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DEVELOPMENT OF FIBERS CONTAINING
A REACTION PRODUCT OF CHLOROMETHY-
LATED STYRENE POLYMER AND
DIETHYLENETRIAMINE

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Uniroyal, Incorporated

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Fibers with an anion exchange capacity as high as 2.7 meq/g were obtained by preparing ion exchange resins in situ within two phase fiber systems. Initially, blends of polypropylene with acrylonitrile-butadiene (NBR) and a styrene containing polymer (ABS) were melt spun into two phase fibers, then drawn and crosslinked with peroxide or heat. Following this, the - See reverse side -		

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19. <u>KEY WORDS</u>	<u>LINK A</u> <u>Role</u>	<u>LINK B</u> <u>Role</u>	<u>LINK C</u> <u>Role</u>
Development	8	-	-
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Chemical Reactions	-	6	-
Styrene Copolymers	-	6	-
Chloromethylated	-	0	-
Polymerization	-	6	-
Acrylic Acid Copolymers	-	6	-
Diethylenetriamine	-	6	-
Tests	-	-	8
Temperature	-	-	10
Ion Exchange Resins	-	-	10
Evaluation	-	-	u

20. ABSTRACT (Continued)

fibers were chloromethylated with chloromethyl methyl ether and aminated with diethylenetriamine. Unfortunately, the resulting fibers were very weak, e.g., the fibers with 2.7 meq/g anion exchange capacity had a tenacity of only 0.05 g/d.

Attempts were made to scale up the process to obtain larger sample sizes adequate for more extensive testing. At this stage of development, tubes knitted from melt spun fibers were exposed to the chloromethylation and amination steps. However, the highest anion exchange capacity obtained for a knitted fabric was only 1.6 meq/g.

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FOREWORD

The development work described in this report was performed primarily by Malcolm J. Smith of Uniroyal, Inc., under Contract No. DAAG17-72-C-0017, at the company's Oxford Management and Research Center in Middlebury, Connecticut. The contract was conducted in collaboration with Richard N. Macnair, Project Officer and Gilbert N. Arons, Alternate Project Officer of the U.S. Army Natick Laboratories.

Two work phases were used in preparing fibers containing diethylene-triamine/chloromethylated polystyrene copolymers. Phase I was concerned with developing the proper reaction and process variables and preparing small quantities of fiber in a range of compositions and properties. These fibers are identified as Samples A, B, C and D. Phase II was concerned with preparing larger amounts of fiber compositions chosen by these Laboratories after evaluation of the samples from Phase I. Fibers from Phase II were required in sufficient quantities for testing with vapors of toxic Military agents such as HD, GB and VX. These fibers were produced in the form of knitted fabrics identified as Samples AA and DD.

An evaluation of the sample fibers prepared under the contract is described in a separate report prepared by the Project Officer and Alternate Project Officer [1]. The evaluation emphasizes toxic agent testing of Samples AA and DD and compares results with earlier experiments using chemically similar ion exchange beads in impregnated fabrics.

INTRODUCTION

The U. S. Army Natick Laboratories have a continuing interest in materials that can be incorporated into protective clothing to sorb or otherwise render innocuous a variety of toxic chemicals [2], [3]. One material which had shown promise in this respect is an ion exchange bead prepared by chloromethylating a crosslinked polystyrene matrix and subsequently aminating with diethylene-triamine. The purpose of this project has been to prepare substantially the same material in fiber form for comparative evaluation by the Natick Laboratories.

In a previous contract with the Federal Water Quality Administration [4], Uniroyal, Inc., demonstrated the feasibility of producing ion exchange materials in fiber form by melt spinning organic polymers and giving the spun fibers a subsequent chemical treatment. Ion exchange fibers having capacities and selectivities comparable to conventional ion exchange resins in bead form were prepared. However, in some cases selectivities were found to differ from those found in conventional beads, and in all cases the sorption rates in fibers were faster by as much as two orders of magnitude. Thus, it is possible to obtain quite different properties in a fiber compared to beads having similar sorption sites.

