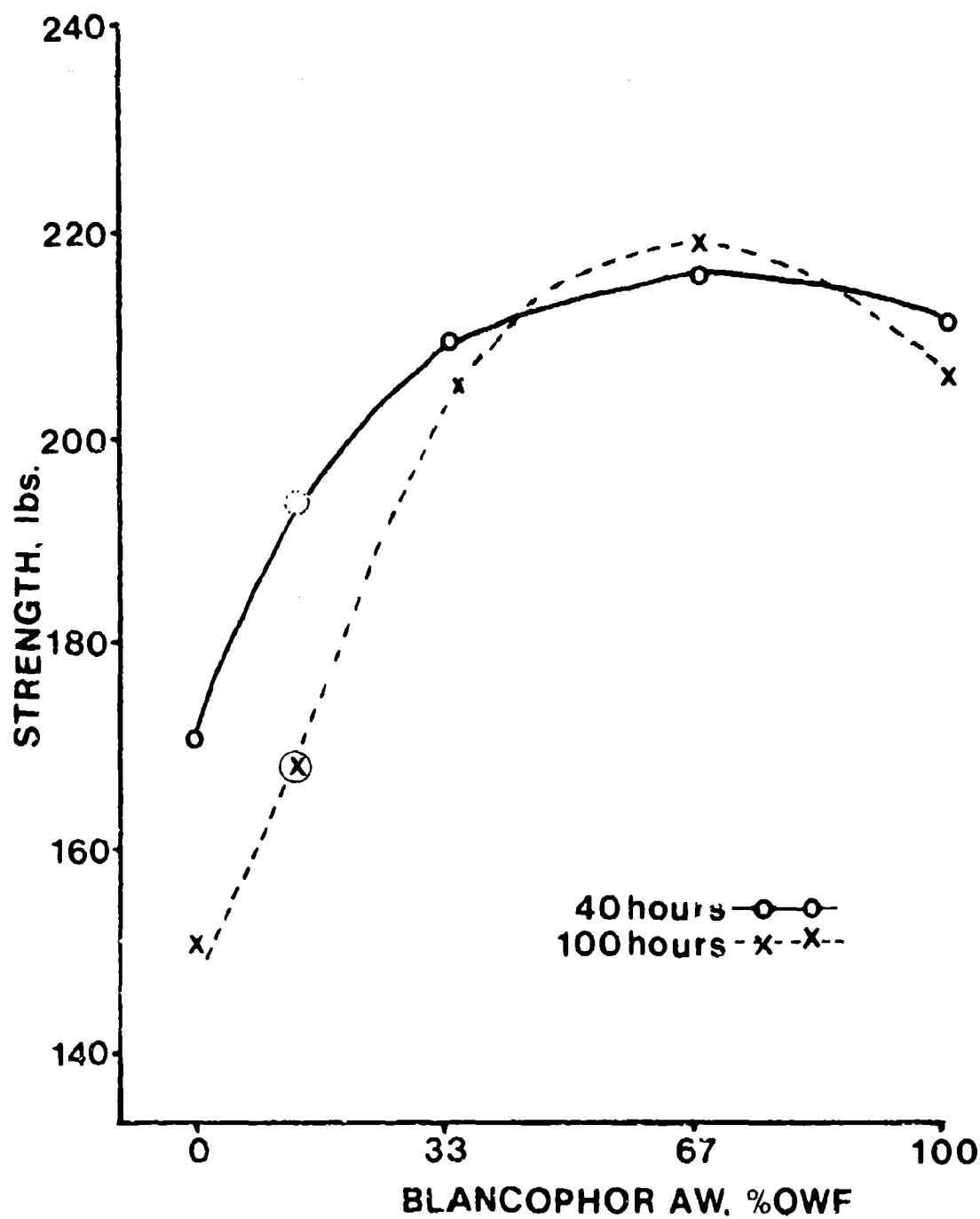


Figure 42. The effect of concentration of Blancophor AW on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-O-meter.

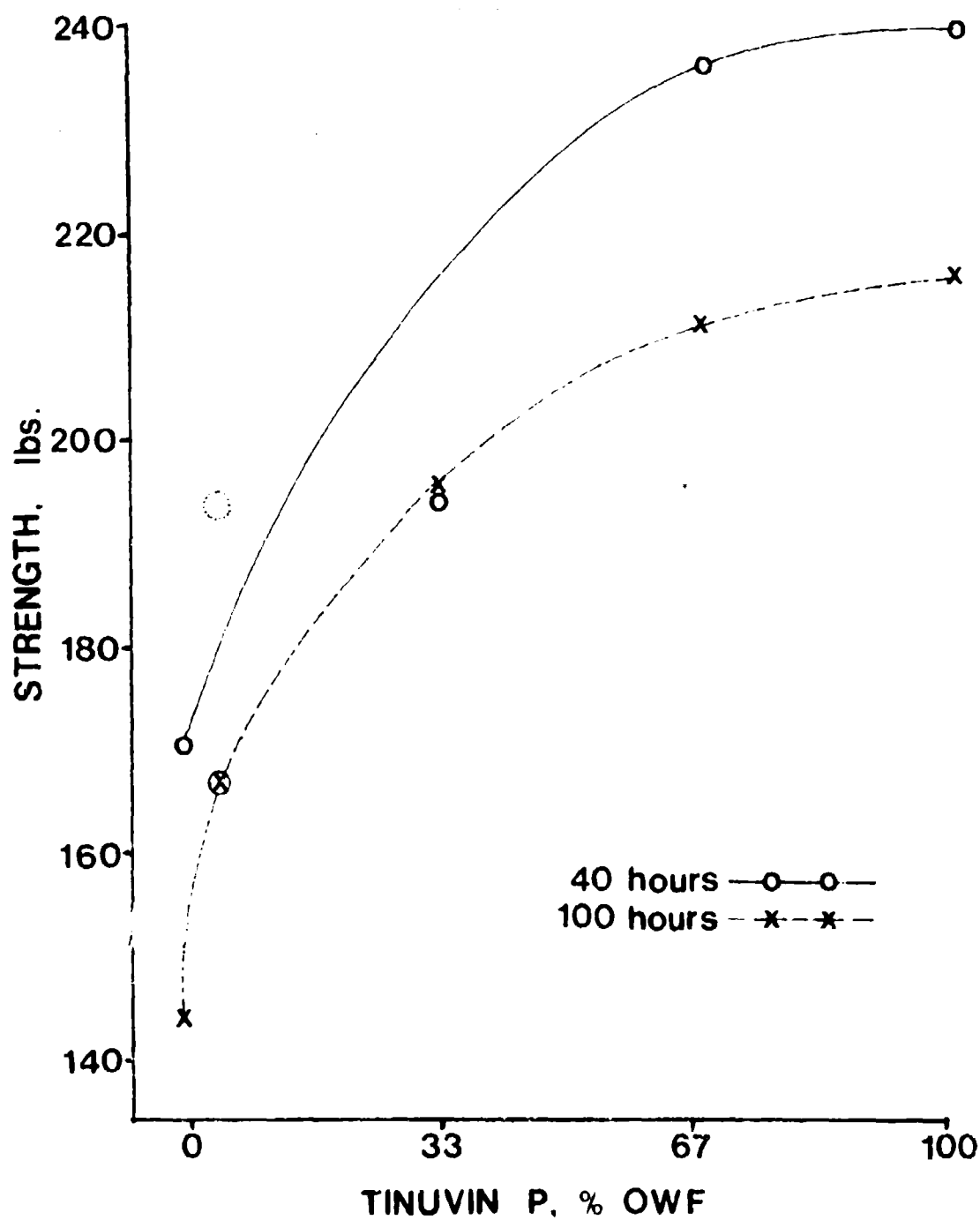


Figure 43. The effect of concentration of Tinuvin P on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer.

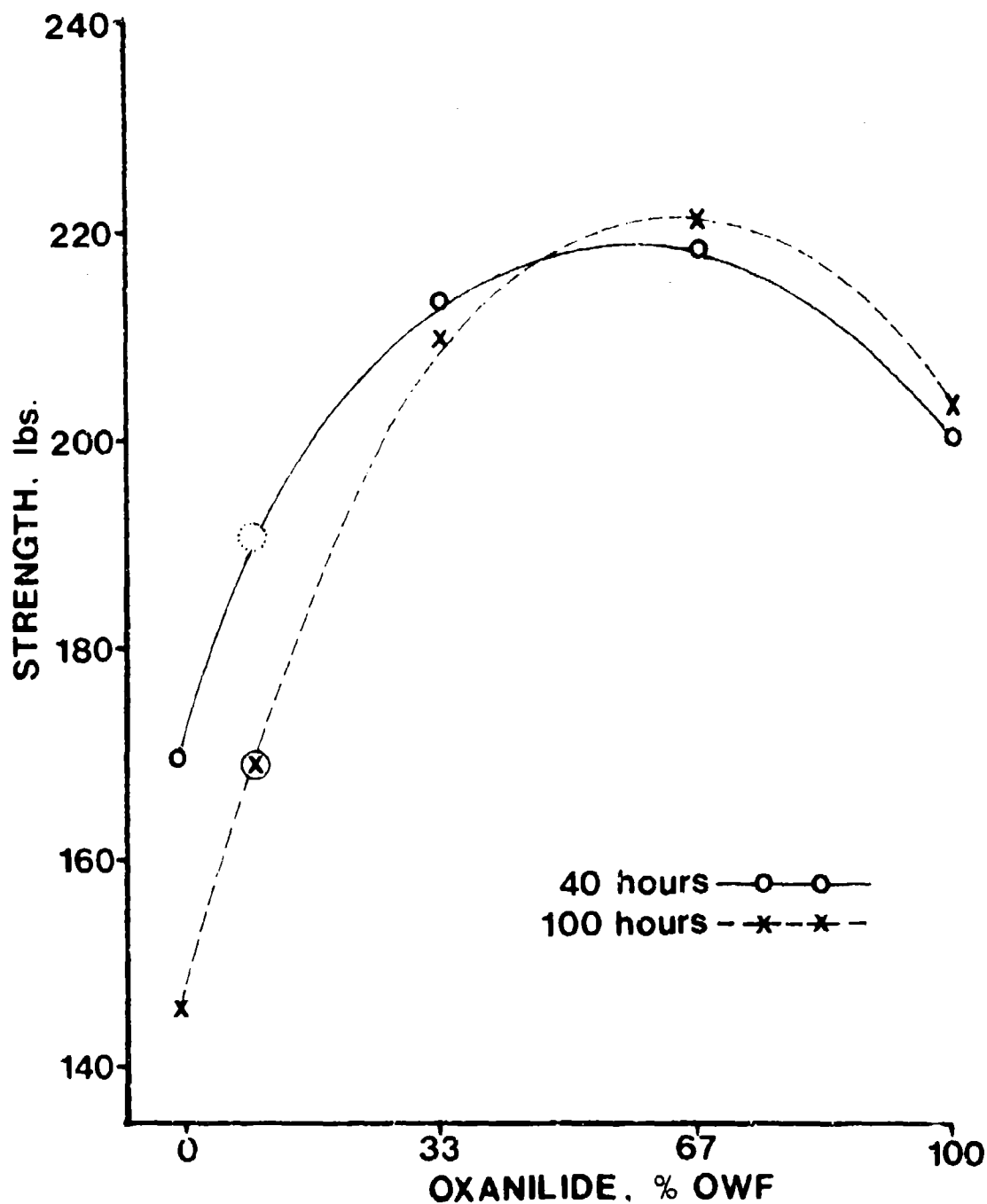


Figure 44. The effect of concentration of oxanilide on strength of Nomex fabrics after exposure for 40 and 100 hours in the carbon arc Fade-Ometer.

