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PERSPIRATION POISONING OF PROTECTIVE CLOTHING MATERIALS.

PART III.

STUDY OF A NEW AGENT SIMULANT, A MODIFIED UNDERGARMENT FABRIC AND THEORETICAL PROTECTIVE LIFE.

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by

(10) J. K. Ferrell
R. W. Rousseau

North Carolina State University
Department of Chemical Engineering
Raleigh, North Carolina

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This report discusses results of experiments on (1) the equilibrium and dynamic adsorption of dichloroethyl ether (DCEE) on carbon-impregnated polyurethane foam, (2) the modification of cotton undergarment fabric and its utilization in the inhibition of the deleterious effects of perspiration on adsorption by protective overgarments, and (3) comparisons of liquid and vapor perspiration poisoning. These results show that vapor in equilibrium with simulated perspiration has no effect on the dynamic adsorption of

CCl_4 vapors. The application of liquid simulated perspiration resulted in a significant decrease in both the amount of CCl_4 adsorbed by a sample and in the breakthrough time. Modification of cotton undergarment fabric, which was then placed between a sweat source and a sample of the protective foam, produced a material that substantially reduced the deleterious effects of perspiration on CCl_4 adsorption by the foam. The most successful modification of fabric was that in which weakly basic ion exchange substituents were grafted to the cellulose chain.

PREFACE

This report describes results of work conducted by investigators at North Carolina State University at Raleigh as a continuation of studies begun in 1972. The original work was begun bacause there were no data available on the effects of sweat on the Suit, Chemical Protective. As data were generated in the initial work under contract DAAG17-72-G-0004, it became apparent that absorption of sweat by the Suit caused a definite reduction in the sorption capacity and could be a problem in the field. It thus appeared worthwhile to develop a system for reducing the effect of sweat and thus to help maintain the protective quality of the Suit. The most logical way to do this seemed to be to keep sweat away from the Suit. This had been done previously with water impermeable or water repellent materials but these approaches prevent or retard passage of water away from the body. A new method being developed by the US Army Natick Research and Development Command is to graft basic functional groups to an undergarment to retain the major components of sweat and prevent them from migrating to the protective material while allowing passage of moisture. Early contract effort showed that this approach had potential. The effort described in this report was designed to develop the method further and also to measure the effects of sweat vapor on the Suit in comparison with the effect of liquid sweat and to investigate a modification of the method for measuring the effects of sweat on garment sorptivity. The work was supported under the project titled Clothing and Equipment Technology. The Project Officer was Dr. Richard N. Macnair.

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PART III

STUDY OF A NEW AGENT SIMULANT, A MODIFIED UNDERGARMENT FABRIC AND THEORETICAL PROTECTIVE LIFE

INTRODUCTION

The development of protective overgarments to adsorb toxic chemical agents has been underway at the U. S. Army Natick R&D Command for several years. Several excellent materials have been developed for this purpose; however, in use their adsorptive capability is decreased by sweat poisoning. This phenomenon occurs when the wearer of the overgarment perspires, causing sweat and sweat components to enter the overgarment material and reduce its adsorptive capacity for toxic agents. Not only is there a reduction in the amount of material which can be adsorbed, but the rate of adsorption is also reduced.

In earlier research under grant agreement No. DAAG17-72-G0004, data were reported which illustrated the effects of sweat on adsorption characteristics of carbon impregnated polyurethane foam and other adsorbent materials. Also, preliminary tests were made on techniques for reducing the influence of sweat on the adsorption dynamics of CCl_4, and a mathematical model which would be used to simulate the adsorption behavior of these systems was developed. These efforts are discussed in reports by Ferrell, Rousseau, and Aneja[1] and by Ferrell, Rousseau, and Branscome.[2]

In this report research continuing the earlier efforts is reported. Specifically, results are presented on the following:

(a) Equilibrium and dynamic adsorption of dichloroethyl ether on carbon-impregnated foam,

(b) modification and testing of cotton undergarment fabric for reduction of sweat poisoning,

(c) comparisons of liquid and vapor sweat poisoning,

(d) predictions of mustard vapor adsorption properties from data on CCl_4 and a numerical model provided by the US Army Natick Research and Development Command (NARADCOM).