The preparation of these ion exchange fibers has generally been carried out in four stages: 1) melt spinning of a polymer mixture containing styrene polymer as one of the phases, 2) crosslinking of the polymer in the fiber, 3) chloromethylation, and 4) amination. This contrasts with ion exchange bead preparation in that the bead is crosslinked during polymerization of the styrene through the incorporation of divinylbenzene, thus obviating a separate crosslinking step. It is not generally possible or practical to attain the same degree of crosslinking in the fiber as in the bead as this would certainly lead to a very brittle fiber. However, the presence of "inert" fiber formers such as polypropylene in the ion exchange fiber somewhat lessens the need for a high degree of crosslinking. Nevertheless, high capacity fibers require considerable crosslinking to prevent solubility of the fiber during the subsequent chemical treatments. Therefore, capacity and strength must be balanced, and this trade in properties generally results in lower ion exchange capacities in fibers than in the corresponding beads.

EXPERIMENTAL

PHASE I

Fiber Preparation

The feedstock for fiber spinning was prepared by thoroughly mixing raw powdered ingredients by hand and melt extruding these through a single hole (1/8 inch diameter) die at 230° to 260°C. The extruded material was chopped to produce pellets about 1/4 inch long. All fibers were melt spun from these pellets in a 1-inch Modern Plastics Machinery Co. extruder feeding a size 1/2 gear pump. The melt emerged from an eight hole die (0.020 in hole diameter) at temperatures ranging from 230° to 260°C and at an approximate rate of 5 grams/minute. The fiber was taken up at 200 to 300 ft/min, and wound on a cylindrical package. Because of the slow take-up of the fibers, they were generally in the area of 100 denier. Therefore, before any chemical treatment, the fiber was drawn in order to reduce the diameter and increase the strength. The fiber was oven drawn at 130°-150°C with draw ratios ranging from 1.25:1 to 4.2:1, the higher draw ratios required two or more steps.

Eight polymer mixtures were melt spun for this project. The compositions of the fibers are given in Table I and some physical properties are given in Table II. Samples MS-NC-2 and -7 are identical in composition; slightly different take up rates during spinning account for the difference in physical properties. The last three columns of Table I give the compositions in terms of the chemically important components - styrene, butadiene, and inert (polypropylene plus acrylonitrile). Further information on the composition of the polymers is given in the Glossary. Mixture MS-NC-1 had the highest butadiene content, 12.7%; but because of thermal decomposition in the extruder, this material did not spin well. Thus, it appears that the practical limit for butadiene content is about 11% as in MS-NC-8. In previous work [4] we have attempted to spin styrene-butadiene copolymers with high styrene content which would permit better crosslinking than the ABS-NBR mixtures. However, the tendency of these copolymers to gel at extrusion temperatures made spinning impossible.

Crosslinking

Since styrene is soluble in the chloromethylating agents, it is necessary to provide substantial crosslinking prior to the chloromethylation step. The chloromethylation itself gives some crosslinking, but only after a fairly high degree of chloromethylation has been achieved. Crosslinking of the residual double bonds in the butadiene copolymers with fuming sulfuric acid catalyst (H_2SO_4 : 5% SO_3) at 0°C was attempted with some success. This method was considered to be unsatisfactory, however, since the accompanying sulfonation reaction yielded about 0.5 meq/g styrene sulfonic acid.

TABLE I
COMPOSITIONS OF MELT SPUN FIBERS

<u>Sample</u>	<u>% ABS*</u>	<u>% NBR</u>	<u>% PP</u>	<u>% Styrene</u>	<u>% Butadiene</u>	<u>% Inert</u>
MS-NC-1	50	10	30	46.2	12.7	41.1
MS-NC-2	70	5	25	53.9	9.2	36.9
MS-NC-3	60	5	35	46.2	8.4	45.4
MS-NC-4	80	0	20	61.6	5.6	32.8
MS-NC-5	55	5	40	42.4	8.1	49.5
MS-NC-6	75	5	20	57.8	9.5	32.7
MS-NC-7	70	5	25	53.9	9.2	36.9
MS-NC-8	70	7	23	53.9	10.8	35.3

*Compositions and sources of polymers given in Glossary.