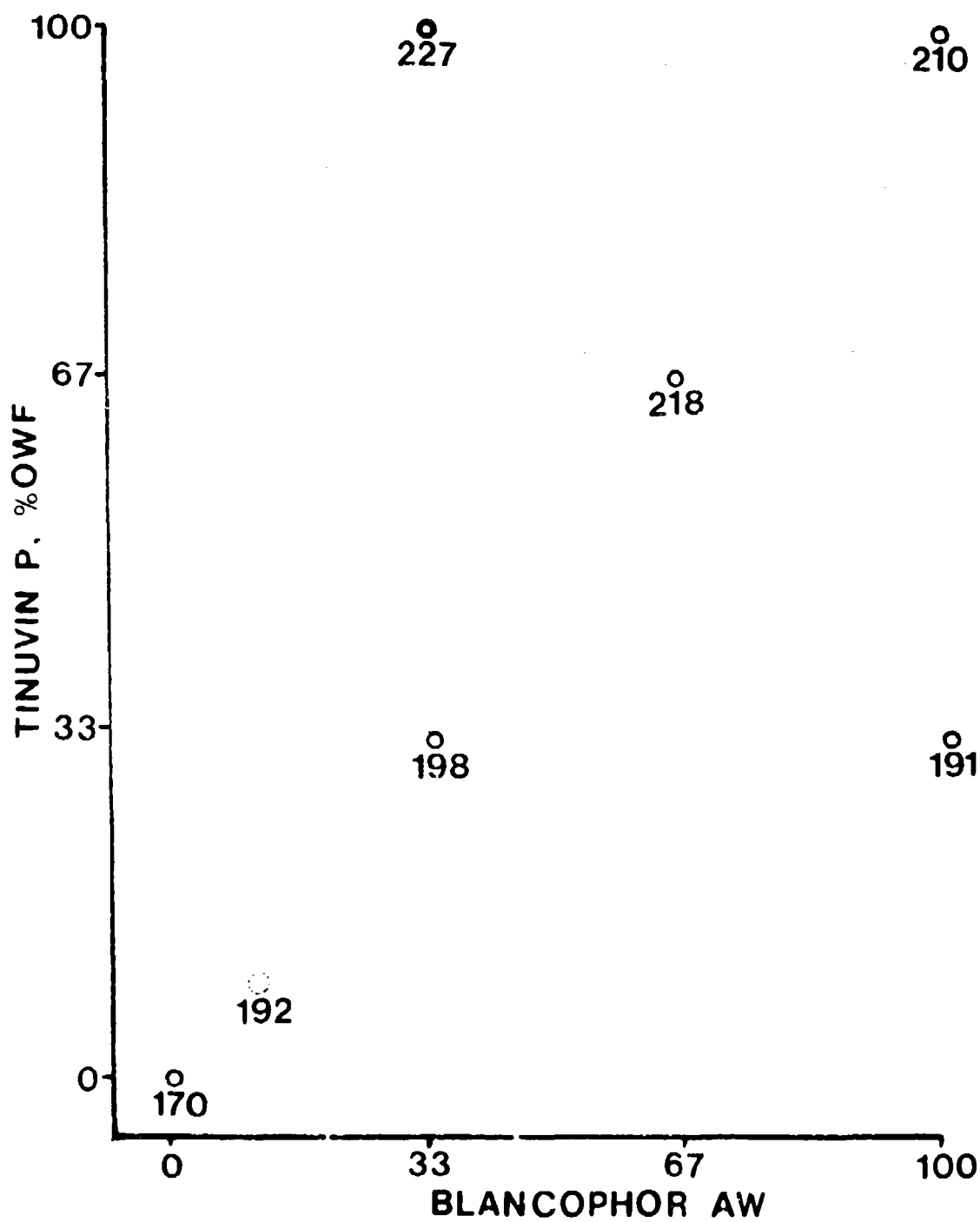


Figure 4b. Strength after 40 hours exposure of fabric samples containing Blancophor AW and Tinuvin P.

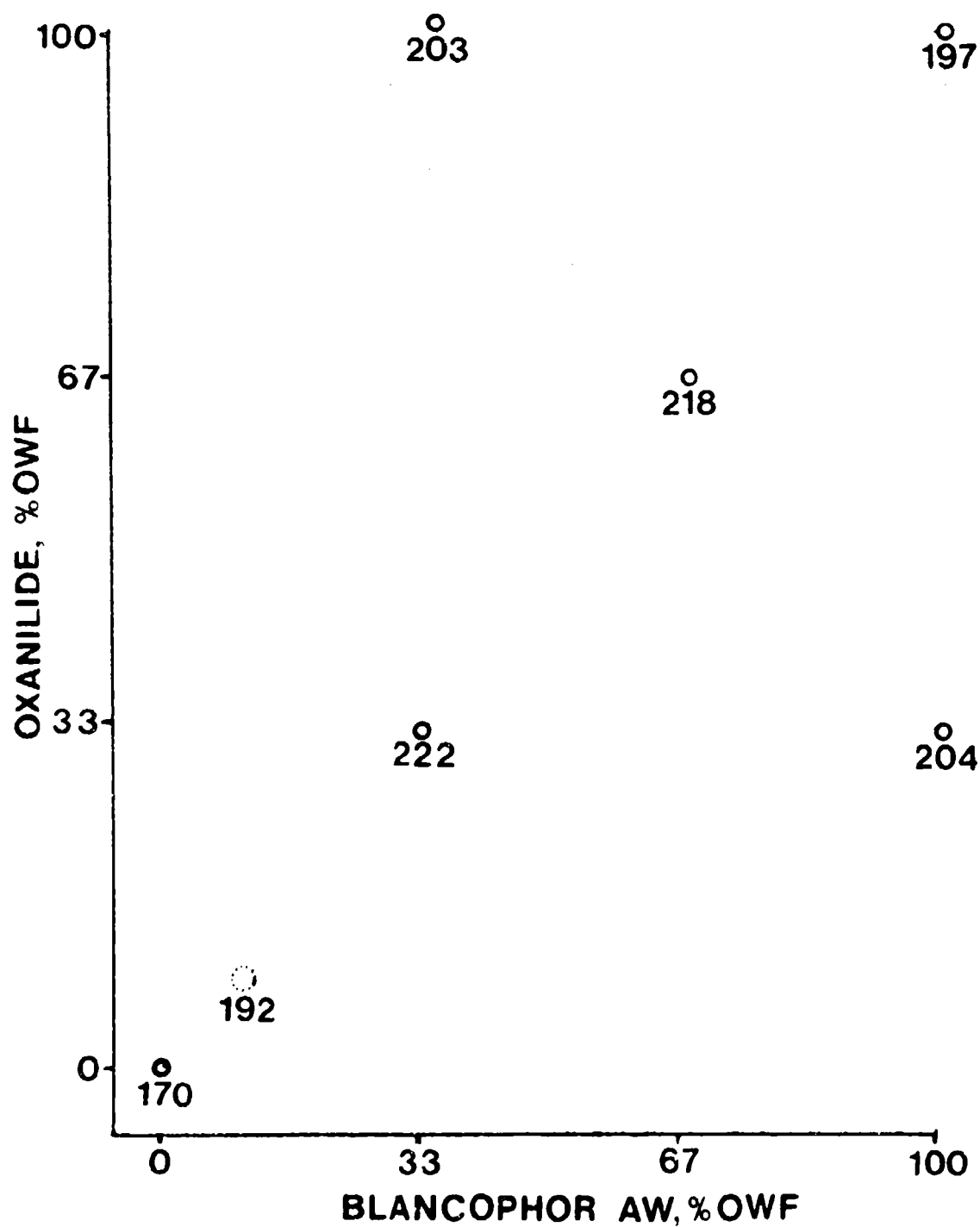


Figure 46. Strength after 40 hours exposure of fabric samples containing oxanilide and Blancophor AW.

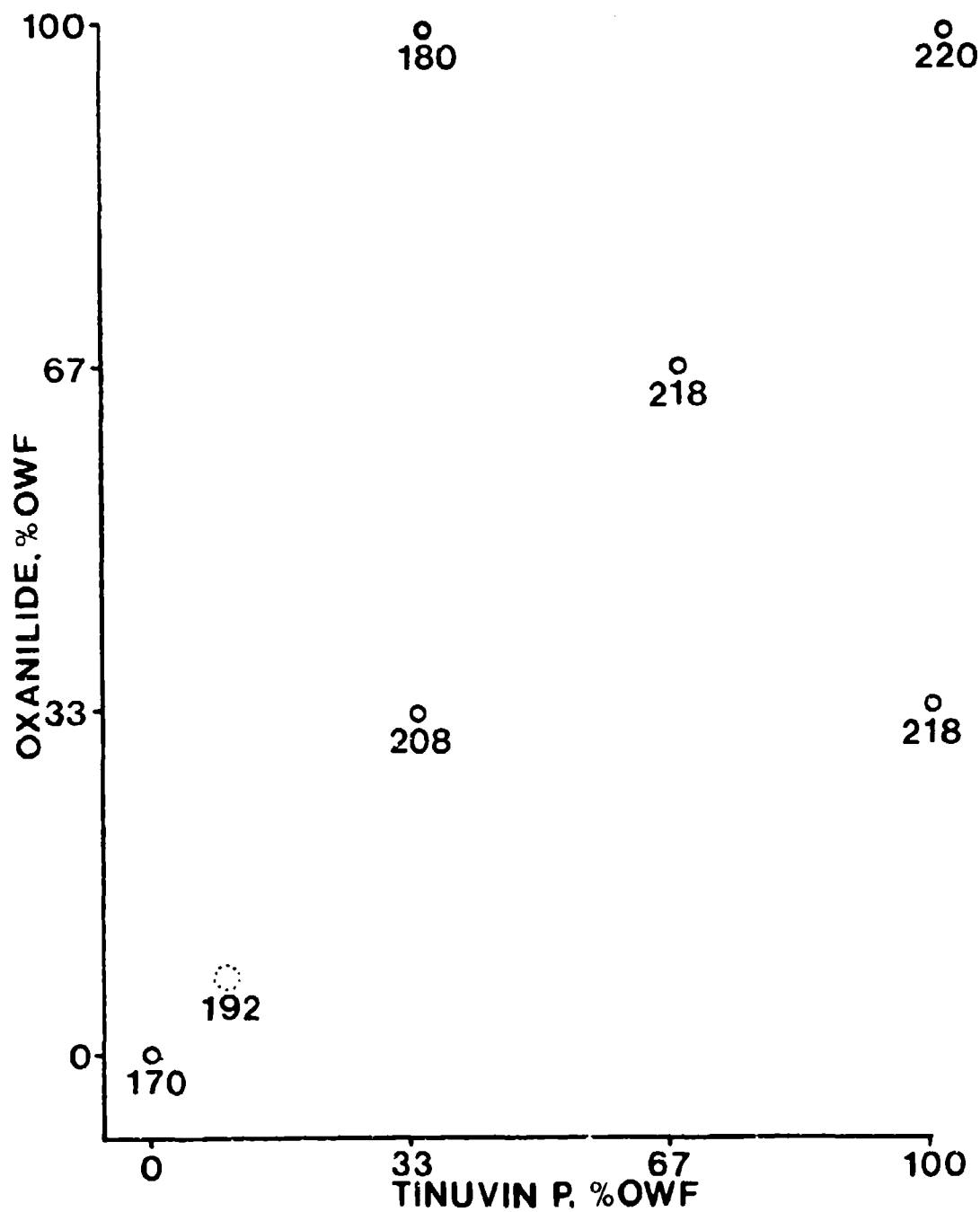


Figure 47. Strength after 40 hours exposure of fabrics samples containing oxanilide and Tinuvin P.

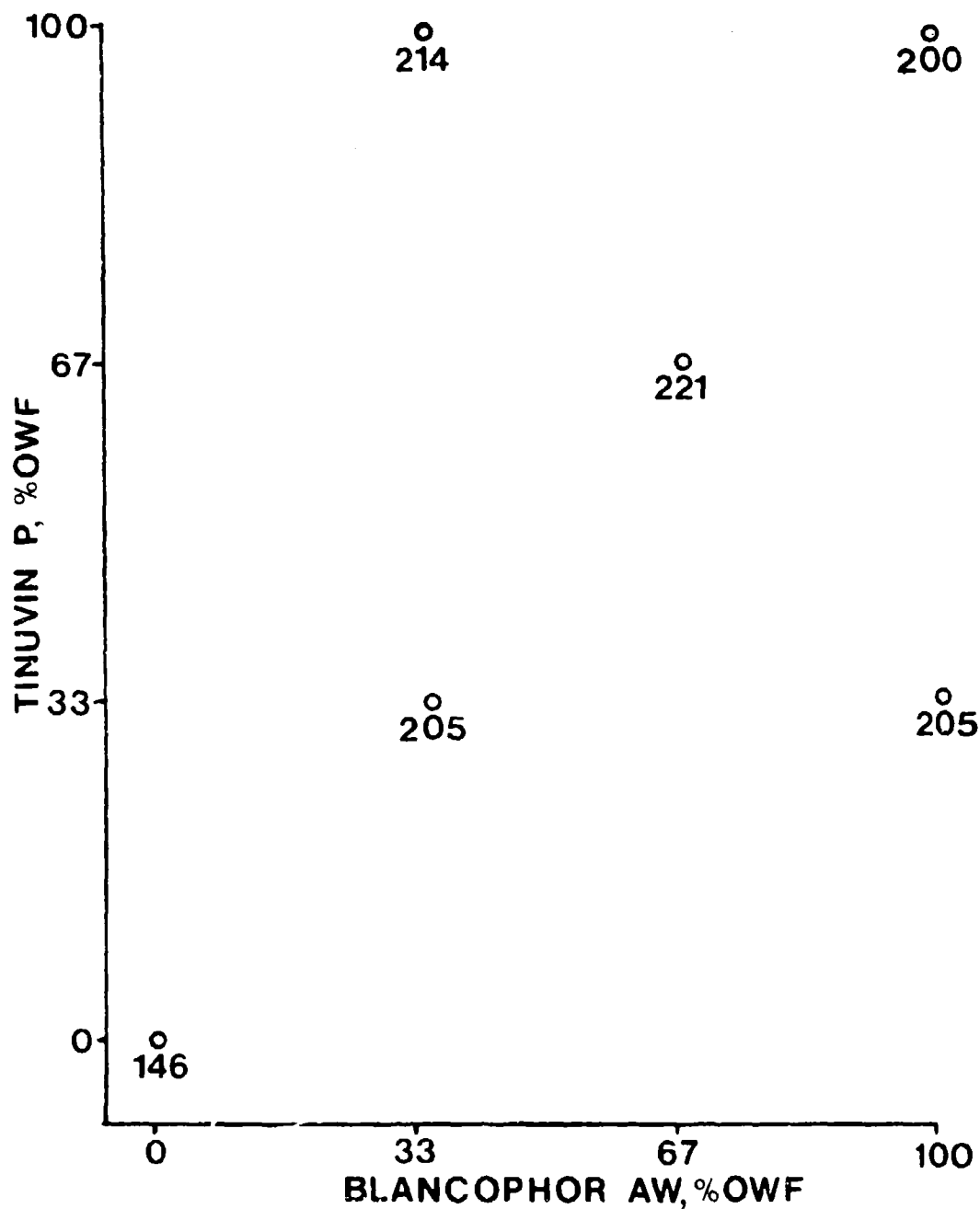


Figure 48. Strength after 100 hours exposure of Nomex fabric containing Blancophor AW and Tinuvin

