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NOMEX ULTRAVIOLET INHIBITORS

John F. Krasny, et al

Gillette Company Research Institute

Prepared for:

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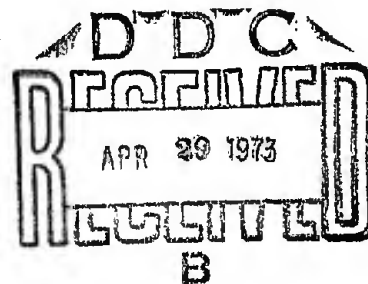
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## NOMEX ULTRAVIOLET INHIBITORS

*JOHN F. KRASNY AND A. M. SCHWARTZ*  
*THE GILLETTE COMPANY RESEARCH INSTITUTE*

TECHNICAL REPORT ASD-TR-72-104

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13. ABSTRACT  Investigation has been made of several systems intended to improve the resistance of Nomex fabric and webbing to actinic degradation. All of these consisted in applying to the Nomex a material that absorbs actinic radiation in the range 360 - 390 nm, which is known to be the wavelength involved in the photochemical degradation. Several materials are available that meet this primary requirement, but relatively few meet the added requirements of stability, safety in application and use, and lack of undesirable effects on the fabric. A major problem proved to be the durable and satisfactory bonding of the protective material to the Nomex. Best results were obtained by applying a pigment that was opaque to the harmful radiation (carbon-black) in a lacquer type polymeric "tie-coat" or binder. A vinyl resin was used as the major ingredient of the tie-coat.  As a stipulated part of this investigation a complete survey was made of the technical literature relating to actinic degradation of polyamides. This is included as an appendix.			

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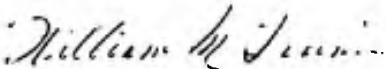
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## FOREWORD

This final technical report was prepared by The Gillette Company Research Institute, 1413 Research Boulevard, Rockville, Maryland 20850, under Contract F33657-70-C-0858, Nomex Ultraviolet Inhibitors. The program was sponsored by Life Support System Program Office. Technical direction was provided by the Nonmetallic Materials Division, Air Force Materials Laboratory, Directorate of Laboratories, with Mr. P. C. Opt as Technical Monitor.

The work herein reported was performed during the period April 1970-September 1972. This report was submitted for approval November 1972.

This technical report has been reviewed and is approved.



WILLIAM M. QUINN, Colonel, USAF  
System Program Director  
Life Support System Program Office  
Deputy for Subsystems

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## I. INTRODUCTION

The aromatic polyamide fiber, Nomex\*, is of particular interest for a number of Air Force applications because it exhibits some of the physical characteristics of nylon, but has much higher thermal stability; does not support combustion; and does not melt when in contact with a flame. However, Nomex is susceptible to serious actinic degradation from natural and artificial light sources. Items such as parachute packs discolor and lose strength from exposure to sunlight when stored in ready-to-use position in aircraft on alert. The present program was initiated to investigate the use of chemical systems to reduce actinic degradation of Nomex.

Basically, the program consisted of an extensive literature search (Appendix II) and an experimental phase. In the literature search emphasis was placed on the actinic degradation of Nomex and on means to overcome it. However, references to the actinic degradation of all polyamides, not only to the aromatic polyamide, Nomex, are included.

It became apparent in the beginning of this program, as a result of our literature search, discussions with duPont, and some of our preliminary experiments, that Nomex absorbs light at a higher wavelength than most other polymers. The degradation of the strength of Nomex occurs within the wavelength region of 310 - 390 nm with a peak between 360 - 390 nm. Since most commercial u.v. absorbers rapidly lose effectiveness at wavelengths above 340 - 365 nm, extension of the effective protection range was required. This might logically be accomplished by including with the u.v. absorber a material which absorbs strongly in the 360 - 390 nm region. We shall refer to such materials as extenders. Based on this information, a series of compositions was selected for application to Nomex fabrics and webbings. These consisted of commercial u.v. absorbers, alone and in combination with various extenders.

Methods for applying such compositions to Nomex have not previously been described, and their development was accordingly a pioneering effort. Various techniques analogous to dyeing were tried. These included applications from aqueous baths with and without carriers, and from swelling and nonswelling \*Registered trade mark for E.I. du Pont de Nemours high temperature resistant aromatic polyamide.

solvents. Best adhesion of the protective systems to Nomex was achieved by compounding them with resins, plasticizers, and heat stabilizers to form a paint which could be applied as a coating to the fabric. The binder portion of this paint (polymer, plasticizer, etc.) is referred to as the "tie coat" or "tie coating". Extenders were found which provided good protection against actinic light. These materials which (like the uv absorbers) were soluble in the vinyl resin tie coating mixture, bloomed out of it on drying. An attempt was then made to use insoluble pigment protective systems in the tie coating. The first pigment tried, carbon black, resulted in good adhesion, no blooming, and promising protection against actinic degradation.