TABLE II
PHYSICAL PROPERTIES OF MELT SPUN FIBERS

<u>Sample</u>	<u>Nominal Draw Ratio</u>	<u>Denier/Filament</u>	<u>% Elongation</u>	<u>Tenacity (g/d)</u>
MS-NC-2	-	76	0	0.44
"	1.25:1	54	31	0.61
MS-NC-3	-	68		0.48
"	1.25:1	62	13	0.49
MS-NC-4	-	71	102	0.67
"	1.25:1	52	31	0.93
MS-NC-5	-	131		-
"	1.25:1	100	29	0.58
"	1.5:1	95	17	0.65
MS-NC-6	-	83	5	0.39
MS-NC-7	-	92	4	0.38
MS-NC-8	-	58	4	0.53

Treatment of the fiber with peroxide gave about the same degree of crosslinking as sulfuric acid, and so this method was used for most of the preparations. The fiber was soaked in a 5 to 10% solution of di-tert-butyl peroxide in ethanol for 12-16 hours at room temperature. Then, the fiber was oven treated at 110°C to 130°C for several hours. This procedure usually rendered the fiber insoluble in carbon tetrachloride at room temperature, but still soluble in toluene and chloromethyl methyl ether. Some crosslinking was afforded by heat aging alone, presumably through polymer degradation. However, the thermal degradation was accompanied by excessive strength loss making this method impractical.

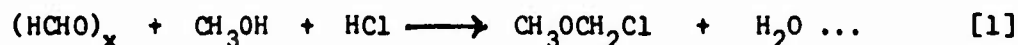
The Project Officers at Natick Laboratories conducted some crosslinking experiments by exposing melt spun fibers to two different sources of ionizing radiation, i.e., a LINAC (10 MEV electrons) and Cobalt 60. Separate samples of MS-NC-2 and MS-NC-4 in nitrogen were exposed, respectively, to 10 MR from each source. LINAC exposure was at ambient temperature whereas Cobalt 60 exposure was at - 30°C. After irradiation, crosslinking was allowed to continue for 24 hours at room temperature.

Irradiated fibers and untreated controls were tested for swelling (fiber diameter increases) after immersion in toluene at room temperature for 24 hours. The Control Samples MS-NC-2 and -4 swelled to high levels of 1570% and 2400%, respectively. The LINAC irradiated Samples MS-NC-2 and -4 swelled only 300% and 275%, respectively. The Cobalt 60 irradiated Samples MS-NC-2 and -4 swelled to the high and low extremes of 1170% and 150%, respectively.

Chloromethylation

The introduction of aryl chloromethyl sites was carried out by reacting the fiber with chloromethyl methyl ether (CME) in the presence of a Friedel-Crafts type catalyst. The solvent systems generally consisted of a non-polar substance such as heptane and a chlorinated hydrocarbon, for example, carbon tetrachloride.

The CME was prepared in the laboratory by passing hydrogen chloride through a mixture of paraformaldehyde and methanol at 0 - 10°C. The ratio of paraformal-



dehyde to methanol was varied from 1:1 to 2:1 in the first several preparations, after which a ratio of 1.5:1 was adopted for the remaining preparations. Above 1.5:1 the reaction did not proceed to completion, leaving paraformaldehyde suspended in the CME product. The product resulting from a 1:1 ratio did not give good chloromethylation reactions. Preparation of the CME required about four to six hours to consume all of the paraformaldehyde. After slight warming the reaction mixture separated into two phases, and the lower layer was discarded. The upper layer, containing CME, HCl, and biproducts of the reaction, was dried over calcium chloride but otherwise given no further purification. The CME was generally prepared biweekly although we had no firm evidence that longer shelf life should not be expected.

Four catalysts for the chloromethylation reaction were investigated - AlCl_3 , FeCl_3 , SnCl_2 and ZnCl_2 . Based on chlorine analysis after chloromethylation ZnCl_2 was found to give the highest degree of chloromethylation. Examples of the effect of catalyst are given in Table III. All of the reactions in Table III were carried out at room temperature for 18 hours.