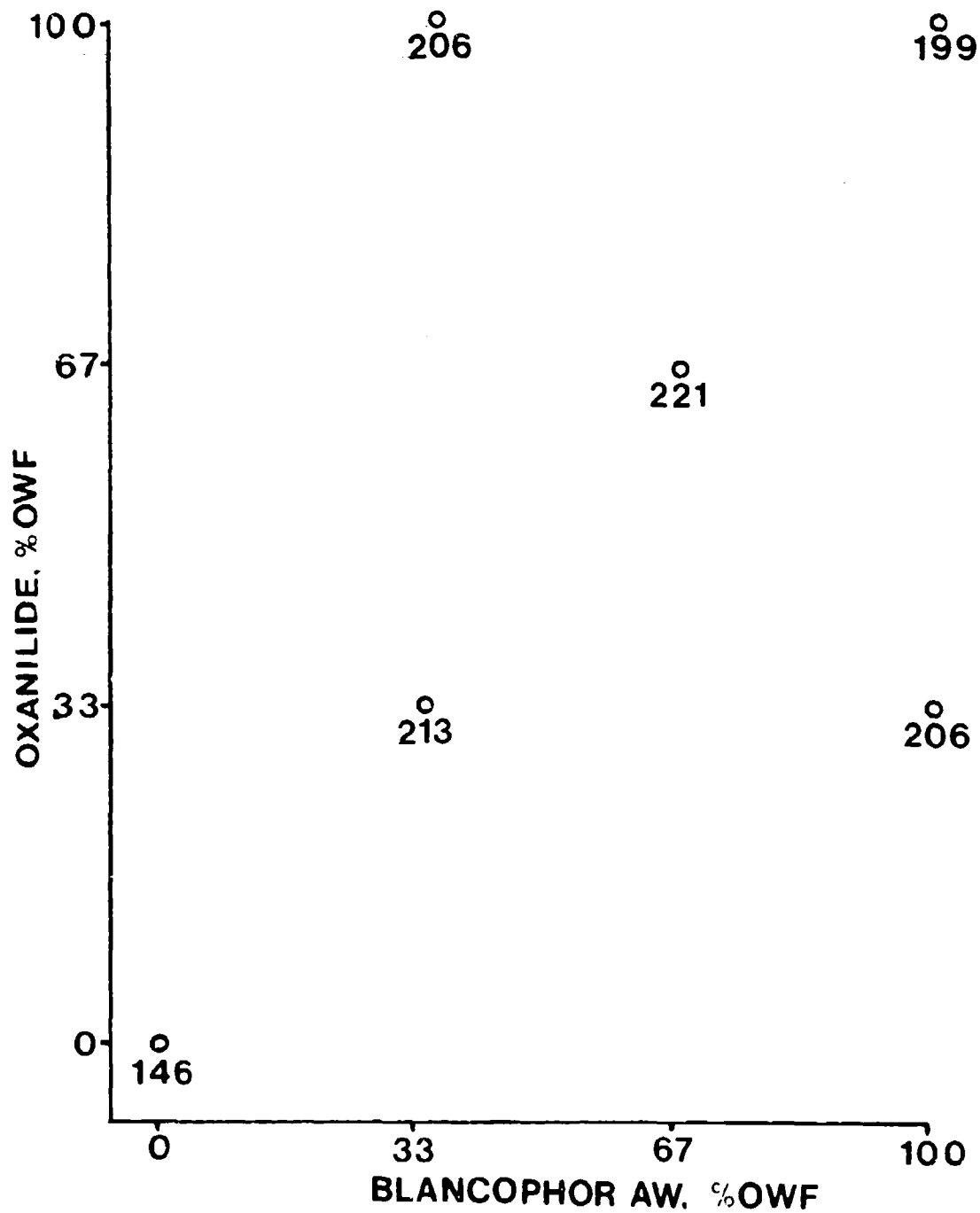


Figure 49. Strength after 100 hours exposure of Nomex fabrics containing oxanilide and Blancophor AW.

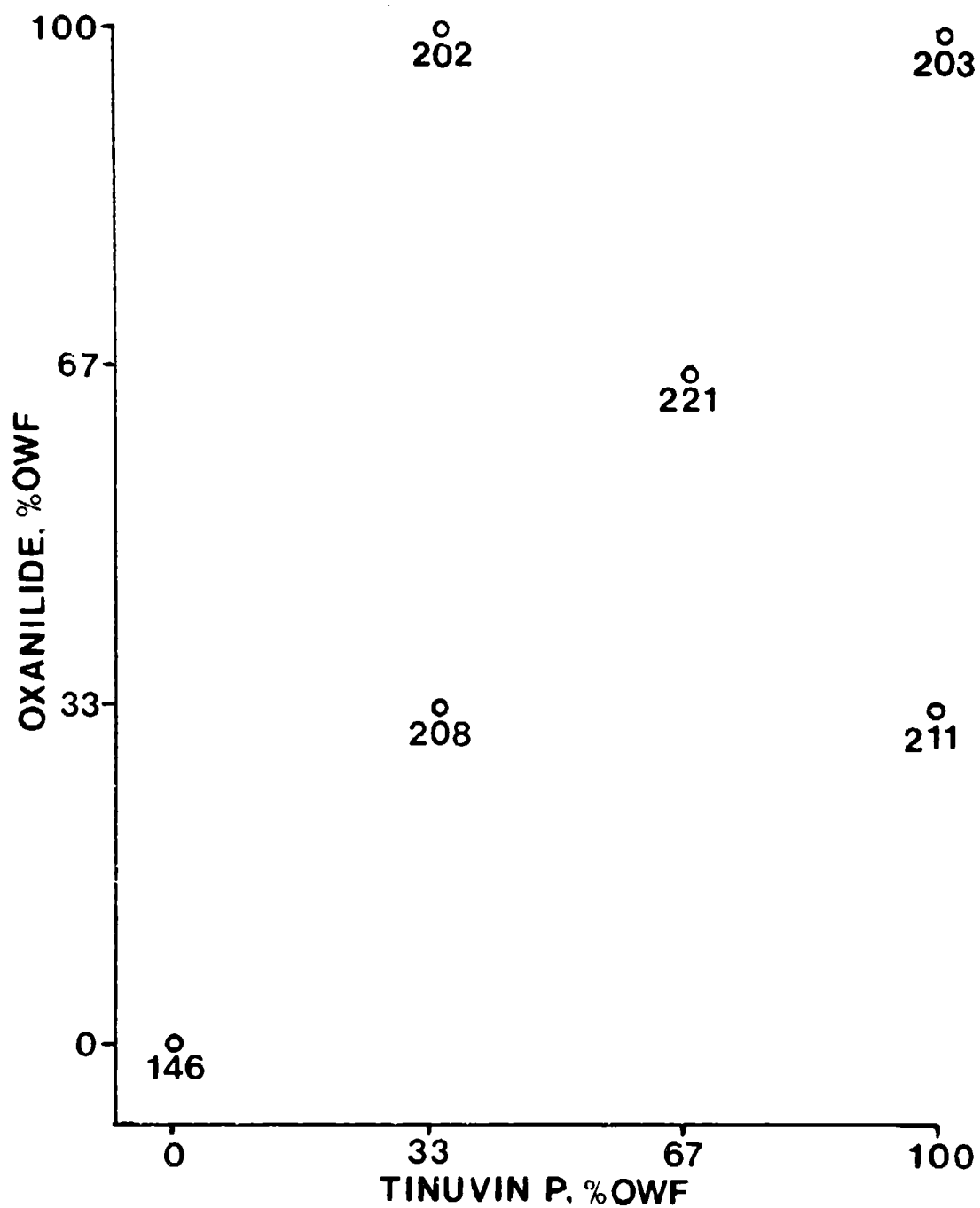


Figure 50. Strength after 100 hours exposure of Nomex fabrics containing oxanilide and Tinuvin P.

systems were selected which do not contain Blancophor AW to avoid the reduced dye lightfastness previously mentioned. Third, combinations were selected in which the level of Tinuvin P were usually higher than the other stabilizers. One of the selected systems was similar to the factorial sample which gave exceptionally high strength values both initially and after exposure.

The four systems selected for study were:

1. Blancophor AW 33%, Tinuvin P 33%, Oxanilide 33%
2. Blancophor AW 15%, Tinuvin P 50%, Oxanilide 15%
3. Tinuvin P 50%, Oxanilide 33%
4. Tinuvin P 50%

B. Evaluation of Stabilizer Systems

Nomex sage green fabric (Mil-C-38351, Type II, Class 1) obtained from Stern and Stern Textiles, Inc. was used in preparation of these samples. Pieces 10 inches by 15 yards (approximately 700 grams) were cut from the fabric and treated in a sample size Smith Engineering pressure jig dyeing machine. The fabric was attached to one of the jig rollers with surgical tape and the controller set to automatically cycle the fabric back and forth through the bath. The bath was filled with 29 liters of water and heated to the boil by means of an enclosed steam coil. Additives for a given run were weighed into a large beaker and mixed with 500 ml of the dyeing assistant, Chemo-carrier FPN. The well dispersed additives were then added to the hot dyebath by pouring 1/4 of the mixture alternately in the two sides of the bath during one complete cycle of the jig. The jig was then closed and the pressure raised to 21-23 pounds per square inch (260°F) by injecting live steam into the bath. The fabric was cycled through the bath for 2 hours.

At the conclusion of the treatment cycle the fabric was washed at least 3 times in a standard washer and tumble dried to remove excess dyeing assistant and treatment chemicals.

A "blank-dyed" sample was also prepared which was subjected to the same treatment procedure as the treated samples except that no stabilizers were added to the bath. The sample identification numbers for the treated and control samples are given below:

<u>Sample Number</u>	<u>Treatment</u>
109-68-D	Control
109-68-A	Blank-dyed
109-68-E	33% Blancophor AW, 33% Tinuvin P, 33% Oxanilide
109-68-F	15% Blancophor AW, 50% Tinuvin P, 15% Oxanilide
109-68-C	50% Tinuvin P, 33% Oxanilide
109-68-B	50% Tinuvin P

In addition to tests in the Georgia Institute of Technology Laboratories, portions of each of the above samples were submitted to the Air Force Materials Laboratory for evaluation.

All samples were exposed to the carbon arc Fade-O-meter for periods of 50,100,150, and 200 hours. Before and after exposure the breaking load and elongation were determined by the 1" ravel strip method with the Instron tensile tester. Results are shown in Tables 4,5 and 6. The results are plotted in Figures 51 through 55 where the percent retention of breaking strength and elongation is plotted for each sample compared to the blank-dyed sample (109-68-A).

These data suggest that samples 109-68-E and 109-68-F showed greater resistance to UV degradation than the control or blank-dyed samples. Sample 109-68-E had 75% retention of breaking strength after 150 hours exposure which was the target objective for this project. Samples 109-68-B and 109-68-C showed less improvement than 109-68-E and 109-68-F. This was undoubtedly due to the presence of Blancophor AW in both samples E and F. Sample E showed by far the best performance of any of the samples in strength retention.