The following properties were evaluated:

Effectiveness against actinic degradation of the Nomex, as measured by the retention of load-elongation properties of yarns after carbon arc exposure;

Load-elongation properties of the Nomex fabric and webbings after treatment: These do not always remain constant, e.g., application of uv absorbers from swelling solutions changed the load-elongation characteristics so extensively that fabrics and webbings would have to be reengineered;

Resistance to laundering, solvents, and abrasion or effectiveness of treatments (tumble drying and passing through buckles were employed as simulants of in-service abrasion);

Discoloration: compromises had to be made in this area because compounds which protect against radiation in the 360 - 390 nm region are yellow, and protective pigments also discolor the fabrics and webbings;

Flexibility: this was a problem with the resin coatings but could be minimized by the use of plasticizers;

Stability in storage: this presented great difficulties in some of the most successful protective systems applied with resin tie coatings;

Medical safety in both application and use.

This final report summarizes the technical effort leading to the pilot scale application of the treatment using carbon black pigment in a tie coat. The treatments which were eliminated during the lengthy effort because of one or more deficiencies are described only briefly. The products used in this work are described in chemical terms in Appendix I.

## II. METHODS AND MATERIALS

### A. Fabrics and Webbing

The Nomex yarn required to accomplish this program was purchased from E. I. duPont de Nemours and Company, Inc. by our weaver subcontractors. The Nomex webbing was purchased from Alliance Webbing, Inc. It conforms to MIL-W-38283 (U.S.A.F.) specification, Type XII, sage green, 200 denier, with the finish omitted. The Nomex fabric was purchased from Stern and Stern Textiles, Inc., according to MIL-C-38351 specification, Type II, Class 1, sage green, again with the finish omitted. A similar white fabric was obtained from the same manufacturer, and used in much of the screening effort, because the white fabric was more subject to actinic degradation than the sage green fabric and discoloration could be more easily detected. In addition to untreated Nomex fabrics and webbing, nylon fabric (MIL-C-7219, Type III) and webbing (MIL-W-4088, Type XXII) were used as controls in the carbon arc exposures.

### B. Protective Systems

The protective systems are listed in Table I, along with information pertaining to the method of application. Basically, they consisted of commercial u.v. absorbers; "extenders", i.e., compounds which offer protection in the wavelength range in which Nomex is most sensitive, 360 - 390 nm, and which is beyond the effective range for commercial u.v. absorbers; elemental iodine; protective pigments; and specially synthesized adducts of polyethyleneimine and commercial u.v. absorbers.

### C. Methods of Application

The original contract called for treatment and carbon arc exposure in yarn form. However, this was found difficult, because of excessive fraying of the yarns, and fabric samples were treated except at the inception of the work. In crossover tests, the yarns from the fabrics seemed to suffer at least as much actinic degradation as those exposed in yarn form. All fabrics and webbing were cleaned by repeated immersion in solvent.

Most applications of protective systems were made by padding, double dip-double nip, or triple dip, triple nip, followed by slow drying and exposing the sample in an oven to the melting temperature of the tie coating, u.v. absorber, or extender, to obtain better coverage and adhesion. In the case of the adduct of an uv absorber and a polyethyleneimine, samples were immersed in beakers and shaken. Other samples were exposed to iodine vapor in closed systems. In the padding treatments several different solvents were used. These included both swelling and non-swelling solvents and carrier solvents for the actinic absorbing materials. Times and temperatures of immersion were varied. In some of the treatments a resinous tie coat was used to improve retention of the actinic absorber by the fiber.

### D. Exposure of Nomex to Carbon Arc Weather-Ometer

For exposure to the carbon arc light (Fed. Std. 191 Textile Test Methods 4804 and 5804), the fabrics were cut into strips with the warp in the length direction. Most samples were exposed at both ambient conditions in the Weather-Ometer, as well as at approximately 100% r.h. This latter was accomplished by placing 30 ml of distilled water in Pyrex test tubes, 38 mm in diameter. The samples were suspended between two binder clips and lowered in the tubes so that they remained above water level. A copper wire was attached to the lower clamp to prevent the sample from twisting during exposure. The upper clamp was suspended from the wall of the tube. The tube was capped with aluminum foil, and attached to the Weather-Ometer with tape.

## E. Evaluation

The effect of exposure was assessed by removing yarns from the fabric and recording their load-elongation curve on an Instron Tester. Test conditions were two inch gauge length and 33%/minute extension rate. The breaking load was read from the recorder chart.

The shapes of the load-elongation curves for exposed and unexposed Nomex yarns were similar, except for the breaking point, so that load at break sufficiently characterizes the yarns. Yarns exposed to a swelling solvent, e.g., LiCl in DMF (dimethylformamide) showed changed load-elongation characteristics even before carbon arc exposure. The durability of the treatments was determined by one cycle of laundering and tumble drying in home laundering equipment according to AATCC Test Methods 124-1969, I.B. In some cases, webbing was passed five times through the buckle of a parachute harness, to test the effect of the abrasion under typical use conditions.

## III. EXPERIMENTAL AND RESULTS

The systems applied to Nomex fabric and webbing are summarized in Table I, along with information on their advantages and disadvantages.

Two systems, one containing u.v. absorbers and extenders in resin tie coatings, and the other elemental iodine, offered good protection against actinic degradation. However, neither system could be recommended because the protective agents proved to be toxic, and could not be affixed to the Nomex so that they would not rub or flake off. The extenders bloomed from the resin coating, i.e., they continued to emerge from the surface during prolonged storage even after being removed repeatedly by leaching or laundering. The iodine also bloomed, even when covered with a resin coating. Both systems could rub off on skin or could allow escape of noxious vapors into the atmosphere.