TABLE III
EFFECT OF CATALYST ON CHLOROMETHYLATION

Sample	C_7H_{16} (ml)	CCl_4 (ml)	CME(ml)	Catalyst-(Wt.)	Fiber-(wt.)	% Cl
III-60g	75	25	4	AlCl_3 (1.5g)	MS-NC-2(2.3g)	3.4
III-60i	75	25	4	FeCl_3 (1.5g)	" (2.2g)	trace
III-99a	-	50	25	AlCl_3 (2g)	MS-NC-5(1.8g)	5.9
III-99b	-	50	25	ZnCl_2 (2g)	" (1.8g)	13.7
III-99c	-	50	25	SnCl_2 (2g)	" (1.4g)	10.3

The highest degree of crosslinking appeared through the use of AlCl_3 based on visual inspection of fiber swelling in toluene. Thus, AlCl_3 was used in most experiments, but in some of the later preparations a mixed AlCl_3 - ZnCl_2 catalyst was employed. It was always difficult to remove all of the ZnCl_2 from the fiber after chloromethylation whereas AlCl_3 was easily removed. Another possible disadvantage of ZnCl_2 is that its use usually resulted in a greatly weakened fiber; however, this observation was not firmly established. Chloromethylations described in the literature [5] generally call for 0.1 to 0.5 mole of catalyst for each mole of polystyrene, the catalyst requirement being inversely proportional to polystyrene concentration. This was borne out by the present experiments where, because of the low polystyrene concentrations (in a heterogeneous system), it was advantageous in some cases to use several moles of catalyst for each mole of polystyrene.

Since the styrene in the fibers is soluble in CME, it was necessary to keep CME concentrations at low levels. In most cases a mixed solvent of heptane with a chlorinated hydrocarbon was used in order to limit the extraction of styrene from the fiber. The chlorinated hydrocarbons tried were 1,2-dichloroethane, 1,2-dichlorobutane, 1,4-dichlorobutane, and carbon tetrachloride. None of these appeared to have any special effect on the chloromethylation. Although the extraction of styrene varied among these solvents, the effect could be compensated by the amount of heptane in the mixed solvent. Thus, for the sake of consistency, carbon tetrachloride was chosen for most of the preparations. In initial experiments the heptane to carbon tetrachloride ratio was generally 3:1, but as improvements in crosslinking were achieved, the ratio was reduced to 1:1 and in some cases the heptane was eliminated altogether.

Under mild reaction conditions - room temperature, 1 to 10% CME in 1:1 heptane: carbon tetrachloride - the chloromethylation reaction was quite slow, requiring up to 24 hours to reach a quasi steady state. By raising the temperature to 45°C the reaction time was reduced to less than 12 hours, but as a general practice, the reaction was given at least 16 hours in order to enhance cross-linking. Commencing the chloromethylation reaction at high temperature and high CME concentration generally failed because too much styrene was extracted by these extreme conditions. However, after the reaction had proceeded for several hours the temperature could be raised and the CME concentration increased without deleterious effect.

The most reliable judgement of the outcome of the chloromethylation was based on analysis of the chlorine content of the fiber, and this analysis was carried out in many instances. However, as a practical matter, the time delay in obtaining chlorine analyses necessitated other means of evaluation. A reasonable correlation was found between the anion exchange capacity after amination under mild conditions and the chlorine content, exemplified by Table IV.