An evaluation of the effects of treatment to increase UV stability on other fabric properties was also carried out for the six fabrics. The properties measured and the methods employed are given below.

TABLE 4
BREAKING STRENGTH AND ELONGATION BEFORE AND
AFTER UV EXPOSURE

		Hours Exposed				
		<u>0</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
109-68-D	Breaking Load	241.6	161.2	126.2	158.4	132.8
	Elongation	54.0	23.1	16.7	21.5	18.9
109-68-A	Breaking Load	241.3	182.0	131.4	125.2	122.4
	Elongation	54.2	26.2	19.2	23.0	21.8
109-68-E	Breaking Load	247.4	193.0	180.2	186.0	199.0
	Elongation	57.0	29.8	27.3	27.6	28.9
109-68-F	Breaking Load	253.6	196.6	146.0	132.8	149.0
	Elongation	63.2	28.4	27.5	27.2	32.6
109-68-C	Breaking Load	241.4	184.8	120.0	106.6	118.0
	Elongation	54.0	26.1	22.2	23.0	23.0
109-68-B	Breaking Load	218.8	145.2	125.4	130.2	126.6
	Elongation	49.9	25.2	27.2	25.7	25.6

TABLE 5

TENSILE STRENGTH RETENTION (%)

	Hrs. Exposed			
	50	100	150	200
109-68-D	66.7	52.2	65.6	55.0
109-68-A	75.4	54.5	51.9	50.7
109-68-E	78.0	72.8	75.2	80.4
109-68-F	77.5	57.6	52.4	58.8
109-68-C	76.5	49.7	44.2	48.9
109-68-B	66.4	57.3	59.5	57.9

TABLE 6
ELONGATION RETENTION (%)

<u>Sample</u>	Hours Exposure			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
109-68-D	43	31	40	35
109-68-A	48	35	43	40
109-68-E	52	48	48	51
109-68-F	45	44	43	52
109-68-C	48	41	43	43
109-68-B	51	55	51	58

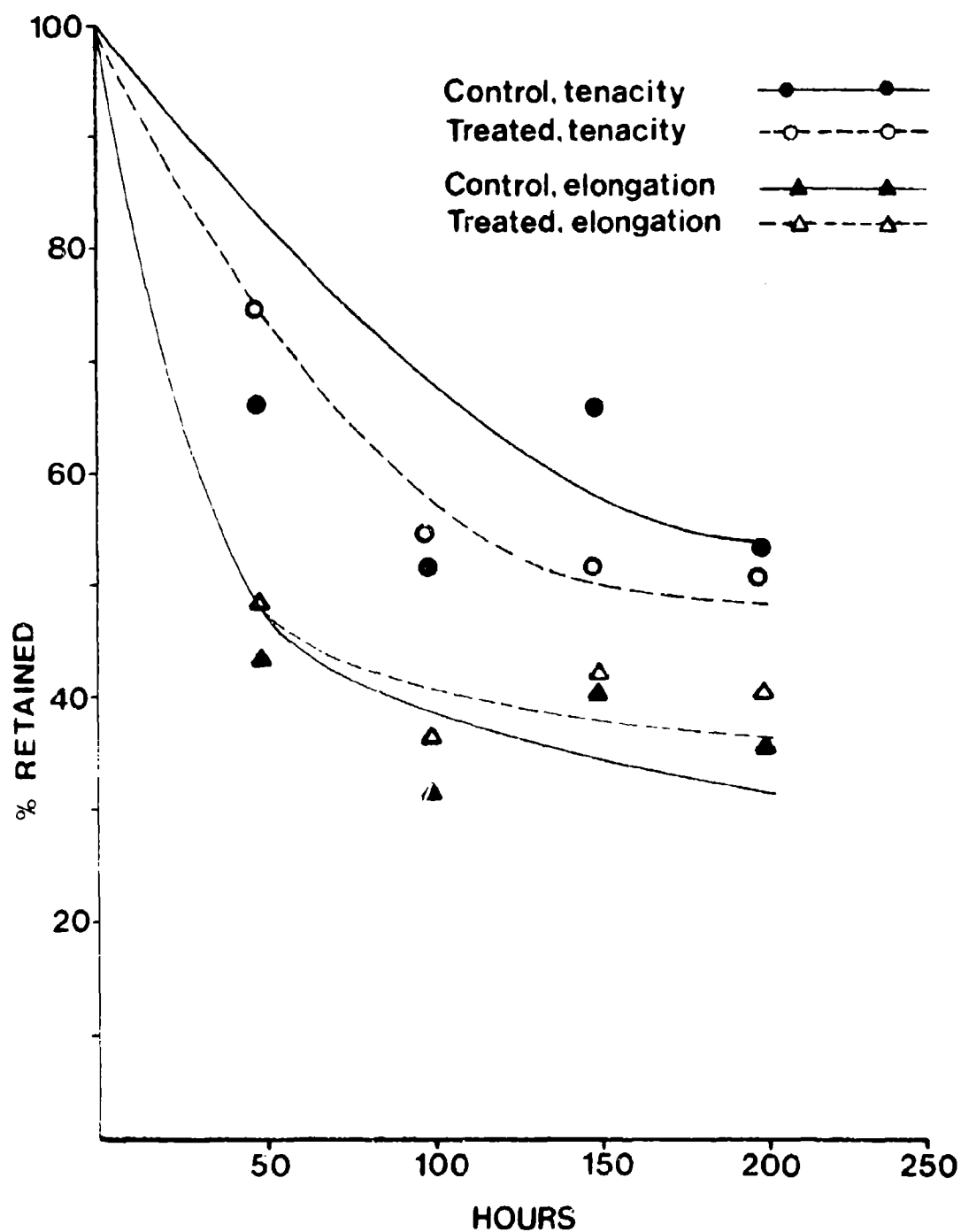


Figure 51. Retention of breaking strength and elongation of treated (a) and control (D) Nomex fabric after exposure in the carbon arc Fade-Ometer.

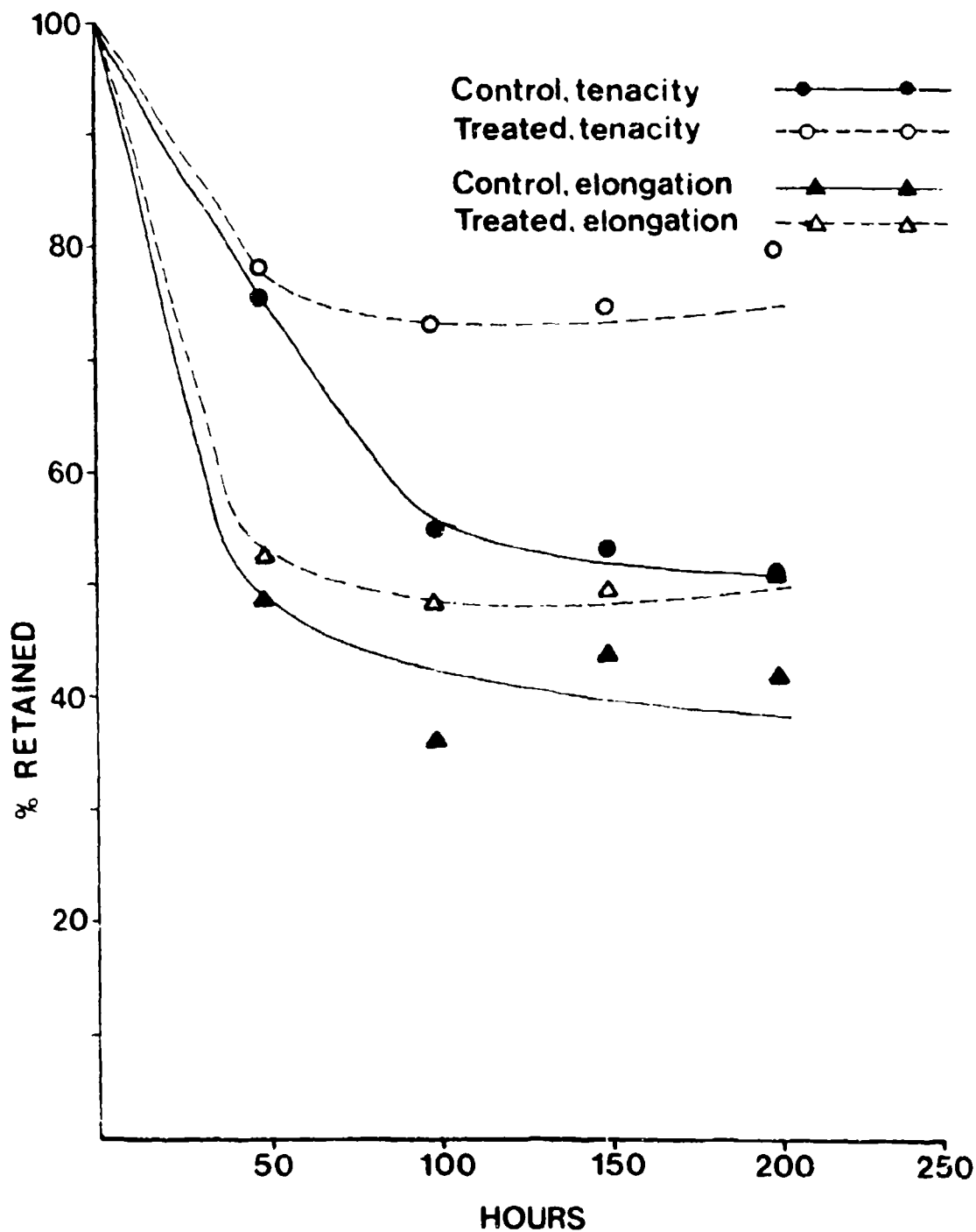


Figure 52. Retention of breaking strength and elongation of treated (E) and control (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

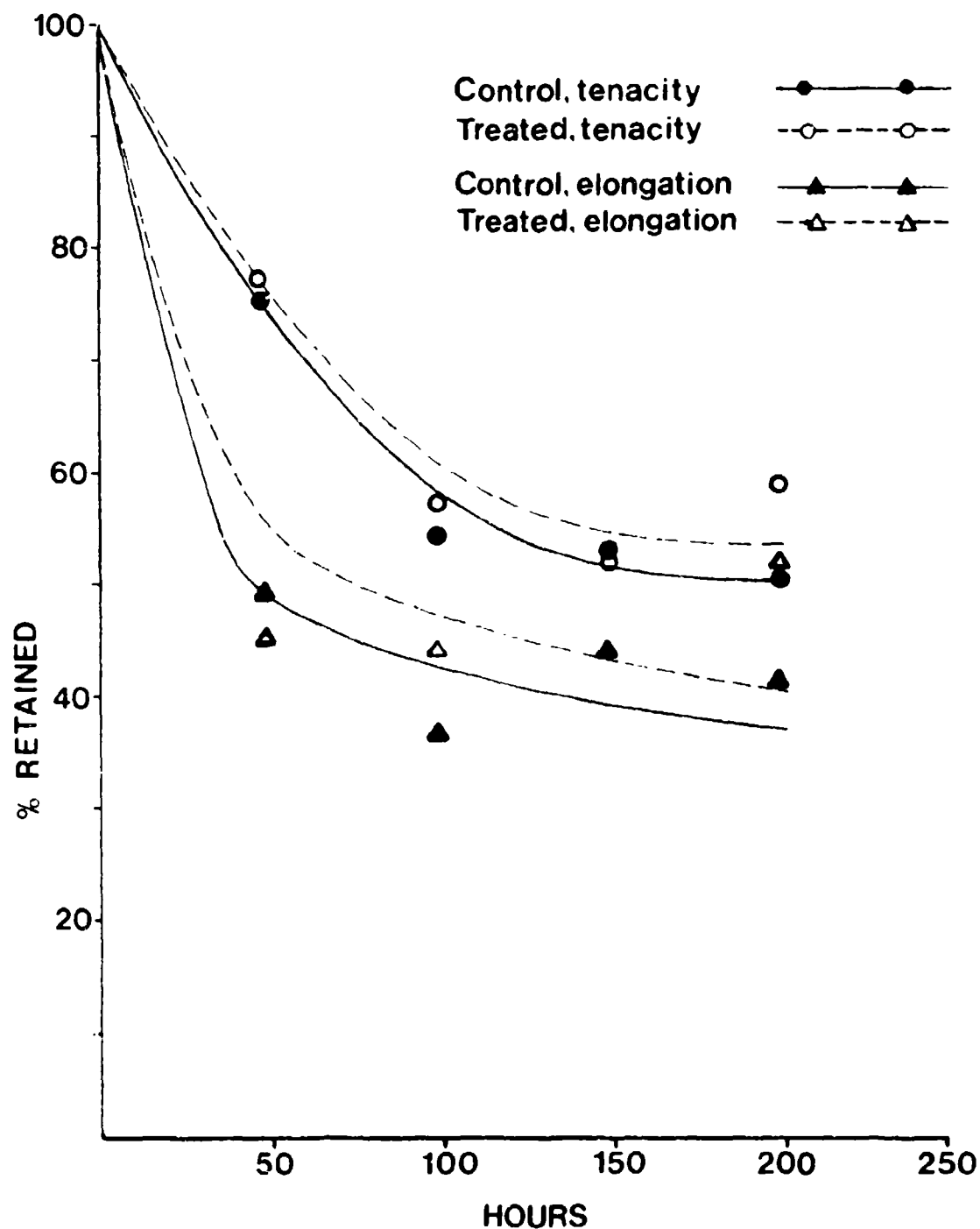


Figure 53. Retention of breaking strength and elongation of treated (F) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