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[1] J. K. Ferrell, R. W. Rousseau and A. P. Aneja, "Perspiration Poisoning of Protective Clothing Materials - Part I - Experimental Results and Evaluation," June 1974, Report No. TR-76-13-CEMEL, U. S. Army Natick R&D Command.

[2] J. K. Ferrell, R. W. Rousseau and M. R. Branscome, "Perspiration Poisoning of Protective Clothing Materials - Part II - Mathematical Model for a Complex Adsorption Bed", June 1974, Report No. TR-75-55-CEMEL, US Army Natick R&D Command.

EXPERIMENTAL

Most of the experimental equipment and procedures are discussed in detail in Reference 1. The discussion of these items in this section will, therefore, be brief.

Dynamic Adsorption-Apparatus

A schematic of this equipment is given in Figure 7 of Reference 1. The apparatus supplied a stream of vapor in nitrogen at varying compositions to a sample of carbon-impregnated foam in a sample holder at constant temperature. The flow rate of the vapor through the sample was measured and controlled at a constant value during any given run. The concentration of vapor in nitrogen was fixed by mixing a vapor-saturated stream of nitrogen, that had been saturated by bubbling through pure liquid, with a stream of pure nitrogen. Concentrations of vapor in nitrogen were measured with a gas chromatograph equipped with a gas sampling valve. Flow rates were measured with rotameters calibrated over the appropriate ranges.

Sample Holder

A photograph of the sample holder used with the dynamic vapor test apparatus is given in Figure 9 of Reference 1. The inside diameter of the holder was 10.16 cm giving a flow area of 81.1 cm^2.

Sweat Applicator

A device to apply sweat to the foam material in a manner simulating the transfer of sweat from the human body to a garment was used in many of the experiments to be reported. A schematic of this device is shown in Figure 14 of Reference 1. The sweat application procedure consisted of positioning the foam sample against the applicator, with the nylon side closest to the sweat source. A measured volume of simulated sweat was then forced from the applicator into the foam. The treated sample was then removed and dried before being run in the dynamic vapor test apparatus. To test the influence of treated or untreated undershirt material, a sample of this material was placed between the foam and the sweat source so that the simulated sweat had to pass through this material before entering the foam.

Absorbent Material

The absorbent material was developed by the U. S. Army Natick R&D Command. It consisted of a layer of polyurethane foam bonded to a nylon tricot fabric and impregnated with activated carbon held in place by a latex binder. Reference 1 contains further details on the material. The foam used in these experiments was designated Bolt 4 material in Reference 1. It is considered representative of material produced in pilot scale runs since it passed the specification requirement for carbon tetrachloride sorption.

Undergarment Material

Tests were performed using cotton undershirt material supplied by the U. S. Army Natick R&D Command. This material was tested in unmodified and modified forms for the removal of sweat components that affect deleteriously the adsorbent properties of carbon-impregnated foam.

Determination of Breakthrough Curves

Breakthrough curves were generated by sampling the gas stream exiting the sample holder in the dynamic vapor test apparatus and determining the vapor concentration in this stream as a function of time. Sampling frequency was limited to three minutes because this amount of time was required to allow the chromatograph system to return to baseline conditions after a sample was analyzed.

McBain Balance

This apparatus, shown in Figure 13 of Reference 1, was used to measure adsorption isotherms. The amount of vapor adsorbed on a sample of adsorbent material was determined by measurement of the extension of a calibrated spring holding the sample.

ADSORPTION OF DICHLOROETHYL ETHER (DCEE)

Since dichloroethyl ether (DCEE) is considered a more realistic simulant than CCl_4 for toxic gases of interest to the Natick R&D Command, a series of adsorption experiments was performed with DCEE adsorption on carbon-impregnated foam. Except for the variations noted below, the experimental conditions were identical to those used in CCl_4 experiments described in Reference 1.