TABLE IV
RELATION OF CHLORINE CONTENT TO CAPACITY

<u>Sample</u>	<u>C₇H₁₆</u>	<u>CCl₄</u>	<u>CME</u>	<u>AlCl₃</u>	<u>% Cl</u>	<u>Capacity (meq/g)</u>
III-87a	40	40	2	1.5	1.6	0.4
III-87b	40	40	5	2.5	4.8	0.9
III-87c	40	40	10	4.0	10.7	1.9

The chloromethylation reactions in Table IV were carried out on 2g samples of crosslinked MS-NC-5; this was done under somewhat special conditions insofar as all samples were reacted at room temperature for 18 hours. The aminations consisted of three hours of refluxing in a 6% DET solution of 1:1 heptane-toluene. The correlation between percent chlorine and anion exchange capacity is not linear because amination was not complete. The main difficulty in this otherwise straightforward method of evaluation was that in some cases the amination resulted in significant extraction of chloromethylated styrene from the fiber resulting in an apparent low degree of chloromethylation. Nevertheless, this method of evaluation was of great use from a practical standpoint since the ultimate interest lay in the anion exchange capacity.

Amination

Aminations were first carried out by placing the fiber in a refluxing solution of diethylenetriamine (DET), 5 to 10%, and toluene. Boiling toluene proved to be too severe on the fiber, and subsequent aminations with toluene included about 50% heptane. Amination under refluxing conditions (about 100°C) required 2 to 4 hours. By reducing the temperature to 70-80°C the extraction of styrene from the fiber was reduced, but reaction times were increased several-fold. The temperature effect was partially compensated by increasing the DET concentration. Dioxane was ultimately chosen as the amination solvent over toluene because its swelling effect on the fiber could be simply controlled by the addition of water and the solvent was easily removed from the fiber after amination.

As implied in the section on chloromethylation, the anion exchange capacity after amination did not always correlate with the chlorine content prior to amination. It is possible in some cases that the catalyst was not completely removed from the fiber, thus giving high chlorine content. Also, by following the weight of fiber before and after amination it was obvious in some cases that material was extracted from the fiber. Aside from the above cases there was a rough correlation between anion exchange capacity and chlorine content. Based on the addition of one DET molecule at each chloromethyl site the maximum possible capacity is calculated to be 0.8 meq amine/g fiber/1% chlorine. In actual practice one would not expect to reach this calculated capacity because of crosslinking through DET and other inefficiencies. However, the observed capacity was in no case as much as 50% of the ideal theoretical capacity. This may be partly due to extraction of the aminated product from the fiber, but the principal cause for this effect is not understood.

Preparations on Spools

In scaling up the fiber preparation from small loose bundles of about one gram to larger fixed-length samples wound on spools, considerable difficulty was encountered in handling the fiber due to shrinkage. Both the peroxide impregnation and chloromethylation reactions caused shrinkage of the fiber. If the fiber were allowed to dry, the resulting tension on the spool wound fiber caused the fibers to fuse together. The only practical ways found to avoid this situation were either to pre-shrink the fiber or to remove the fiber from the spool when drying. In either case the net result was shrinkage, hence weakening of the fiber. Attempts to dry the fiber by passing the strand through an oven under tension were unsuccessful because of the short (several seconds) residence time in the oven. However, this procedure might be feasible if the oven residence time were increased.

The fiber was wound on a perforated stainless steel cylinder for the chemical treatment. The solutions surrounding the fiber were well mixed, and the fiber appeared to react uniformly throughout the package. Because of the low strength after chloromethylation it was necessary to use 16 and 24 filament yarns to facilitate handling. Also, the yarn was given a twist of about two turns per inch (tpi) to reduce breakage.

Preparation of Samples Submitted to Natick Laboratories

A summary of the procedure used in preparing the four samples submitted to the U. S. Army Natick Laboratories is given in Table V. Included in the table are some final physical properties and chemical analyses. It is first noted that each sample was subjected to the chloromethylation reaction twice. The condition for the first chloromethylation was relatively mild in an attempt to avoid extraction of styrene from the fiber. After the first chloromethylation, a small sample of the fiber was aminated and its anion exchange capacity measured. In all cases the capacity was too low (0.0 to 1.3 meq/g). After the second chloromethylation small samples were again aminated in order to determine the conditions for amination of the larger sample. In the chloromethylation reactions, the catalyst and CME were added in two or three parts over a period of several hours.