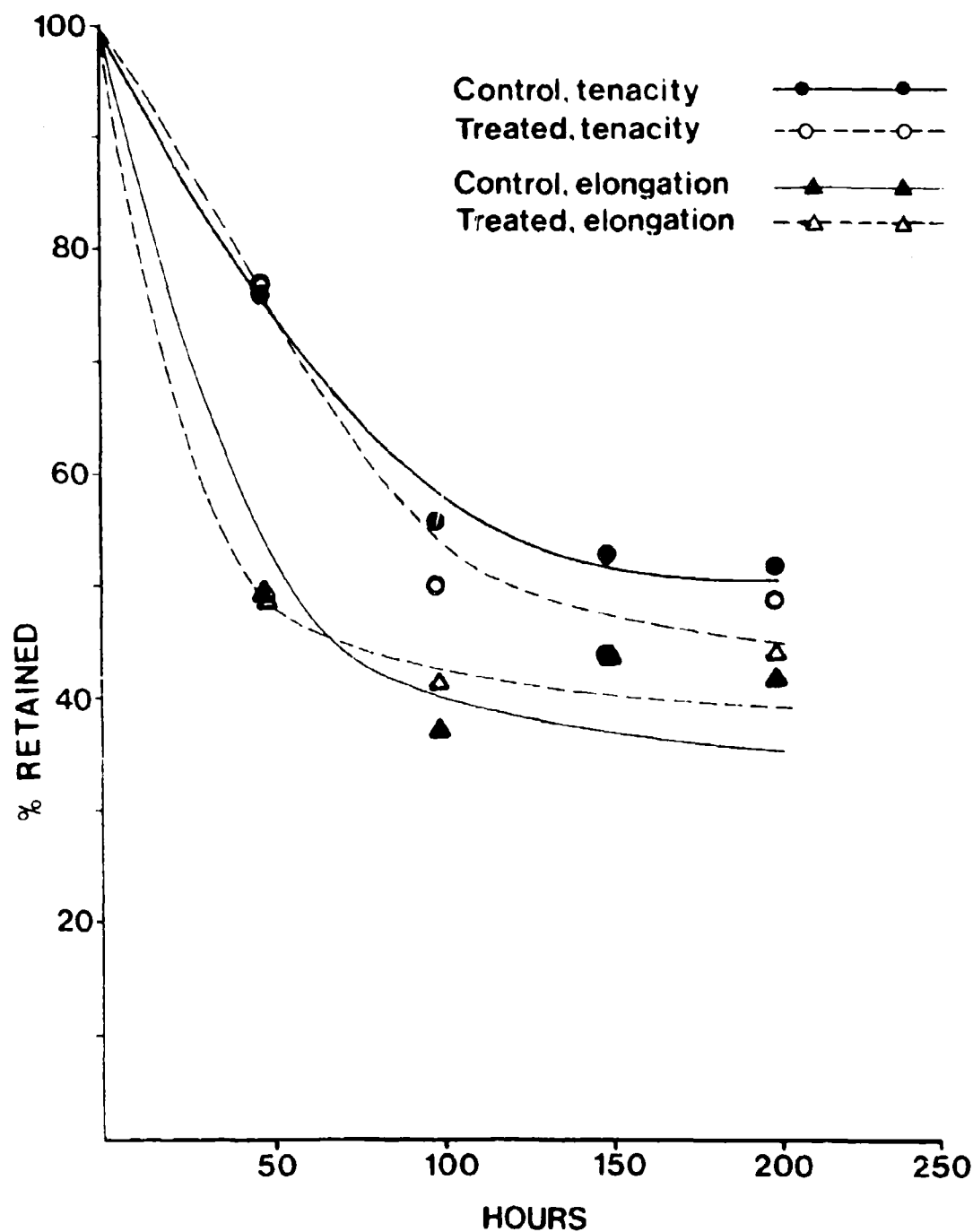


Figure 54. Retention of breaking strength and elongation of treated (C) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

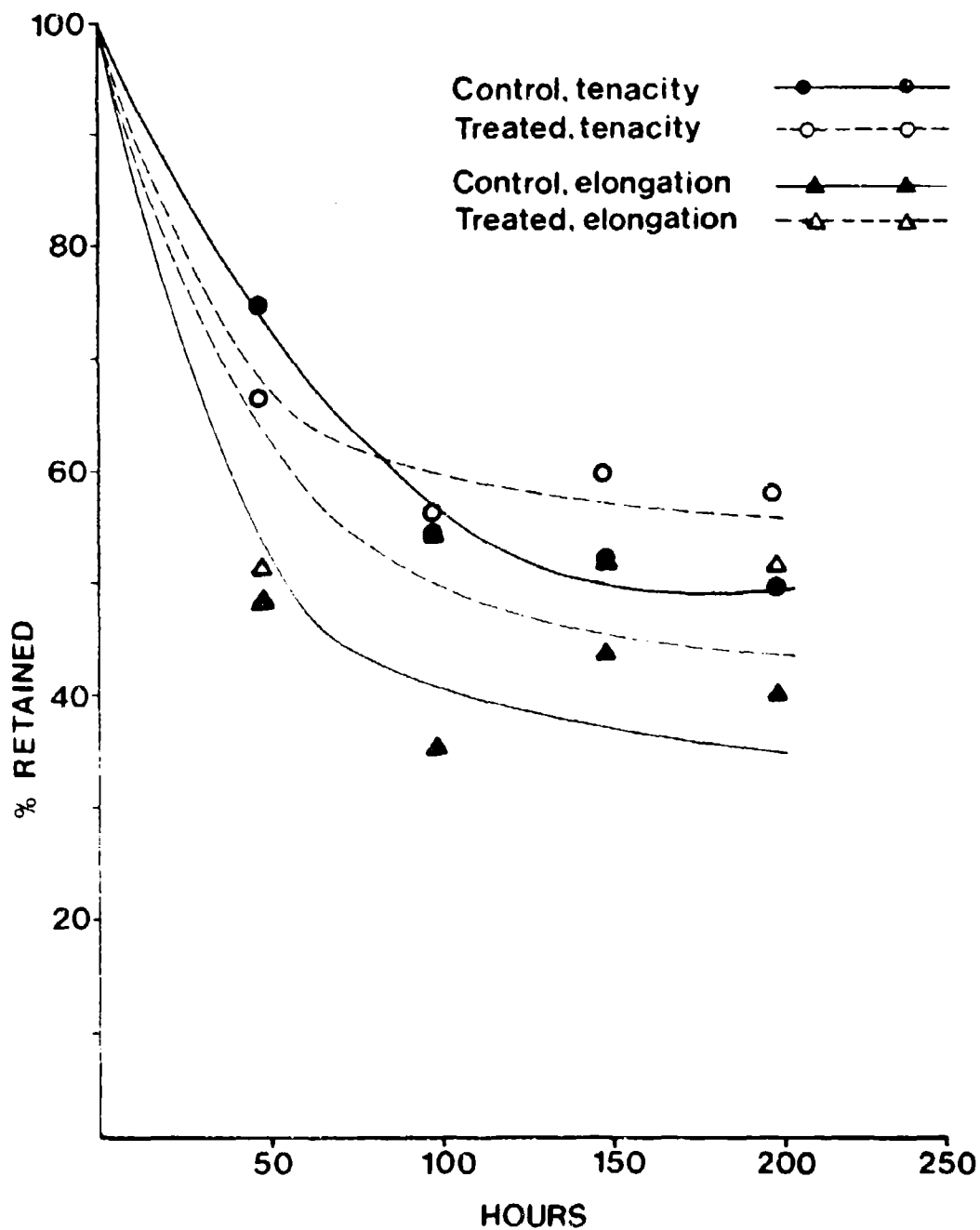


Figure 55. Retention of breaking strength and elongation of treated (B) and blank-dyed (A) Nomex fabric after exposure in the carbon arc Fade-Ometer.

Yarns per Inch

Warp ends per inch and filling picks per inch were measured as directed in Method 5050, Federal Test Method Standard 191. Results are shown in Table 7 and indicate that fabric construction was identical for all of the experiment fabrics.

Fabric Weight

Weight of the experimentally treated fabrics was measured according to Method 5041 of Federal Test Method Standard 191. Results are also shown in Table 7 and indicate a large difference in the measured weights among the samples, with the differences being related to the take-up of the UV stabilizer compounds by the fabric.

Thickness

Fabric thickness was measured according to Method 5030. Thickness varied among the several samples approximately the same as fabric weight and again is related to the take-up by the fabric of the UV resistant compound.

Flexibility

Flexibility was determined by measurement of bending length of the fabric in both the warp and filling directions. ASTM method D 1388, Stiffness of Fabrics, Option A-Cantilever Method, was used. Results indicate no consistency in bending length measurements among the several samples. Explanation of the differences observed will require a further examination.

Air Permeability

Air permeability was measured by the Frazier air permeability tester according to ASTM method D 737. The results indicate very high resistance to air passage through the fabric for all of the samples.

TABLE 7

PROPERTIES OF EXPERIMENTALLY-TREATED NOMEX FABRICS

Property	109-68-E	109-68-C	109-68-A	109-68-F	109-68-B	109-68-D
Warp Ends per Inch	63.2	62.8	62.0	62.6	63.0	62.2
Filling Picks per Inch	49.0	49.0	48.8	49.0	49.0	48.4
Weight, oz/sq.yd.	7.23	7.09	6.42	7.16	7.46	6.27
Thickness, inch	.012	.012	.010	.011	.011	.009
Flexibility: Bending Length, inches: Warp	4.77	4.10	3.53	4.56	4.40	3.23
Fill	7.07	3.44	3.55	5.70	3.62	4.20
Air Permeability, cu.ft./min.sq.ft.	3.2	2.6	1.7	1.9	2.2	2.4
Breaking Strength, lbs. Warp	247	241	241	254	219	242
Breaking Strength, lbs. Fill	189	176	177	185	186	170
Abrasion Resistance: Breaking Strength, lbs.: Warp	197	227	191	212	232	88
Breaking Strength, Retained	79	94	79	84	106	36
Breaking Strength, lbs., Fill	179	189	145	190	179	64
Percent Strength Retained	95	107	82	103	96	38

Breaking Strength

Breaking strength was measured according to ASTM method D 1682, 1-inch ravelled strip test. Filling strength of all samples was approximately the same, while warp strength of sample B was lower than that of the other samples.

Abrasion Resistance

This property was measured following ASTM method D 1175, flexing and abrasion method. Specimens 1 1/2" x 10" were ravelled to a width of 1 inch and abraded for 900 cycles with a tension load of 4 pounds and a head load of 1 pound. Strength of the abraded specimens was measured according to ASTM method D 1682. Percent breaking strength retained is shown in Table 7 and indicates that all of the treatments, including the blank dyeing, improved the abrasion resistance.

Results of the warp ends and picks per inch indicate that little dimensional change occurred during the treatment. The weight measurements show a 13 to 19% increase in weight as a result of treatment. From the appearance of the fabric it is probable that at least part of this weight increase is due to chemicals on the fabric surface which were not completely removed by the after-scouring step. Fabric flexibility was decreased somewhat as a result of the treatment.

One result which was not expected was the increase in abrasion resistance observed for the treated fabrics and the blank-dyed fabric. It is apparent that the dyeing operation has a very beneficial effect on abrasion properties and may be due to either lubrication of the fabric by carrier components or to changes due to thermal treatment during the process.