The DCEE used in the experiments was obtained by distilling commercial DCEE in a Vigreaux column at 16.3 mm Hg over the range 70^{o}C to 71^{o}C. A small fraction of the commercial material was more volatile than DCEE, while a significant fraction was less volatile.

Adsorption Kinetics

Data from two sets of experiments on DCEE are presented in Table 1. The objective in the first three runs (18-, 19-, 20-) was to compare the effects of various foam pretreatment procedures on DCEE adsorption. These runs were on as-received foam (AR designation), foam which had been placed in a humid atmosphere for 40 hours (H_2O designation), and foam which had been dried to constant weight in a desiccator (D designation). No significant changes in the amount of DCEE adsorbed per gram of foam, M^*_T, amount of DCEE adsorbed at breakthrough, M^*_b, or breakthrough time, t_b, were observed. The inlet concentrations of DCEE, C_o, varied due to changes in the bubbler temperature. These runs were also subject to variations in the foam material, as each run was performed on a different foam sample. There was no attempt at regeneration. It is apparent from these data that adsorbed water is not a major poison for DCEE adsorption, as it is for CCl_4.

Table 1. Adsorption of DCEE on Carbon Impregnated Foam Material.

Run No.	T	Q (l/min)	C_o(mg/ℓ)	t_b	M_t^*(mg/g foam)	M_b^*(mg/g foam)
18-B_4AR-1	35°C	0.40	7.00	107.39	122.08	83.55
19-B_4H_2O-1	35°C	0.40	7.74	90.83	112.74	76.74
20-B_4D-1	35°C	0.40	7.15	94.44	109.19	72.72
21-B_4AR-1	35°C	0.46	8.34	75.00	125.84	73.50
22-B_4AR-1	35°C	0.97	8.19	20.92	119.88	42.46
23-B_4AR-1	35°C	0.95	8.93	21.34	121.99	46.51
24-B_4AR-1	35°C	0.95	8.19	29.95	123.01	60.14

The objective in the second set of experiments was to determine the effect of flow rate on DCEE adsorption (Runs 21-, 22-, 23-, 24-). These runs were all on as received foam. No significant changes in the total amount of DCEE adsorbed per gram of foam were observed. However, when the flow rate was cut in half the breakthrough time, t_b, increased by more than a factor of 2. There was lesser and inconsistent increase in the amount of DCEE adsorbed per gram of foam at breakthrough, m_b*. The effect of DCEE flow rate on t_b was the same as it is for CCl_4 but the effect on m_b* was greater, i. e., no effect has been observed for CCl_4.

Influence of Sweat on DCEE Adsorption Kinetics

An experimental procedure was used to evaluate the effects of sweat treatment on DCEE adsorption kinetics. The essential features of the procedure are that adsorption-desorption runs were repeated on a foam sample in the dynamic adsorption apparatus until successive adsorption runs were identical. The sample was then removed from the system and treated with a fixed quantity of simulated sweat and dried in a desiccator. The sample was returned to the dynamic adsorption apparatus and an adsorption run made. These steps were taken to isolate the influence of sweat from sample variability.

Results of the experiments are shown graphically in Figures 1 through 4. The first two of these figures are for runs in which the DCEE inlet concentration , C_0, was not controlled as well as it was for runs described in the latter two figures. Figures 3 and 4 show that sweat treatment did have an effect on both the breakthrough time and total amount adsorbed. Breakthrough time was reduced by about 7% while total amount adsorbed was reduced by about 7.5%. Although there is uncertainty in the actual magnitude of the effects, analysis of the chromatographic data upon which the breakthrough curves are based clearly showed an earlier breakthrough for sweat-treated samples. Data points showing earlier breakthrough are not shown on Figures 3 and 4 because of the scale of the drawings. Under similar conditions for experiments on carbon tetrachloride, sweat treatment reduced breakthrough time by about 30% and total amount adsorbed by about 15%. These data show that sweat has a more significant effect on the adsorption of CCl_4 than adsorption of DCEE. Since it was shown in the previous section that moisture did not influence significantly the adsorption of DCEE, the results of these experiments on sweat poisoning are not altogether surprising.