The nitrogen analyses of the samples generally agree with the calculation of combined acrylonitrile and amine. However, the calculations are only approximate since the extent of extraction of styrene-acrylonitrile polymer from the fiber is not known. For example, in sample A the starting fiber contained 4.85% N based on acrylonitrile content. If the weight of the fiber is adjusted for the addition of 2.7 meq/g of amine the nitrogen due to acrylonitrile is reduced to 3.7%. The amine nitrogen corresponding to 2.7 meq/g is 3.8%, thus giving a total nitrogen content of $3.7 + 3.8 = 7.5\%$ (cf. analysis of 7.4%). Residual chlorine in the samples could be from unreacted chloromethyl sites or chlorine ion. The high chlorine content of sample D may indicate insufficient conversion from the amine hydrochloride to free amine.

A small sample submitted in addition to those listed in Table V is coded III-101a. This sample has an ion exchange capacity of 3.1 meq/g. The fiber was prepared as follows: 1) fiber MS-NC-5 was soaked in 6% t-butyl peroxide for 16 hours, then dried at 127°C for 3 hours; 2) the fiber (about 2g) was placed in 40 ml heptane, 40 ml carbon tetrachloride, 10 ml CME, and 4g $AlCl_3$ for 18 hours at room temperature; and 3) about 1g of the fiber was heated at 109°C for 17 hours in a solution of 50 ml dioxane and 25 ml DET. The rather mild conditions of the chloromethylation resulted in 10.7% Cl in the fiber corresponding to chloromethylation of about 90% of the styrene. This result could not be reproduced in subsequent experiments. The fiber also has strength suitable for practical processing (about the same strength as sample C).

TABLE V

DATA ON SAMPLE PREPARATIONS

<u>Sample</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Starting Fiber	MS-NC-4	MS-NC-8	MS-NC-5	MS-NC-8
Heat Shrinking	-	105°C, 7 hr	-	105°C, 7 hr
t-butyl peroxide (4%) in ethanol	40°C, 2 hr	20°C, 12 hr	20°C, 11 hr	20°C, 12 hr
Heating	118°C, 36 hr	82°C, 18 hr 105°C, 24 hr	110°C, 14 hr	65°C, 120 hr 82°C, 18 hr 105°C, 24 hr
Approx. fiber wt.(g)	10	21	26	15
CHLOROMETHYLATION-I				
C ₇ H ₁₆ (ml)	150	0	125	0
CCl ₄ (ml)	150	325	145	325
AlCl ₃ (g)	6	25	15	25
CH ₃ OCH ₂ Cl (ml)	25	55	35	55
Thermal record	35°C, 5 hr 50°C, 1/2 hr	30°C, 1-1/2 hr 40°C, 18-1/2 hr 60°C, 1 hr	25°C, 18 hr	30°C, 1-1/2 hr 40°C, 1-1/2 hr 60°C, 1 hr
CHLOROMETHYLATION-II				
CCl ₄ (ml)	275	250	250	250
AlCl ₃ (g)	8	15	5	15
ZnCl ₂ (g)	5	10	0	10
CH ₃ OCH ₂ Cl (ml)	30	50	25	50
Thermal record	60°C, 15 hr	60°C, 18 hr	50°C, 13 hr 60°C, 1 hr	60°C, 18 hr

TABLE V (Continued)

<u>Sample</u>	<u>DATE ON SAMPLE PREPARATIONS</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
AMINATION				
dioxane (ml)	240	0	260	200
toluene (ml)	0	200	0	0
DET (ml)	50	100	50	110
Thermal record	95°C, 62 hr	114°C, 19 hr	95°C, 40 hr	160°C, 16 hr
FINAL PROPERTIES				
denier/filament	76	78	124	78
no. filaments in yarn	24	24	16	24
breaking force (g)	103	39	660	86
tenacity (g/d)	0.05	0.02	0.33	0.04
breaking force-wet(g)	243	52	420	154
anion exchange cap. (meq/g)	2.7	2.3	0.7	2.5
%N	7.4	7.2	5.2	6.8
%Cl	1.1	1.5	2.5	6.6