Application of u.v. absorbers and extenders from numerous solutions was tried, and was generally unsuccessful. Somewhat promising results were obtained when application was made from solutions which swell Nomex, hot

DMF and DMF with 1% LiCl. However, these treatments reduced the modulus and yield point, and increased the elongation at break of the yarn even before exposure, though they did not greatly affect the breaking load. This approach was abandoned, because it would require re-engineering of the Air Force fabrics and webbings to obtain the desired load-elongation characteristics.

A system consisting of a tie coating and dispersed carbon black has afforded the best all around result of any of the systems tried to date. It was fully stable, exhibiting no blooming or exudation. It gave reasonably good protection on webbing (Table II) although the protection on fabric was marginal. Carbon black was the first pigment chosen for trial when it was decided that pigmented resin systems should be examined. Since this decision was made late in the program, carbon black is the only pigment tried to date. It is used in the pigmented resin system being applied to 250 yards of webbing and 100 yards of fabric in fulfilling one of the requirements of this project.

#### Systems Containing Extenders

The extenders were selected from tables in the "Handbook of Organic Structural Analysis"\* which lists the chemical composition as well as the log maximum absorption coefficient and the wavelength at which it occurs for a wide range of organic compounds. The extenders with which most work was performed were:

- DMAB - p-dimethylaminoazobenzene
- ADPH - acetone-2,4-dinitrophenylhydrazone
- PNA - p-nitroaniline
- PPAA - p-phenylazoaniline

Applications of DMAB and ADPH, together with a commercial uv absorber, from solvents and from carriers resulted in some improvement of the resistance to actinic degradation, but adhesion of the protective systems seemed

\*Y. Yukawa, Editor, W. A. Benjamin Inc., New York, N. Y., 1965.

poor. Consequently, it was decided to apply these systems in a tie coating, i.e., from solutions containing the u.v. absorber, the extender, and a resin. Table III shows that these latter treatments resulted in quite effective protection. On the basis of the results, DMF was chosen as the preferred solvent, and VMCH polyvinyl chloride terpolymer as the preferred resin. Geon 222 coatings appeared to be less effective, and Butvar B98 polybutyral tie coatings are reported to be more flammable than polyvinyl chloride (however, this resin is presently applied to nylon webbing for the Air Force). VMCH was found, however, to have poor drycleaning resistance. ADPH used as the extender seemed to provide better adhesion than DMAB and to be somewhat less yellow. ADPH is also cheaper than DMAB, and was chosen as the preferred extender for further studies. The next objective was to overcome the stiffness of resin coated fabrics and webbings, by means of plasticizers. Phosphate-based plasticizers were chosen because of their known flame resistant characteristics. The stiffness of present nylon webbing, Mil-W-27265, CON R could be matched with these plasticized formulations. Addition of a heat stabilizer, dibutyltin-di-2-ethyl hexoate, eliminated tackiness. Results of carbon arc exposure of such systems are shown in Table IV.

The following was found:

Protection against the effects of carbon arc exposure was afforded by these tie coating systems on both webbing and fabric, unlaundered and laundered, exposed at ambient conditions and at 100% r.h., and after abrasion by passing webbing repeatedly through a harness buckle.

Relatively high concentrations of Cyasorb uv 24 and ADPH were needed to provide protection, although recommendations for normal use of uv absorbers rarely exceed 1%.

Heating the bath did not improve the effectiveness of the treatments.

Choice of plasticizers or their concentration did not affect the results; concentration could then be chosen on the basis of the desired stiffness.

The unlaundered fabrics exhibited blooming, i.e. flaking off of the ADPH. The bloom was removed by laundering and did not recur immediately, but reappeared after prolonged storage. Because ADPH is toxic the treatment was not practical.

It was thought that perhaps a tie coating in which the extender was soluble in the plasticizer (ADPH was not) would not exhibit blooming. The solubility of several promising extenders in plasticizers was determined, and tie coatings containing two such products, PNA and PPAA, were applied. Table V shows the results; again, reasonable protection could be obtained but blooming persisted.

#### Systems Containing Elemental Iodine

It is reported (by the personnel at the duPont company) that elemental iodine protects Nomex from actinic degradation. We applied iodine to test the concept, in the hope that we could firmly attach it to the fabrics either by treatment from a swelling solution or by applying a tie coating on top of it. However, all such treatments resulted in flaking off, sublimation, and/or blooming of the iodine. They could not, therefore, be considered practical because of iodine's toxicity. The results of the carbon arc exposure are given in Table VI. Application from hot DMF provided good protection but resulted in decreased modulus and yield point, and increased elongation at break, before and after carbon arc exposure. Obviously, this change in load-elongation properties would require re-engineering of the fabric and webbing; if it were not due to molecular reorientation, but due to retained solvent which would eventually evaporate, toxicity problems as well as undesirable aging effects would be encountered. Exposure to iodine vapor worked well in the laboratory but would present serious difficulties on a plant scale; we know of no installed equipment which could be used. In addition, iodine has permeated all of the subsequently applied tie coatings that have been tried to date, and it is evident that containing this reactive element would be a problem.