Treated, control and blank-dyed samples were tested also in accordance with DOC-FF-3-71. Measurement of after-flame times, afterglow times and char lengths are given in Table 8. Afterglow times were comparable for all the samples tested and with the exception of sample 109-68-E, the char lengths were similar. Greater variation was observed in the afterflame times. Samples 109-68-E and 109-68-C appear to have higher afterflame times. Since samples 109-68-E and 109-68-C both have 33% Oxanilide,

TABLE 5
RESULTS OF VERTICAL FLAME TEST ON CONTROL,
TREATED, AND BLANK-DYED FABRICS

<u>Sample</u>	<u>Afterflame Time (sec.)</u>	<u>Afterglow Time (sec.)</u>	<u>Charlength</u>
109-68-D warp	4.4	0.9	1.5
109-68-D filling	3.8	4.5	1.4
109-68-A warp	4:1	0.0	1.4
109-68-A filling	3.5	0.2	1.2
109-68-E warp	9.8	0.0	3.3
109-68-E filling	10.8	0.0	4.8
109-68-F warp	2.6	0.8	1.0
109-68-F filling	3.8	0.0	1.6
109-68-C warp	14.1	0.0	2.1
109-68-C filling	15.9	0.0	1.4
109-68-B warp	8.1	0.0	2.5
109-68-B filling	2.1	0.6	0.9

this component of the treatment system may have an adverse effect on flammability. Reduction in the level of oxanilide in the treatment selected for final recommendations was considered as this appears to be the least effective component in improving the UV stability of Nomex.

C. Improvement in Treating System

Some disadvantages of the treatment system were noted during preparation of the six samples described above. The dyeing assistant used was not properly emulsified for use in a low agitation system such as the pressure jig. Accumulation of solids during the treatment cycle made cleanup of the jig and the fabric at the end of the treatment a major problem.

A survey of dyeing systems that would be useful for Nomex treatment was conducted and a jet dyeing machine was evaluated for this purpose. The jet machine with high agitation of the dye liquor was expected to offer some advantages over the pressure jig.

Jet dyeing was investigated as a means of treating Nomex fabric. A sample of fabric 12 inches by 30 feet was treated in a mini-jet dyeing machine at the Celanese Laboratory in Charlotte, North Carolina. The treatment bath contained 33% Blancophor AW, 15% Tinuvin P and 7% Oxanilide. Results of testing of this sample (109-68-H) compared to the two best samples from dyeing (109-68-E and 109-68-F) are shown in Table 9. The 73% retention of tensile strength and 54% retention of elongation after 150 hours exposure to the carbon arc are remarkable good considering that the weight pick-up in jet dyeing was only 5.42% (compared to 15.3% for sample 109-68-E and 14.2% for 109-68-F). Jet dyeing was the treatment technique selected for preparation of large samples of Nomex fabric.

D. The Selected Treatment System

Data on strength retention for all treated fabric samples are summarized in Table 10. The quantity of each of the additives (in percent owf) in the treatment bath are shown in parenthesis for Blancophor AW, Tinuvin P, and Oxanilide, respectively. The xenon and carbon arc exposures were conducted at the Georgia Tech laboratories, the sunshine arc exposures at U.S. Testing Laboratories and the outdoor exposures at the South Florida Testing Service.

TABLE 9

COMPARISON OF NOMEX SAMPLES TREATED IN
A JET AND JIG DYEING MACHINETensile Strength

<u>Sample</u>	<u>0 hrs</u>	<u>50 hrs</u>	<u>100 hrs</u>	<u>150 hrs</u>	<u>200 hrs</u>
109-68-E	247	193	180	186	199
109-68-F		197	146	133	149
109-68-H	229	167	157	167	161

Elongation

<u>Sample</u>	<u>0 hrs</u>	<u>50 hrs</u>	<u>100 hrs</u>	<u>150 hrs</u>	<u>200 hrs</u>
109-68-E	57	30	27	28	29
109-68-F	63	28	28	27	33
109-68-H	63	37	34	34	31

TABLE 10

STRENGTH RETENTION (%) OF TREATED NOMEX
FABRICS AFTER EXPOSURE

Carbon Arc Exposure

Sample	% Tensile Strength Retention			
	50 hr	100 hr	150 hr	200 hr
109-68-E (33,33,33)	78	73	75	80
109-68-F (15,50,15)	76	58	52	59
109-68-C (0,50,33)	77	50	44	49
109-68-B (0,50,0)	66	57	60	58
109-68-D (0,0,0)	67	52	66	55

Sunshine Arc Exposure

Sample	% Tensile Strength Retention			
	50 hr	100 hr	150 hr	200 hr
109-68-E (33,33,33)	72	77	70	55
109-68-F (15,50,15)	69	63	63	54
109-68-C (0,50,33)	65	62	55	53
109-68-B (0,50,0)	70	67	62	60
109-68-D (0,0,0)	63	64	53	48

Xenon Arc Exposure

Sample	% Tensile Strength Retention			
	50 hr	100 hr	150 hr	200 hr
109-68-E (33,33,33)	90	86	82	80
109-68-F (15,50,15)	89	82	79	73
109-68-C (0,50,33)	79	70	66	61
109-68-B (0,50,0)	87	74	72	67
109-68-D (0,0,0)	77	73	67	67

Florida Sunshine

Sample	% Tensile Strength Retention		
	1 month	2 months	3 months
109-68-E (33,33,33)	73	50	50
109-68-F (15,50,15)	69	52	47
109-68-C (0,50,33)	68	53	47
109-68-B (0,50,0)	72	60	55
109-68-D (0,0,0)	69	53	49

It is apparant from these data that, with the exception of the South Florida exposures, those fabrics with all three additives (Samples 109-68-E and 109-68-F) performed best. In the South Florida exposures Sample 109-68-B containing only Tinuvin P was comparable to 109-68-E. It was decided that the treatment system used for large fabric samples should contain both Blancophor AW and Tinuvin P at 33% (owf) in the treatment bath. It was decided that oxanilide, although apparantly effective in the three component systems, was more effective at lower concentrations. Also, flammability studies reported earlier suggested that oxanilide at high levels may increase the flammability as measured by the vertical flame test. Therefore, an oxanilide level of 50% (owf) was selected for the large fabric and webbing samples.

SECTION IV

PREPARATION AND EVALUATION OF FABRIC AND WEBBING SAMPLES

A. Preparation of Fabric Sample

Final evaluation of the selected stabilizer system was carried out by treating 200 yards of Nomex sage green fabric (Mil-C-38-351, Type II, Class I) and 100 yards of Nomex sage green webbing (Mil-W-38283, Type XII). The fabric was obtained from Stern and Stern Textiles and the webbing was produced by Murdock Webbing Company.

The fabric sample was treated in a Gaston County 100# Jet Dyeing Machine at the Monsanto Textile Company laboratories in Decatur, Alabama.

The dyeing machine was filled with 350 gallons of water, the fabric (109 pounds) was entered and wet-out by passing through the jet at 150 yards per minute. The temperature was raised to 120°F at 3°F per minute prior to addition of the treatment chemicals. A treatment solution concentrate was prepared by dispersing

36 pounds Blancophor AW	(33% owf)
36 pounds Tinuvin P	(33% owf)
5.5 pounds Oxanilide	(5% owf)

in 17.5 gallons of Chemocarrier FPN (Tanatex). The Blancophor AW and Oxanilide were soluble in the carrier but the Tinuvin P is not soluble at room temperature. The treatment solution was placed in the add tank, heated with steam to approximately 120°F and added to the jet machine by circulating part of the bath through the add tank. After complete addition of the stabilizer the temperature was raised to 270°F at 3°F per minute and held at 270°F for 2 hours. The bath was cooled to 160°F at 3°F per minute and overflow rinsed for 10 minutes (about 2 bath volumes). The bath was then discharged and the dyeing machine refilled with water and heated to 160°F. A scouring agent, Merspol LFH (1%), was added and the fabric run for 10 minutes followed by 10 minutes of overflow rinsing. The bath was then dumped and the scouring step repeated twice. Following the scouring, the sample was overflow rinsed for 10 minutes, unloaded, vacuum extracted to remove excess water and dried (33 seconds at 250°F followed by 33 seconds at 300°F).

B. Preparation of Webbing Sample

Approximately 100 yards of Nomex webbing (Mil-W-38283, Type XII) were given the selected treatment to improve resistance to UV degradation. The webbing was woven by Murdock Webbing Company, Inc. and treated in a Gaston County Sample Jet Dyeing Machine, Model PBJ-1100, at Hoechst Fibers laboratories in Greenville, South Carolina. The webbing was loaded in the jet machine (25 pounds) and the machine filled with 125 gallons of water at 120°F. The temperature was raised to 190°F at approximately 3°F per minute. The treatment solution containing 8.25 pounds of Blancophor AW, 8.25 pounds of Tinuvin P, and 1.25 pounds of oxanilide dispersed in 6.25 gallons of Chemocarrier FPN was added through the expansion tank at 190°F. The treatment bath was heated to 265°F at 3°F per minute and held at that temperature for 2 hours. Following the treatment, the bath was lowered to 190°F and dropped. The sample was then hot rinsed at 170°F for 5 minutes and overflow rinsed at 160°F for 15 minutes. The webbing was scoured at 160°F for 5 minutes in 2% (owf) Mergol LFH followed by a 5 minute overflow rinse at 160°F. The sample was then given a cold running rinse for 20 minutes squeezed dry in a pad and dried at 300°F in a 20 foot dryer at 2 yards per minute. The treated webbing was returned to Murdock Webbing Company for resin treatment as specified for Mil-W-38283, Type XII.

C. Evaluation of Treated Fabric

Specimens of treated and untreated fabric were exposed for periods of 50, 100, 150 and 200 hours to the xenon arc, carbon arc, and Sunshine arc lamps. Breaking load and elongation were determined in the warp and filling direction after each exposure period by the 1" ravel strip method described previously. Breaking strength and elongation before and after exposure to xenon, carbon and Sunshine arc lamps are given in Tables 11, 12 and 13; the retention of breaking strength (in percent) in Tables 14, 15 and 16; and the retention of elongation (in percent) in Tables 17, 18, and 19.

It is apparent from these data that the treatment system resulted in significant improvement in the UV resistance of the Nomex fabric. Tensile strength for the treated fabric after 150 hours exposure to the Sunshine arc was 89% in the warp direction and 87% in the filling direction compared to 49% and 46% for the untreated fabric. Similar results (83 and 78% versus 58 and 53%)

TABLE 11

BREAKING STRENGTH AND ELONGATION OF UNTREATED
AND TREATED NOMEX SPECIMENS BEFORE AND AFTER
EXPOSURE TO SUNSHINE ARC LIGHT.

<u>Material and Pull Direction</u>		<u>Hours Exposed</u>				
		<u>0</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated						
Warp -	Breaking Load	249.2	166.6	137.8	123.0	104.6
	Elongation (%)	47.8	21.3	16.9	15.9	18.9
Filling -	Breaking Load	199.0	123.6	91.8	91.8	59.2
	Elongation (%)	39.9	12.1	7.2	6.7	6.1
Treated						
Warp -	Breaking Load	247.8	220.6	222.2	220.8	208.2
	Elongation (%)	54.5	41.3	42.0	40.3	38.9
Filling -	Breaking Load	209.4	178.2	185.0	181.8	179.2
	Elongation (%)	43.6	23.7	24.4	24.3	24.6

TABLE 12
BREAKING STRENGTH AND ELONGATION OF UNTREATED
AND TREATED NOMEX SPECIMENS BEFORE AND AFTER
EXPOSURE TO XENON ARC LIGHT.

<u>Material and Pull Direction</u>		<u>Hours Exposed</u>				
		<u>0</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated						
Warp -	Breaking Load	249.2	179.2	159.4	144.0	134.6
	Elongation (%)	47.8	24.6	20.8	18.2	16.5
Filling -	Breaking Load	199.0	148.6	125.6	105.2	90.4
	Elongation (%)	39.9	14.9	9.7	7.8	7.0
Treated						
Warp -	Breaking Load	247.8	226.4	212.4	204.6	208.6
	Elongation (%)	54.5	41.3	37.2	34.0	35.1
Filling -	Breaking Load	209.4	180.4	171.6	163.8	167.0
	Elongation (%)	43.6	25.3	21.6	19.0	20.8

TABLE 13

BREAKING STRENGTH AND ELONGATION OF UNTREATED
AND TREATED NOMEX SPECIMENS BEFORE AND AFTER
EXPOSURE TO CARBON ARC LIGHT.