PHASE II

Chloromethylation and Amination of Knitted-Fabric

The following describes the preparation of samples A and D (see Table V) as a knitted fabric under Phase II of the contract. Starting mixtures for samples A and D were MS-NC-4 and MS-NC-8, respectively, the compositions of which are given in Table I. Approximately three pounds of each mixture were melt spun according to the procedure used under Phase I. Fiber MS-NC-4 was drawn 4:1 in two stages, and fiber MS-NC-8 was drawn 3.7:1 in three stages. The drawing was generally difficult because of the weakness of the fiber. Input speed in the drawing was usually limited to about 30 ft/min in order to minimize breaks which cause difficulty in the knitting. Prior to the last drawing stage the fiber was given a twist of 1-2 tpi in order to prevent bellowing during knitting as well as to help hold broken ends intact. Again because of the weakness of the fiber and unavoidable breaks, the knitting process was very slow (1-3 hours/yd of tube). Approximately 25 yds of MS-NC-4 and 11 yds of MS-NC-8 were knitted (much of MS-NC-8 was lost during spinning and drawing).

Attempts to chloromethylate the fiber were carried out using the procedure outlined in Table V except that the reaction vessel was vented through a sodium hydroxide trap in order to prevent evolution of the chloromethyl methyl ether into the air. After several failures using this procedure, experiments were begun on a small scale to try to rectify the difficulties. It was found that at least part of the problem was due to the sodium hydroxide trap which was effectively removing the hydrogen chloride vapor pressure over the reaction mixture. Saturation of the reaction mixture with hydrogen chloride appears to be beneficial if not absolutely necessary for the chloromethylation reaction. Therefore, subsequent chloromethylation reactions were carried out in a closed system. This improved the chloromethylation results, but it was not possible to achieve the capacities previously obtained.

In the case of sample D, peroxide crosslinking was found to be ineffective; instead, the same results could be obtained by simple heat treatment. Therefore, because the crosslinking process caused considerable deterioration of the fabric; this step was eliminated for sample D. In fibers of this type the unsaturation is largely concentrated in relatively small domains. Thus, crosslinking of the butadiene results in localized regions of crosslinking with the bulk of the styrene not crosslinked. While peroxide crosslinking of the polystyrene is feasible, it could not be carried out without losing the integrity of the fabric. Although the crosslinking reaction was carried out on sample A, it is doubtful what any crosslinking took place aside from that obtained by heat aging.

Data on Preparation of Samples Submitted to Natick

Since the samples submitted to Natick for evaluation were not prepared precisely according to the scheme in Table V, they will be referred to as samples AA and DD, corresponding to fabric made from MS-NC-4 and MS-NC-8 fibers, respectively. The following table gives the scheme for preparation of these samples.

TABLE VI
PREPARATION OF FABRIC SAMPLES AA AND DD

<u>Sample</u>	<u>AA</u>	<u>DD</u>
Starting Fiber	MS-NC-4	MS-NC-8
di-t-butyl peroxide (5%) in ethanol	25°C, 16 hr	-
Heating	100°C, 40 hr	105°C, 24 hr
Approx. Fiber Wt.(g)	30	50
CHLOROMETHYLATION-I		
C ₇ H ₁₆ (ml)	250	290
CCl ₄ (ml)	215	290
AlCl ₃ (g)	5	20
CH ₃ OCH ₂ Cl (ml)	25	40
Thermal record	45°C, 8 hr	48°C, 17 hr
CHLOROMETHYLATION-II		
CCl ₄ (ml)	575	500
AlCl ₃ (g)	7	10
ZnCl ₂ (g)	-	10
CH ₃ OCH ₂ Cl (ml)	50	60
Thermal record	48°C, 6 hr	50°C, 10 hr
CHLOROMETHYLATION-III		
CCl ₄ (ml)	525	-
AlCl ₃ (g)	10	-
ZnCl ₂ (g)	5	-
CH ₃ OCH ₂ Cl (ml)	50	-
Thermal record	55°C, 5 hr	-
AMINATION		
dioxane (ml)	150	150
DET (ml)	450	450
Thermal record	95°C, 18 hr	100°C, 18 hr
Anion Exchange Capacity (meq/g)	1.0	1.6