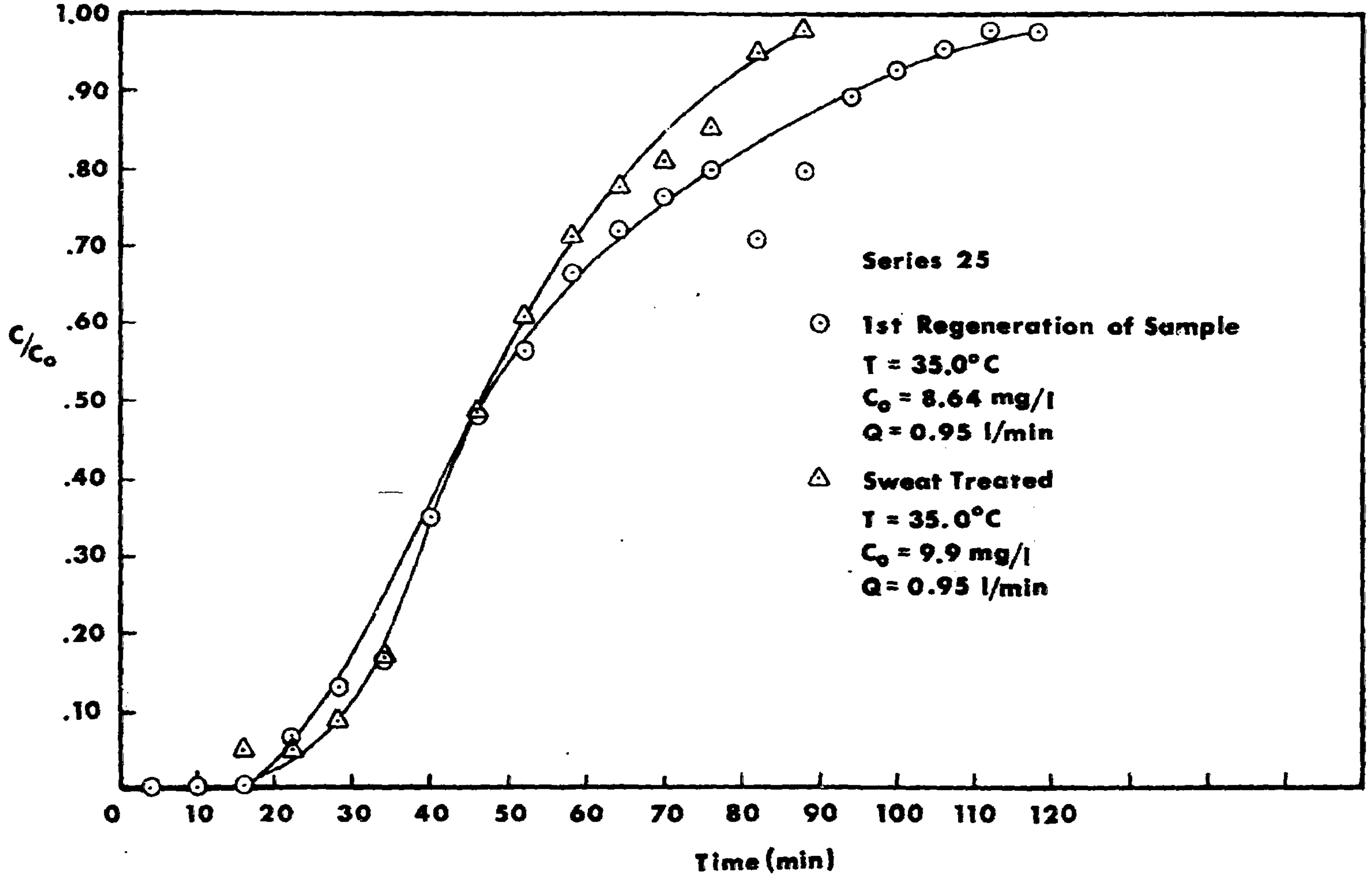


Figure 1. Effect of Sweat on DCEE Adsorption-Series 25