### Pigmented Tie Coat Systems

The various extenders which were tried gave good uv protection, but failed in that they were not retained by the tie coating. It was decided to try a pigment to replace the extender, because pigments opaque to the harmful wavelengths of light could be found, and these pigments would presumably be retained by the tie coating. Carbon black was tried first. It is a common paint pigment, retained well by most polymeric coating materials, is opaque to visible and near ultraviolet light, and was therefore expected to provide protection.

The carbon black selected for use was available commercially as a dispersion with Vinylite VYHH in methyl ethyl ketone (see Appendix I). Three mixtures were made up based on this material, differing from one another in concentration of resin, plasticizer and pigment. These mixtures were applied to fabric and webbing in the same manner as previous tie-coating mixtures, i.e. by padding in three passes at room temperature. The treated goods were cured at 150° C for 5 minutes. The treatment appeared to be quite uniform, resulting in an even coating. No blooming or leaching in water occurred with either fabric or webbing. Test results are shown in Table II. On the basis of these results the composition of Sample # 1451-74 was chosen for semi-plant application. This composition contains 5% carbon black, 7.5% Vinylite VYHH (vinyl chloride-vinyl acetate copolymer), 20% plasticizer, 7% u.v. absorber and 1% stabilizer.

### Semi-Plant Scale Applications

The composition of Sample #1451-74 was applied to 250 yards of the webbing and 100 yards of the fabric. The apparatus consisted of two double roll padders in series separated by a knife scraper. The material was passed through at 10 feet per minute and a roll pressure of 3.5 pounds. It was taken up on a screen rack and passed into a solvent recovery chamber, held at 150°F to eliminate all the solvent, then passed to a curing oven, and finally cooled and rolled up. This was essentially identical to the procedure used in the laboratory applications.

The webbing took the treatment satisfactorily. The fabric was splotchy in appearance, and the finish was obviously distributed unevenly. The degree of unevenness was difficult to estimate and it is quite possible that the uv protective effect did not vary from point to point on the surface nearly so much as the appearance. In any event the finish obtained in this semi-plant run was much less uniform than that obtained with the identical formulation in the laboratory. This is ascribed to at least two factors, neither of which is inherent in the process. One is that the fabric was too wide for the padder that was used, and was put through folded. The second is that the solvent evaporated too fast for the speed of throughput; i.e. the rate of solvent evaporation was not matched to the fabric speed nor to the roll pressure. It is very probable that this could be corrected by adjustment and/or by modification of the solvent.

#### IV. CONCLUSIONS

Materials which absorb strongly in the wavelength region of 360 - 390 nm afford protection to Nomex against actinic degradation, when they are applied as a coating to the fabric surface. Of the numerous materials examined the only one that meets subsidiary requirements and appears to afford protection against actinic degradation is a coating consisting essentially of carbon black pigment in a plasticized vinyl resin vehicle. It is expected that this type of coating ultimately will prove optimal, but that it can be improved upon, presumably along the lines of more effective pigmentation and binders of greater all around suitability.

TABLE 1

SUMMARY OF EXPERIMENTAL U.V. PROTECTIVE SYSTEMS FOR NOMEX

Protective Agents	Solvent	Protection	Resistance to Laundering and Abrasion	Discoloration	Variables Investigated	Note	Details in Report
<b>A. Protective Pigments in Tie Coating<sup>1</sup></b>							
Carbon black	MEK	poor to modest	good	grey	Conc. of carbon black resin and plasticizer.	Acceptable hand can be attained by use of plasticizer.	Final Report
<b>B. U.V. Absorber and Extenders<sup>2</sup> in Tie Coating</b>							
Cyasorb UV-24 + ADPH	MEK	good	fair to good	yellow	Conc. of Cyasorb extenders, resin, plasticizers; heat stabilizers, resin types, plasticizer type; treatment time/temperature	Bleaching and leaching in water of extenders makes systems unacceptable	Final and Monthly Reports No. 10, 11, 18, 19, 18, 19
" " + DUCD							
" " + PMA							
" " + PPA							
<b>C. Elemental Iodine</b>							
From solution	DMF Xylene CCl <sub>4</sub>	good poor poor	good ---- ----	browen to gold	time/temperature ---- ---- ----	Danger of sublimation makes iodine medically unacceptable; hot DMF changes load-elongation properties of Nomex	Final and Monthly Reports No. 10, 11
Vapor treatment		good	fair to good				
<b>D. U.V. Absorber-TIE Additive</b>							
DS-49-TIE	Water	poor	poor	none	FEI mol. wts.; degree of substitution of adduct, conc., time/temp.	Not promising	Quarterly Report No. 3, Monthly Report No. 7
<b>E. U.V. Absorbers and Extenders in Solvent</b>							
Cyasorb UV-24 and ADPH	various swelling and non-swelling solvents; carriers	poor to slight	poor to slight	yellow	Conc.; addition of "quencher" time/temperature	Not promising	Quarterly Report No. 3 and Monthly Report No. 7.
Cyasorb UV-24							
TiMavis 320	various swelling and non-swelling solvents; carriers	poor	poor	----	conc. Conc. ----	Not promising	Quarterly Reports No. 2, 2, 3
Dv(ou) DS-49							

1. PVC resins, phosphate plasticizers, heat stabilizer.

2. Extenders: compounds with peak absorption between 360 - 380

TABLE II

EFFECT OF CARBON ARC EXPOSURE ON NOMEX TREATED WITH CARBON BLACK AND U.V. ABSORBER DISPERSED WITH PVC RESIN, PLASTICIZER, AND HEAT STABILIZER. 50 HOUR EXPOSURE. SAGE GREEN FABRIC AND WEBBING.