DISCUSSION

PHASE I

The results of Phase I experiments, while showing that the preparation of anion exchange fibers with diethylenetriamine functionality is feasible, indicate a number of difficulties which must be overcome in order to prepare improved fibers. The most important need for improvement lies with the crosslinking reaction. It is also important to achieve the necessary crosslinking without excessive strength loss, although some strength loss and almost complete loss of elongation is inevitable. Crosslinking by chemical and/or thermal catalysis is probably not suitable for high capacity fibers because the crosslinking network excludes part of the styrene polymer.

Ionizing radiation was investigated on a limited basis as an alternate method of crosslinking. Fiber swelling data shows that this method yields significant crosslinking and suggests potential for improvement over the other methods.

Most difficulties with chloromethylation and amination could be obviated by more uniform crosslinking. Without the concern of fiber solubility, the chloromethylation and amination reactions could be carried out under more vigorous conditions leading to shorter reaction times and higher capacities. Again, these reactions are expected to lead to some loss in strength.

The batch type method of preparation was adopted because of the long reaction times. However, this necessitated shrinking the fiber giving reduced strength. Thus, it is still desirable to process the fiber (at least through the crosslinking stage) on a continuous basis holding the fiber under tension.

PHASE II

The low results on anion exchange capacity under Phase II cannot be explained in light of the preparations shown in Table V where higher capacities were obtained. The key step in the preparation appears to be the first chloromethylation where it is essential that enough crosslinking take place to prevent extraction of styrene from the fiber. The use of heptane in the first chloromethylation was effective in reducing the swelling of the fiber. Further, the use of high temperatures and excess catalyst were found to promote crosslinking. However, the crosslinking obtained was still inadequate.

CONCLUSIONS

1. The Phase I goal of obtaining fibers with a minimum anion exchange capacity of 2.5 meq/gm was demonstrated as possible. Unfortunately such fibers were very weak with tenacities of only 0.04 or 0.05 gm/d.
2. The Phase II goal for preparing the higher capacity fibers of Phase I in a larger quantity was not met because the anion exchange capacity dropped below 2.5 meq/gm. The exact reasons for this capacity drop were not clear, but crosslinking and chloromethylation difficulties were obvious.
3. Considerable additional work would be required to optimize anion exchange capacity and tenacity. Improved crosslinking is a major factor in such work in which the ionizing radiation approach showed some promise.

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REFERENCES

1. G. N. Arons and R. N. Macnair, Evaluation of Fibers Containing a Reaction Product of Chloromethylated Styrene Polymer and Di-ethylenetriamine, U.S. Army Natick Laboratories Report 74-52-CE, Series C&PLSEL - 128, dated June 1974.
2. Final Report, Contract No. DA-19-129-AMC-481(N), MSA Research Corp., Nov. 1, 1965, AD 373-109.
3. Final Report, Contract No. DA-19-129-AMC-2107(X)(01-7008), MSA Research Corp., Oct. 16, 1963, AD 344-693, Classified Secret.
4. R. W. Fuest and M. J. Smith, "Feasibility Study of Regenerative Fibers for Water Pollution Control", Contract No. 14-12-815, Program No. 17040 DFC, Federal Water Quality Administration, June 1971.
5. For examples: G. D. Jones, Ind. & Eng. Chem., 44, 2686, (1952). See also references 2 and 3 above.

G L O S S A R Y

Materials Cited in Preparation of Fiber

ABS	acrylonitrile-butadiene-styrene (16:7:77) blend of butadiene-styrene copolymer and acrylonitrile-styrene copolymer. Dow "Tybrene" 213.
NBR	15:85 copolymer of acrylonitrile and butadiene, Arco "Poly BD, CN-15".
PP	powdered polypropylene, Hercules "Profax, 6501"
DET	diethylenetriamine, Fisher Scientific, technical grade.
CME	chloromethyl methyl ether, prepared in laboratory.