<u>Material and Pull Direction</u>		<u>Hours Exposed</u>				
		<u>0</u>	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated						
Warp -	Breaking Load	249.2	170.2	134.2	122.0	106.4
	Elongation (%)	47.8	22.5	18.7	22.6	20.4
Filling -	Breaking Load	199.0	125.6	97.0	79.0	63.8
	Elongation (%)	39.9	11.9	7.0	7.3	6.7
Treated						
Warp -	Breaking Load	247.8	212.4	180.0	133.2	130.0
	Elongation	54.5	36.6	29.5	27.1	25.9
Filling -	Breaking Load	209.4	174.4	135.2	101.8	96.4
	Elongation (%)	43.6	21.5	15.3	11.0	8.9

TABLE 14
TENSILE STRENGTH RELATION (%)
(SUNSHINE ARC LIGHT)

<u>Sample</u>	<u>Duration of Exposure in Hours</u>			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated Nomex				
Warp	66.9	55.3	49.4	42.0
Filling	62.1	46.1	46.1	39.7
Treated Nomex				
Warp	89.0	89.7	89.1	84.0
Filling	85.1	88.3	86.8	85.6

TABLE 15
TENSILE STRENGTH RETENTION (%)
(XENON ARC LIGHT)

<u>Sample</u>	<u>Duration of Exposure in Hours</u>			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated Nomex				
Warp	71.9	64.0	57.8	54.0
Filling	74.7	63.1	52.9	45.4
Treated Nomex				
Warp	91.4	85.7	82.6	81.2
Filling	86.2	81.9	78.2	79.8

TABLE 16
TENSILE STRENGTH RETENTION (%)
(CARBON ARC LIGHT)

<u>Sample</u>	<u>Duration of Exposure in Hours</u>			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated Nomex				
Warp	68.3	53.9	49.0	42.7
Filling	63.1	48.7	39.7	32.1
Pre-treated Nomex				
Warp	85.7	72.6	53.8	52.5
Filling	83.3	64.6	48.6	46.0

TABLE 17
 ELONGATION RETENTION (%)
 (SUNSHINE ARC LIGHT)

<u>Sample</u>	<u>Duration of Exposure in Hours</u>			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated Nomex				
Warp	44.6	35.4	33.3	39.5
Filling	30.3	17.6	16.8	15.3
Treated Nomex				
Warp	75.8	77.1	73.9	71.4
Filling	54.4	56.0	55.7	56.4

TABLE 18
 ELONGATION RETENTION (%)
 (XENON ARC LIGHT)

<u>Sample</u>	<u>Duration of Exposure in Hours</u>			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated Nomex				
Warp	51.5	43.5	38.1	34.5
Filling	37.3	24.3	19.5	17.5
Treated Nomex				
Warp	75.8	68.3	62.4	64.4
Filling	58.0	49.5	43.6	47.7

TABLE 19
ELONGATION RETENTION (%)
(CARBON ARC LIGHT)

<u>Sample</u>	<u>Duration of Exposure in Hours</u>			
	<u>50</u>	<u>100</u>	<u>150</u>	<u>200</u>
Untreated Nomex				
Warp	47.1	39.1	47.3	42.7
Filling	29.8	17.5	18.3	16.8
Treated Nomex				
Warp	67.2	54.1	49.7	47.5
Filling	49.3	35.1	25.2	20.4

were obtained for xenon arc exposure. The carbon arc appears to be a much more severe exposure source as the treated fabric retains 54 and 49% of the tensile strength in the warp and filling direction and the untreated sample only 49 and 40%. Retention of elongation after exposure of treated and untreated samples shows trends that are very similar to the tensile strength retention data.

D. Evaluation of Webbing Samples

The breaking strength of webbing samples was determined in accordance with FED-STD-191-4108 except that only 3 specimens were tested for each condition. This modification was made due to the very large quantity of material required for each test. Data on breaking strength of webbing (treated and untreated) before and after 150 hours exposure to the Sunshine arc are given in Table 20. There is little loss in breaking strength due to exposure of the webbing to UV light. This is undoubtedly due to the thickness of the webbing. Most of the fibers are not exposed to the UV light in this type structure. The control fabric retained 93% of the original strength and the treated fabric was essentially undegraded by the exposures. More extensive exposures were not undertaken, again, due to the large quantity of webbing required for breaking strength tests.

TABLE 20

TENSILE STRENGTH OF NOMEX WEBBING
BEFORE AND AFTER SUNSHINE ARC EXPOSURE

<u>Tensile Strength (pounds)</u>		
Untreated	<u>0 hours exposure</u>	<u>150 hours exposure</u>
	6300	5860
	6260	5860
	<u>6240</u>	<u>5840</u>
	AV 6267	AV 5853
Treated	5660	5640
	5720	5720
	<u>5660</u>	<u>5660</u>
	AV 580	AV 5673

SECTION V

CONCLUSIONS

The objective of this project was the development of a treatment system for Nomex fabric which would yield 75% retention of the tensile strength after 150 hours exposure to the Atlas Sunshine Carbon Arc Fade-Ometer. This objective was achieved by treatment of fabric samples with a solution containing 33% (owf) Blancophor AW, 33% (owf) Tinuvin P, and 5% (owf) Oxanilide using Chemocarrier FPN as a carrier in a modified jet dyeing procedure. Retention of tensile strength of treated samples was 89% in the warp direction and 87% in the filling direction after exposure for 150 hours to the sunshine arc lamp. Untreated fabrics show less than 50% retention of tensile strength under similar exposure conditions.

Most typical UV stabilizers have little effect on the stability of Nomex to UV exposures. Seventy five materials were screened for effectiveness in stabilizing Nomex but only Blancophor AW, Oxanilide, and Tinuvin P improved the light stability.

SECTION VI

RECOMMENDATIONS

Attempts should be made to optimize the stabilizer system to achieve more economical treatment. It may be possible to reduce the quantity of stabilizers used significantly with little or no reduction in UV stability.

A "standing bath" solvent treatment technique would probably be preferred to the modified drying procedure used in the present work. Such a system could substantially reduce the cost of treating Nomex to improve UV stability.

More extensive outdoor exposure studies should be conducted on treated Nomex samples for comparison with the data obtained by carbon arc and xenon arc exposure.

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APPENDIX A

LITERATURE SURVEY

The computer search of Chemical Abstracts from July, 1968, to Dec. 1975, has been completed using the list of descriptors shown in Table 1. The computer listed over 1,000 citations of which 188 were selected for inclusion in the bibliography shown in the Appendix. Many references to new aromatic amide compositions showing improved thermal stability and references to the more prosaic and standard stabilizers for thermal degradation of aliphatic amides were not included in the list as these subjects are less pertinent to the present work. The selected references have been divided into 12 categories.

- A. General Papers on UV Degradation
- B. UV Degradation of Nylon 6 and Nylon 6,6
- C. Thermal Degradation of Nylon 6 and Nylon 6,6
- D. Thermal Stabilizers for Nylon 6 and Nylon 6,6
- E. UV Stabilizers for Nylon 6 and Nylon 6,6
- F. Thermal Degradation of Aramids
- G. UV Degradation of Aramids
- H. Thermal Stabilizers for Aramids
- I. UV Stabilizers for Aramids
- J. Dyeing of Aramids
- K. Stability and Degradation of Phenolic Fibers
- L. Photochemistry of the Amide Bond

In the important area of UV stabilizers for Aramids 13 references were discovered. Many of the stabilizers reported are not practical systems for use on Nomex fabric. The literature, therefore, provided little guidance in selection of compounds for Nomex stabilization.

Twelve references have been found that discuss the mechanism of radiation and UV degradation of Nomex and other aramids. These references were useful in selection of some materials for screening studies.

TABLE 1.
DISCRIPTOR LIST NOMEX DEGRADATION SEARCH

Group	Term No.	Term	Group	Term No.	Term
G001	1	Nomex	G002	23	*Phenyl*
G001	2	Aramid	G002	24	*Phthal*
G001	3	Poly(1,3-Phenylene Isophthalamide)	G002	25	*Tolyl*
G001	4	Poly(1,4-Phenylene Terephthalamide)	G002	26	*Prydyl*
G001	5	Poly(1,3-Phenylene Terephthalamide)	G002	27	*Naphthyl*
G001	6	Poly(1,4-Phenylene Isophthalamide)	G002	28	*Aryl*
G001	7	Poly(4-Aminobenzoic Acid)	G002	29	*Anthryl*
G001	8	Poly(3-Aminobenzoic Acid)	G002	30	Arene*
G001	9	Kevlar	G003	31	Poly*
G001	10	Fiber B	G003	32	Macromol*
G001	11	HT-1	G003	33	Macromol*
G001	12	HT-4	G004	34	*Amide*
G001	13	PRD 49	G005	35	UV
G002	14	Aromatic*	G005	36	U.V.
G002	15	Arom	G005	37	U. V.
G002	16	*Benz*	G005	38	Ultraviolet
G002	17	*Isoquino*	G005	39	Ultra-violet
G002	18	*Indol*	G005	40	Light
G002	19	*Iden*	G005	41	Decompos*
G002	20	*Indazol*	G005	42	Decompn
G002	21	*Indanyl*	G005	43	Degrad*
G002	22	"Fluoren"	G005	44	Degrdrn

TABLE 1. (cont'd.)

DISRIPTOR LIST NOMEX DEGRADATION SEARCH

Group	Term No.	Term	Group	Term No.	Term
G005	45	Breakdown*	G006	61	Thermal
G005	46	Break-down*	G006	62	*Flam*
G005	47	Breaking Down*	G006	63	Fire*
G005	48	Unzip*	G007	64	Resist*
G005	49	Cleav*	G007	65	*Proof*
G005	50	*Stabi*	G007	66	*Retard*
G005	51	*Stable*	G008	67	Nylon*
G005	52	Deteriorat*	G009	68	High Temp*
G005	53	Degenerat*	G009	69	Nonflammable
G005	54	Reaction	G009	70	Non-flammable
G005	55	Depolymeriz*	G010	71	Kynol
G005	56	Depolymn	G010	72	Polybenzimidazole
G005	57	Hydroly*	G010	73	Poly (Benzimidazole)
G005	58	Solvoly*	G010	74	PBI
G005	59	Photoly*	G010	75	P.B.I.
G006	60	Heat	G010	76	P. B. I.

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APPENDIX B

STABILIZERS FOR E-11 NOMEX FABRIC

Samples of the experimental E-11 (which is considered for replacement of Nomex in stable yarn applications) Nomex fabrics have been treated in "dyebaths" containing Tinuvin P and Blancophor AW. The treated fabrics have been exposed for 20 and 60 hours in the carbon-arc fadeometer and the elongation and breaking strength determined in the warp direction by the 1" ravel strip method. Results are shown in Figures B-1 and B-2 where percent retention of breaking strength and elongation are compared for treated and blank dyed samples. These results clearly indicate that systems which stabilize regular Nomex are also effective on E-11 fabrics. The results are consistent with the proposed structure of E-11 yarn (a fiber blend of predominantly regular Nomex with a small quantity of a more thermally stable fiber).

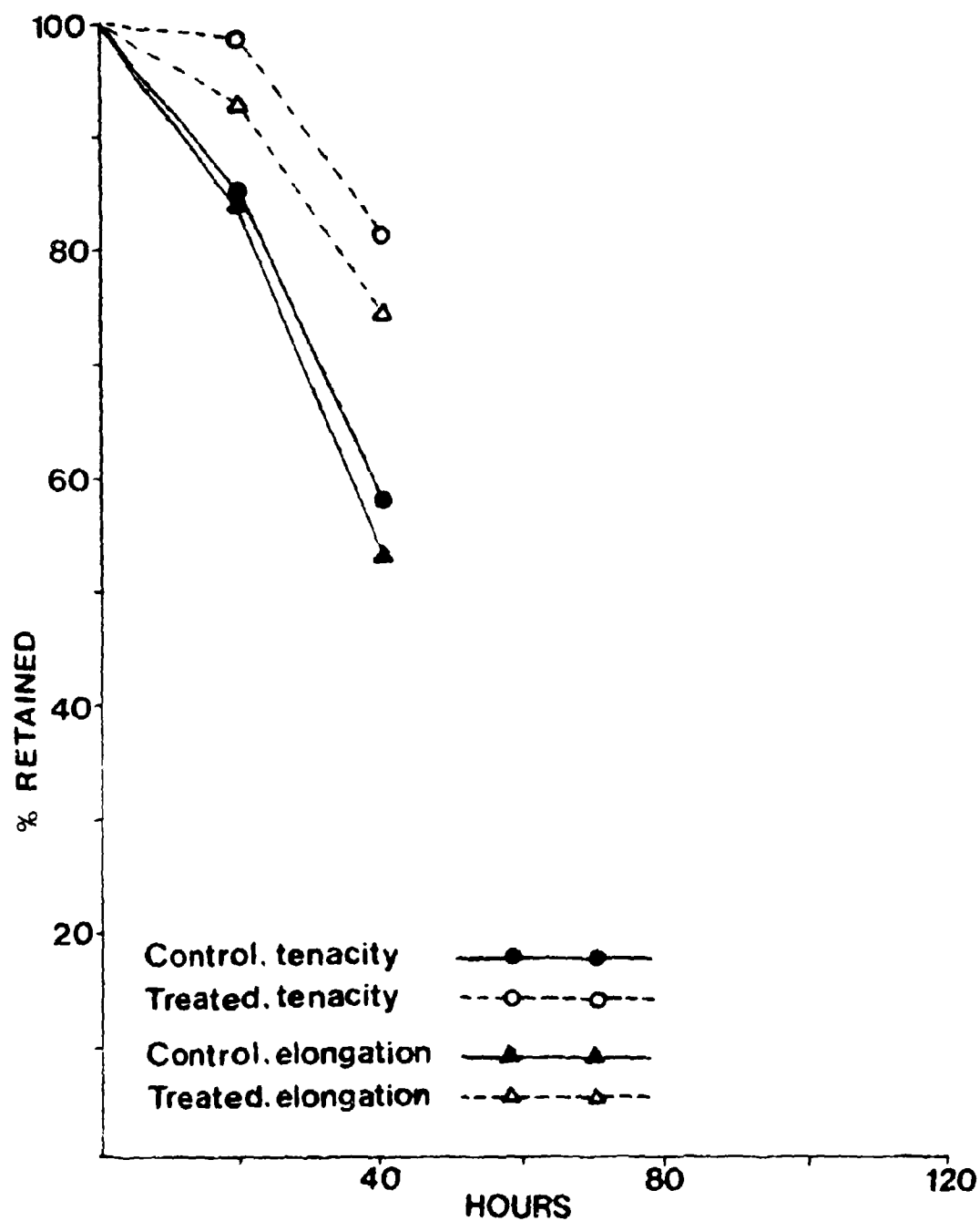


Figure B1. Retention of elongation and breaking strength for E-11 Nomex fabric containing Blancophor AW compared to blank dyed fabric.