Sample No.	Substrate	Treatment <sup>1</sup>			Add on %	Hand	Strength Retention not Laundered Dry Only %	Yarn Breaking Load/lbs.		Elongation at Break/%					
		Resin <sup>2</sup> %	Plasticizer <sup>3</sup> %	Carbon Black %				Not Laundered Dry 100% RH	Laundered + TD Dry 100% RH	Not Laundered Dry 100% RH	Laundered + TD Dry 100% RH				
1451-68	Fabric	11.3	10	7.5	15	15	68	2.8	2.7	---	---	17	16	---	---
1451-78	Webbing				15	15	92	19.8	---	---	---	43	---	---	---
1451-70	Fabric	11.3	15	7.5	25	25	78	3.2	2.8	2.6	2.7	29	15	15	16
1451-79	Webbing				13	13	88	19.0	---	---	---	40	---	---	---
1451-74	Fabric	7.5	20	5	8	8	76	3.1	2.8	3.0	2.7	47	15	20	15
1451-80	Webbing				13	13	93	20.0	---	---	---	42	---	---	---
1451-58	Fabric						71	2.9	2.5	2.8	2.6	47	13	18	14
1451-62	Webbing						72	15.5	---	---	---	20	---	---	---
1451-81	Fabric						100	4.1	---	---	---	56	---	---	---
1451-82	Webbing						100	21.5	---	---	---	48	---	---	---

- 1) Treatment includes: 7% Cyasorb UV-24  
 1% dibutyl tin-di-2-ethyl hexoate, heat stabilizer  
 60% methyl ethyl ketone
- 2) A bakiite resin VHM-copolymer of vinyl chloride and vinyl acetate (87/13)
- 3) Plasticizer was Santicizer 148 - isodecyl diphenyl phosphate

TABLE III

EFFECT OF CARBON ARC EXPOSURE ON NOMEX TREATED WITH  
U.V. ABSORBERS, EXTENDERS, AND RESINS.  
50 HOUR EXPOSURE; WHITE FABRIC, SAGE GREEN WEBBING.

Sample No.	U.V. Absorber + Extenders	Treatment		Strength Retention Not Laundered Dry only	Yarn Breaking Load, lbs.		Elongation at Break, %		Remarks					
		Polymer Coating	Solvent		Add-on %	Not Laundered Dry 100% RH	Laundered Dry 100% RH	Not Laundered Dry 100% RH		Laundered Dry 100% RH				
124-1	5% U.V. 24, 5% DVB	-----	Ethanol	9.7	2.6	2.7	2.4	2.8	9	10	8	10	Gold, stiff, flatish flicks off.	
124-4	5% DVB	-----	Ethanol	5.4	3.2	3.2	2.2	3.0	12	12	9	10		
124-1	5% U.V. 24, 2.5% ADPH	5% VOM	DHF	16	3.2	3.4	3.2	--	17	18	17	--	Yellow, stiff	
124-2 <sup>1)</sup>	5% U.V. 24, 2.5% ADPH	5% VOM	DHF	23	21	--	--	--	8	--	--	--	Yellow cast, stiff	
123-1	5% U.V. 24, 2.5% ADPH	5% Gama 222	MEK	3)	3.0	3.0	3.0	--	11	14	13	--	Yellow, stiff	
123-2 <sup>1)</sup>	5% U.V. 24, 2.5% ADPH	5% Gama-222	MEK	3)	18	--	--	--	20	--	--	--	Yellow cast, stiff	
124-2	5% U.V. 24, 5% DVB	5% Butvar B58	Ethanol	25	3.8	3.8	3.7	3.8	20	20	18	18	Gold, very stiff, yarns glued together, finish flicks off.	
124-3	5% U.V. 24, 5% DVB	Butvar B72A	Ethanol	13	3.8	3.6	3.4	3.6	17	16	17	19		
Controls:														
	White Fabric												46	
	Sage Green Webbing												77	

1) UV 24 - Cyrosorb U.V. 24, a commercial U.V. absorber  
(2,2'-dihydroxy-4-methoxy benzophenone)  
ADPH-- acetone-2,4-dinitrophenylhydrazones  
DVB-- p-dimethyl aminostyrene  
added at ambient conditions

2) Sage green webbing; all other samples were white parachute fabric.  
3) Uneven treatment; add-on figures would be meaningless.

TABLE IV

EFFECT OF CARBON ARC EXPOSURE ON NOMEX TREATED WITH U.V. ABSORBER,  
EXTENDER, PVC RESIN, PLASTICIZER, AND HEAT STABILIZER.  
50 HOUR EXPOSURE: SAGE GREEN FABRIC AND WEBBING.

Sample No.	Substrate	Add-on %	Curing Temp.	Strength Retention Not Laundered Dry only	Yarn Breaking Load, lbs.				Elongation at Break, %					
					Not Laundered Dry	100% RH	Laundered - 7D Dry	100% RH	Abrad. Dry	Not Laundered Dry	Laundered - 7D 100% RH	Abrad. Dry		
<b>A. 35 PMA, 10% Santicizer 148</b>														
24-1A	Fabric	----	150	87	3.4	3.1	2.9	3.0	----	20	16	14	15	--
14-2B	Fabric	20.9	75	74	2.9	2.9	2.8	---	----	15	14	14	--	--
24-7B	Webbing	----	150	92	20.8	---	---	---	14.2	40	--	--	--	25
24-8B	Webbing	----	150	78	17.6	---	---	---	19.2	28	--	--	--	34
24-6A	Webbing	----	150	90	20.4	---	---	---	20.0	35	--	--	--	34
24-7A	Webbing	----	150	96	21.6	---	---	---	18.9	41	--	--	--	30
14-4	Webbing	20.0	75	84	18.9	---	---	---	----	32	--	--	--	--
20-2	Webbing	19.2	75	86	19.4	---	---	---	----	38	--	--	--	--
<b>B. 35 PMA, 10% Santicizer 141</b>														
14-1B	Fabric	23.1	75	100	4.1	3.2	3.0	---	----	39	17	15	--	--
14-3	Webbing	19.2	75	85	19.3	---	---	---	----	34	--	--	--	--
20-1	Webbing	17.4	75	84	18.9	---	---	---	----	33	--	--	--	--
<b>C. 35 PMA, 10% Santicizer 148</b>														
14-2	Fabric	13.7	150	79	3.1	2.8	3.0	---	----	17	14	16	--	--
14-4	Webbing	14.3	150	88	20.0	---	---	---	----	34	--	--	--	--
<b>D. 35 PMA, 10% Santicizer 141</b>														
14-1	Fabric	13.2	150	100	3.9	3.1	2.9	---	----	33	16	15	--	--
14-3	Webbing	15.3	150	80	18.1	---	---	---	----	38	--	--	--	--
20-3	Webbing	12.9	150	76	17.2	---	---	---	----	30	--	--	--	--
<b>E. Exposed Controls</b>														
34-1	Nomex Fabric	----	---	84	2.5	2.6	3.9	7.7	----	11	12	13	12	--
34-2	Nomex Webbing	----	---	86	15.0	---	---	---	14.2	16	--	--	--	13
34-3	Nylon Fabric	----	---	86	5.4	5.8	6.2	5.7	----	29	32	36	31	--
34-4	Nylon Webbing	----	---	84	29.5	---	---	---	30.3	32	--	--	--	34
<b>F. Unexposed Controls</b>														
34-5	Nomex Fabric	----	---	---	3.9	---	---	---	----	39	--	--	--	--
34-6	Nomex Webbing	----	---	---	22.6	---	---	---	----	39	--	--	--	--
34-7	Nylon Fabric	----	---	---	6.3	---	---	---	----	30	--	--	--	--
34-8	Nylon Webbing	----	---	---	35.2	---	---	---	----	32	--	--	--	--

1. Remaining treatment bath composition was: 10% VMCH-Bakelite Resin  
10% Cyasorb UV-24  
1% dibutyl-tin-di-2-ethyl-hexanoate  
methyl ethyl ketone q.s. to 100%

TABLE V

EFFECT OF CARBON ARC EXPOSURE ON NOMEX FABRIC AND WEBBING TREATED WITH U.V. ABSORBER, EXTENDER, PVC RESIN, PLASTICIZER, AND HEAT STABILIZER. 50 AND 100 HOURS EXPOSURE; WHITE AND SAGE GREEN FABRICS; SAGE GREEN WEBBING.

Sample No.	Cyanob UV-26 Absorber %	ADTX Extender %	WHCH Coating %	Plasticizer %	Temp. °C	Substrate	Adhesion %	Tensile Strength, lbs.		Elongation at Break, %		No. Laundered Dry	No. Laundered & Dried	No. Laundered & Dried
								100% RH Dry	100% RH Dry	100% RH Dry	100% RH Dry			
171-10	10	5	10	5/148	24	W F	17.5	50	2.9	2.7	15	11	15	16
	10	5	10	5/148	24	W F	17.5	100	2.5	2.5	12	11	12	12
	10	5	10	5/148	24	S W	15.3	50	18.8	16.2	25	25	25	25
171-11	10	5	10	3/148	24	W F	13.5	50	2.9	3.4	15	17	15	15
	10	5	10	1/148	24	W F	10.5	50	2.9	2.9	15	15	15	15
171-7	10	5	10	5/141	24	W F	15.4	50	2.7	2.4	14	14	14	14
	10	5	10	3/141	24	W F	15.4	100	2.3	2.0	11	11	11	11
	10	5	10	5/141	24	S W	17.4	50	18.0	17.0	26	26	26	26
187-1	10	5	10	5/141	24	S W	17.4	100	17.0	15.4	20	20	20	20
	10	5	10	5/141	24	S F	16.1	50	3.1	3.5	19	15	17	17
171-8	10	5	10	3/141	24	W F	16.0	50	3.0	3.1	17	15	13	13
	10	5	10	3/141	24	S W	30.5	50	17.8	16.7	34	34	34	34
171-9	10	5	10	1/141	24	W F	11.3	50	2.9	3.3	15	16	15	15
	10	5	10	1/141	24	S W	9.6	50	18.2	17.6	23	22	22	22
173-1	10	5	10	3/141	66	W F	11.4	50	2.9	3.3	16	18	13	13
	10	5	10	3/141	66	W F	11.4	100	2.5	1.9	12	12	10	10
	10	5	10	3/141	66	S W	10.3	50	18.0	16.4	26	26	22	22
146-2	5	2.5	5	3/141	24	W F	10.0	50	2.5	2.3	12	12	12	12
	5	2.5	5	3/141	24	S W	10.0	100	2.3	1.7	11	11	11	11
172-2	0	5	10	3/141	66	W F	6.4	50	2.6	2.2	14	15	12	12
	0	5	10	3/141	66	S W	5.5	50	18.2	18.0	23	23	23	23
195-1	10	5	5	3/141	24	S F	9.0	50	3.0	3.1	16	16	16	16