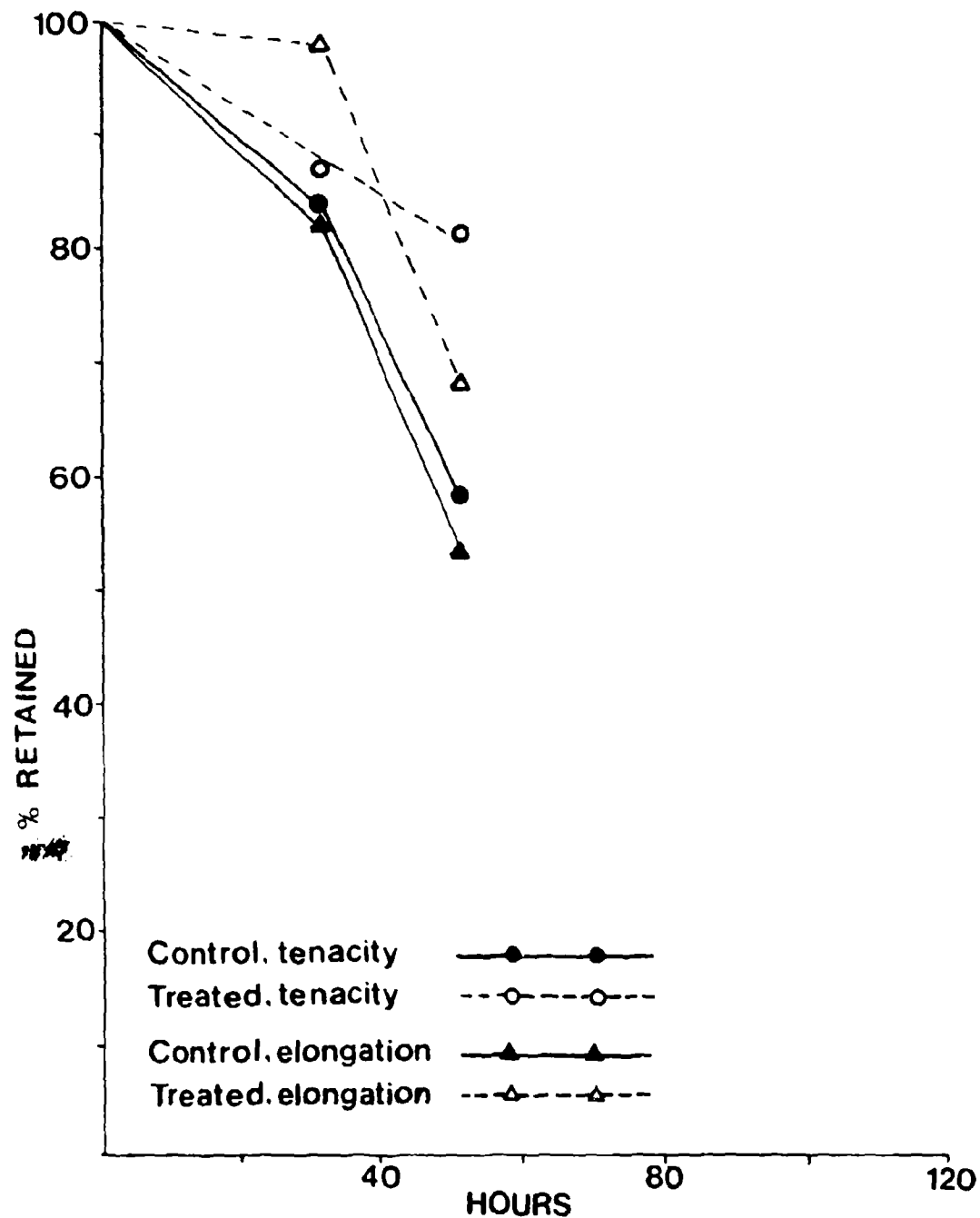
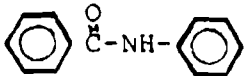
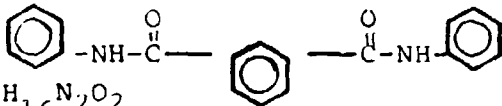
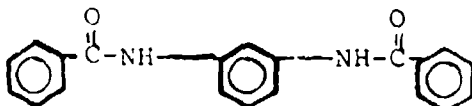


Figure B2. Retention of elongation and breaking strength for E-11 Nomex fabric containing Tinuvin P compared to control sample.

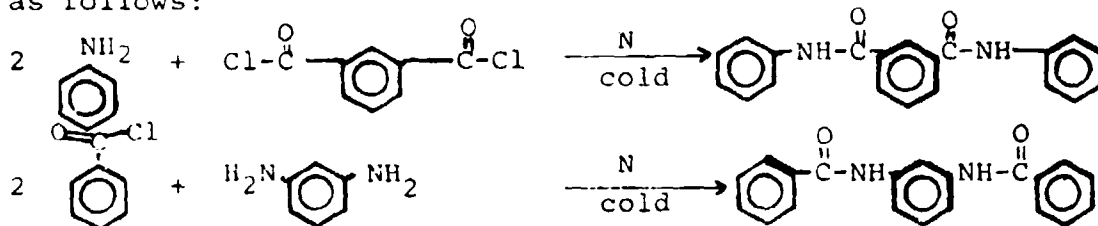
APPENDIX C

FUNDAMENTAL STUDIES ON NOMEX UV DEGRADATION

In order to evaluate the mechanistic characteristics of the UV degradation of Nomex, three model compounds were chosen for study in solid state photolysis experiments. These model Compounds were:

- 1)  Benzanilide
 $C_{13}H_{11}NO$
- 2)  Isophthalanilide or
 $C_{20}H_{16}N_2O_2$ N,N'-diphenyl-1-3-benzene-dicarboxamide
- 3)  N,N'-dibenzoyl-m-phenylene-diamine or
 $C_{20}H_{16}N_2O_2$ N,N'-m-phenylenebisbenzamine

Benzanilide was purchased from Aldrich Chemical Company at 99.9% purity. The other two models must be synthesized as follows:



The analytical data, i.e., IR, NMR, mass spectra, and melting point shown are consistent with the expected products. The thermal stability of these materials was studied by DTA/TGA in air and N_2 and compared with Nomex as shown in Table C-1.

TABLE C-1. THERMAL PROPERTIES OF NOMEX AND MODEL STRUCTURES

	wt. (mg)	Atmos.	Peak temp.	% wt. loss at peak	type peak
 $\text{C}_6\text{H}_5\text{NH}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{NH}-\text{C}_6\text{H}_5$	18.39	air	163°C	0	endo
			325°C	76	endo
			372°C	24	exo
	27.02	N ₂	164°C	0	endo
			360°C	100	endo
 $\text{C}_6\text{H}_5\text{NH}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{NH}-\text{C}_6\text{H}_5$	13.16	air	289°C	0	endo
			410°C	37	exo
	12.10	N ₂	490°C	45	exo
			633°C	18	exo
 $\text{C}_6\text{H}_5\text{NH}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{NH}-\text{C}_6\text{H}_5$	10.30	air	236°C	0	endo
			455°C	69	exo
			660°C	31	exo
	13.62	N ₂	235°C	0	endo
			377°C	31	endo
			478°C	18	exo
			640°C	31	exo
Nomex	15.30	air	312°C	4	endo
			620°C	96	exo
			765°C	96	exo
	15.27	N ₂	380°C	5	exo
			542°C	95	exo
			900°C	95	endo

The data from the DTA/TGA system were plotted as % weight loss vs. temperature. A series of four pairs of curves were obtained and the curves are of the same general shape. The nitrogen and air curves fall on top of one another. This is indicative that the materials undergo similar thermal degradation. As a matter of interest, it should be noted that Nomex in air and N_2 has the exact opposite type of DTA peak initially. In air, there is an endotherm characteristic of bond breaking and in N_2 there is an exotherm characteristic of bond formation. It is felt the exotherm is some cyclization process occurring, and this may be masking the endotherm or the endotherm may not be present at all.

Each model compound was dissolved in DMF and a 1 ml. aliquots from standard solutions were evaporated on a 3" by 1" glass slide. This procedure left behind 10 mg. of material. These samples were then mounted and exposed to UV light from a 2500 watt Xenon arc lamp source at a relative humidity of 52% and black body temperature of 106°F. As the exposure time progressed, samples of the system were removed and examined by IR, fluorescence, and UV. The first samples were removed at 154.8 hours and the last samples after 1316.7 hours. In close examination of the infrared spectra these samples, no noticeable change could be detected in the spectra. Likewise no changes in the UV or fluorescence spectra of the materials were noted. Based on the data, model compounds do not behave as the polymer Nomex on exposure to UV light. The model amides are photochemically stable under the exposure conditions.

Nomex films, however, exposed to the above UV conditions showed extensive degradation after 40 hours, with yellowing and extreme fragileness. Infrared spectra were obtained from these samples and compared to unexposed samples, as well as, differential infrared spectra. There was a shoulder forming at 1720 cm^{-1} and filling in of the troughs in the spectra of the exposed samples. A 1370 cm^{-1} peak was also found in the spectra. These agree with the data Carlson found by attenuated total reflectance infrared studies.

Recently, Roylance and Devriees found that Kevlar contains a radical concentration in the yarn as high as 10^{18} spin/cc. This finding has been confirmed in experiments here. Nomex and Kevlar yarn both contain radicals with Kevlar having the largest number.

Three Nomex and Kevlar samples were prepared so that the same amount of yarn was exposed to irradiation by carbon arc. The samples are as follows:

	<u>wt. (g)</u>	<u>exposure time</u>
1) Nomex	a) 0.1029	0
	b) 0.1048	39
	c) 0.1037	90.1
2) Kevlar	a) 0.2026	0
	b) 0.0986	39.1
	c) 0.2018	90.1
	d) 0.2042	131.1

The standards were not exposed but their electron spin resonance (ESR) spectra were recorded under the same conditions as the exposed samples. The ESR's for the samples were double integrated and the areas compared to the standards. The following data was obtained:

	<u>Area</u>	<u>Relative Amounts</u>	<u>Exposure Time</u>
1) Nomex	a) 12836	1	0
	b) 512100	70	39
	c) 1268880	99	90.1
2) Kevlar	a) 6.45×10^6	1	0
	b) 1.408×10^6	2.2	39.1
	c) 1.018×10^6	1.58	131.2

The data shows a hundred-fold increase in the number of radicals in the 90 hour sample, while the Kevlar concentration remains the same over the duration of the exposure. These differences indicate that Kevlar contains long lived radicals buried in the polymer. Kevlar may contain an equilibrium concentration of radicals since there was no change in the radical concentration. The Nomex, however, generates radicals and these radicals may be the intermediates which cause Nomex's photoinstability. The radicals may be considered short lived relative to Kevlar, since meta substituted systems cannot stabilize the radicals to the same extent as Kevlar. Generation of the radicals in Nomex at least should lead to a drop in the $\bar{M}_w$. The radicals may be quenched before recombination can occur and this would cause a drastic change in the $\bar{M}_w$, as noted by Carlson.

Conclusion

1) The model compounds did not behave as the polymer Nomex in UV exposure experiments.

2) Since the models are dimer units and are stable, one must consider that some unit larger than the repeat unit of Nomex is responsible for degradation. An impurity in the polymer is a second attractive possibility.

3) Large members of stable free radicals are present in Kevlar. Nomex also contains stable radicals and the concentration increases on exposure of Nomex to UV light.