TABLE V (Concluded)

Sample No.	Formulation <sup>a</sup>		Temp. °C	Substrate <sup>b</sup>	Add-on %	Exposure hrs.	Yarn Breaking Load, lbs.		Elongation at Break, %	
	Cysoth UV-26 Absorber	ADPH VMCK Extender Coating					Wet Laundered Dry	100% RH Dry	Wet Laundered Dry	100% RH Dry
B. Controls										
					None					
						0	4.4	---	---	---
						50	2.1	2.2	2.0	37
						100	1.5	1.5	1.5	11
						150	1.4	1.2	---	7
						200	1.3	---	---	4
						0	4.2	---	---	4
						50	2.5	2.6	2.7	43
						100	2.5	2.6	2.6	13
						150	2.5	2.6	2.6	12
						200	2.5	2.6	2.6	16
						0	21.7	---	---	---
						50	15.2	---	---	36
						100	13.5	---	---	13
						150	11.7	---	---	14
						200	11.2	---	---	10
						0	6.3	---	---	12
						50	4.7	6.1	5.0	42
						100	3.2	4.4	3.9	31
						0	35.2	---	---	24
						50	30.7	---	---	30
						100	21.5	---	---	30

a. All ingredients dissolved in MEK; 1% dibutyl-tin-di-β-ethyl-hexanoate - heat stabilizer added to all solutions.  
 b. W F - white fabric; S F - sage green fabric; S W - sage green webbing.  
 c. Abraded by passing five times through buckle of parachute harness.



TABLE VI

EFFECTS OF CARBON ARC EXPOSURE ON NOMEX TREATED WITH ELEMENTAL IODINE.  
50 HOURS EXPOSURE; WHITE FABRIC AND DAGE GREEN WEBBING.

A. Sample No.	Time/Temp. min. °C	Treatment		Add-on %	Substrate	Ave. Str. wt.	Yarn Breaking Load, lbs.			Flingation at Break, %								
		U.V. Absorber	Extender				Resin	Not Laundered 100% RH Dry	Laundered + TD Dry 100% RH Cl.	TD Dry Abr. Dry	Not Laundered 100% RH Dry	TD Dry Abr. Dry	TD Dry Abr. Dry					
141-1	---	Iod. Vapor	---	---	F	71	3.2	3.2	2.9	3.2	3.1	2.4	20	17	19	18	13	
141-2	---	Iod. Vapor	---	---	W	61	12.9	---	---	---	---	---	10	---	---	---	---	
143-1	---	Iod. Vapor + 5% UV-24	2.5% ADPE	5% VMCH	F	72	3.3	3.3	2.9	3.1	3.0	2.3	20	21	16	19	16	10
143-2	---	Iod. Vapor + 5% UV-24	2.5% ADPE	5% VMCH	W	86	10.4	---	---	---	---	---	32	---	---	---	---	---
141-3	---	Iod. Vapor + 5% DMAB	---	5% VMCH	F	72	3.3	2.9	3.1	3.2	3.1	2.6	22	18	20	21	19	13
141-4	---	Iod. Vapor + 5% DMAB	---	5% VMCH	W	61	13.0	---	---	---	---	---	14	---	---	---	---	---
111-2	60/100	Iodine in DMF	---	---	F	71	3.3	3.3	2.9	3.2	---	---	52	42	34	36	31	21
111-1	60/24	Iodine in DMF	---	---	F	45	2.0	---	2.0	---	---	---	10	---	11	---	---	---
111-10	15/100	Iodine in Xylene	---	---	F	44	2.1	---	1.8	---	---	---	8	---	8	---	---	---
111-6	15/100	Iodine in CCl <sub>4</sub>	---	---	F	40	1.8	---	1.8	---	---	---	9	---	9	---	---	---
B. Untreated Controls																		
Nomex					W F	45	2.1	2.0	---	---	1.9	---	6	---	6	---	---	6
Nomex					W W	71	15.2	---	---	---	---	---	12	---	---	---	---	---
Nylon					W F	90	9.7	9.2	---	---	---	---	21	---	27	---	---	---

APPENDIX I

LIST OF PRODUCTS USED

Trade Name or Abbreviation	Chemical Name	Source
<u>A. U.V. Absorbers</u>		
Cyasorb UV-24	2,2'-dihydroxy-4-methoxybenzophenone	American Cyanamid Co.
Tinuvin-320	2-hydroxy-3,5-ditertiarybutylphenyl benzotriazole	Geigy Chemical Co.
Tinuvin-P	2(2'-hydroxy-5'-methylphenylbenzotriazole)	Geigy Chemical Co.
Uvinul DS-49	2,2'-dihydroxy-4,4'-dimethoxy-5-sulfobenzophenone	GAF Corporation
<u>B. Quencher</u>		
AM-105	a nickel complex of a thiobisphenol compound	Ferro Corporation
<u>C. Extenders</u>		
ADPH	acetone-2,4-dinitrophenylhydrazone	Fine Organics, Inc.
DMAB	p-dimethylaminoazobenzene	Fisher Scientific Chem. Co.
PNA	p-nitroaniline	Fisher Scientific Chem. Co.
PPAA	p-phenylazoaniline	Fisher Scientific Chem. Co.
<u>D. Solvents, Carriers and Adduct Materials</u>		
TLF-2791	benzophenotetracarboxylic acid (carrier)	DuPont
M-Pycol	N-methyl-2-pyrrolidone	GAF Corporation
Dymex N	acetophenone derivative (carrier)	Arkansas Co.
PEI-18	polymer of polyethyleneimine (mol wt 1800)	Dow Chemical Co.
PEI-600	polymer of polyethyleneimine (mol wt 60,000)	Dow Chemical Co.

APPENDIX I (Concluded)

<u>Trade Name or Abbreviation</u>	<u>Chemical Name</u>	<u>Source</u>
<u>E. Plasticizers</u>		
Santicizer 140	cresyl diphenyl phosphate	Monsanto Co.
Santicizer 141	2-ethylhexyldiphenyl phosphate	Monsanto Co.
Santicizer 148	isodecyldiphenyl phosphate	Monsanto Co.
Santicizer 160	butylbenzyl phthalate	Monsanto Co.
<u>F. Heat Stabilizers</u>		
K&K #2101	dibutyltin-di-2-ethylhexoate	K and K Labs. Inc.
<u>G. Resins</u>		
VVHH	copolymer of vinyl chloride/vinyl acetate (87:13)	Bakelite Co.
VMCH	terpolymer of vinyl chloride, vinyl acetate and maleic acid, (86:13:1)	Bakelite Co.
Geon 222	vinyl chloride/vinylidene chloride copolymer (low mol. wt.)	B.F. Goodrich Chem. Co.
Butvar B-72A	polyvinyl butyral resin (mol. wt. 180 - 270,000)	Monsanto Co.
<u>H. Pigments</u>		
Black Shield 1611 (carbon black dispersion)	15% carbon black, 22.5% VVHH in methyl ethyl ketone	CDI Dispersions

## APPENDIX II

### REFERENCES

#### A. Literature Searches

The literature search consisted of a survey of Chemical Abstracts by our own staff (1948 to present) and searches ordered from the Defense Documentation Center (1965-1972), the Textile Information Center, Institute of Textile Technology, Charlottesville, Virginia (1965-1970), NASA and Science Information Exchange. The emphasis was primarily on information on the degradation of Nomex due to uv radiation which would help in the selection of the most promising treatments. However, references to the actinic degradation of all polyamides are also listed.

One of the most important references for our immediate purpose is the description of the work by Stephenson and Wilcox (75) who determined the tensile properties of several polymeric materials, including Nomex, after exposure at five wavelengths of light under nitrogen. Nomex, (at the time of this work was still called HT-1) lost strength and elongation at break most rapidly at 340 and 369 nm, less so at 244 nm and least at 214 and 437 nm.

Johnson et. al. (38) compared the photodegradative wavelength dependence of Nomex with that of experimental, thermally resistant fibers; they indicate that degradation of the strength and color of Nomex occurs within the region from 310 to 390 nm with the peak between 360 and 370 nm. Nomex thus absorbs at higher wavelength than most other polymers.

Data on the deterioration of Nomex materials in carbon arc and outdoor exposure have been published by Ross and Opt (62), Little and McGrath (47), and Hargraeves (29-32); we have also received such data from DuPont (70). DuPont also indicated some success with a commercial uv absorber, Tinuvin P (Geigy Chemical Company).

In summary, the literature search helped in establishing the wavelength range in which Nomex shows greatest sensitivity (this was confirmed by obtaining the uv spectra of Nomex in our laboratory using a KBr disc of

ground fiber). Furthermore, it indicated that there seems to be no published work on the application of uv absorbers to Nomex. We, thus had to rely primarily on the experimental approach of choosing absorbers on the bases of the ranges in which they absorb and their expected substantivity to aromatic polyamide.

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B. Patent Search

The search of U. S. Patent Office files from 1950 to 1970 by IF1/Plenum Data Corporation produced no references to agents that may be candidate UV inhibitors for aromatic polyamides (Nomex).

One of us (GA), on a personal visit to the U. S. Patent Office, updated the above patent search from 1970 to March 1972. This again produced no references to our subject. Consultation with two U. S. Patent examiners assured us that the correct classes and subclasses were being searched.

a. Specific Patent Search on Related Topics.

No patents available.

b. General Subject Patent Search:

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81. "Finish for Improved Nylon Filaments," W. Roth and R. Schroth, assignor to VEB Chemiefaserwerk Schwarza Wilhelm Pieck, B.P. No. 1,001,318, August 11, 1965.
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93. "Light-stabilized Nylon," P. V. Papero, assignor to Allied Chemical Co.,  
Germ. Offen. 1,495,018, June 4, 1969, U. S. Appl. October 20, 1961.