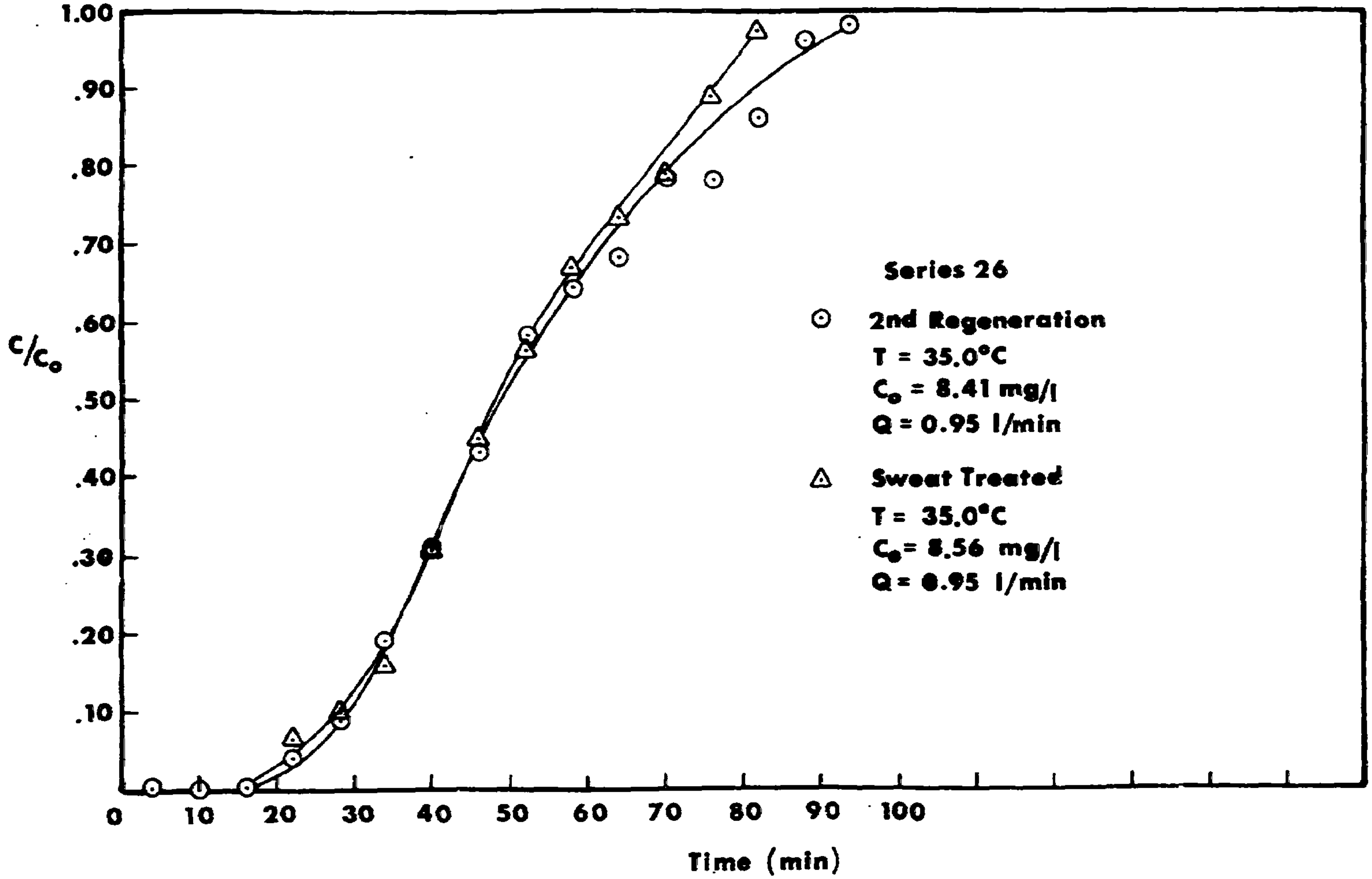


Figure 2. Effect of Sweat on DCEE Adsorption-Series 26

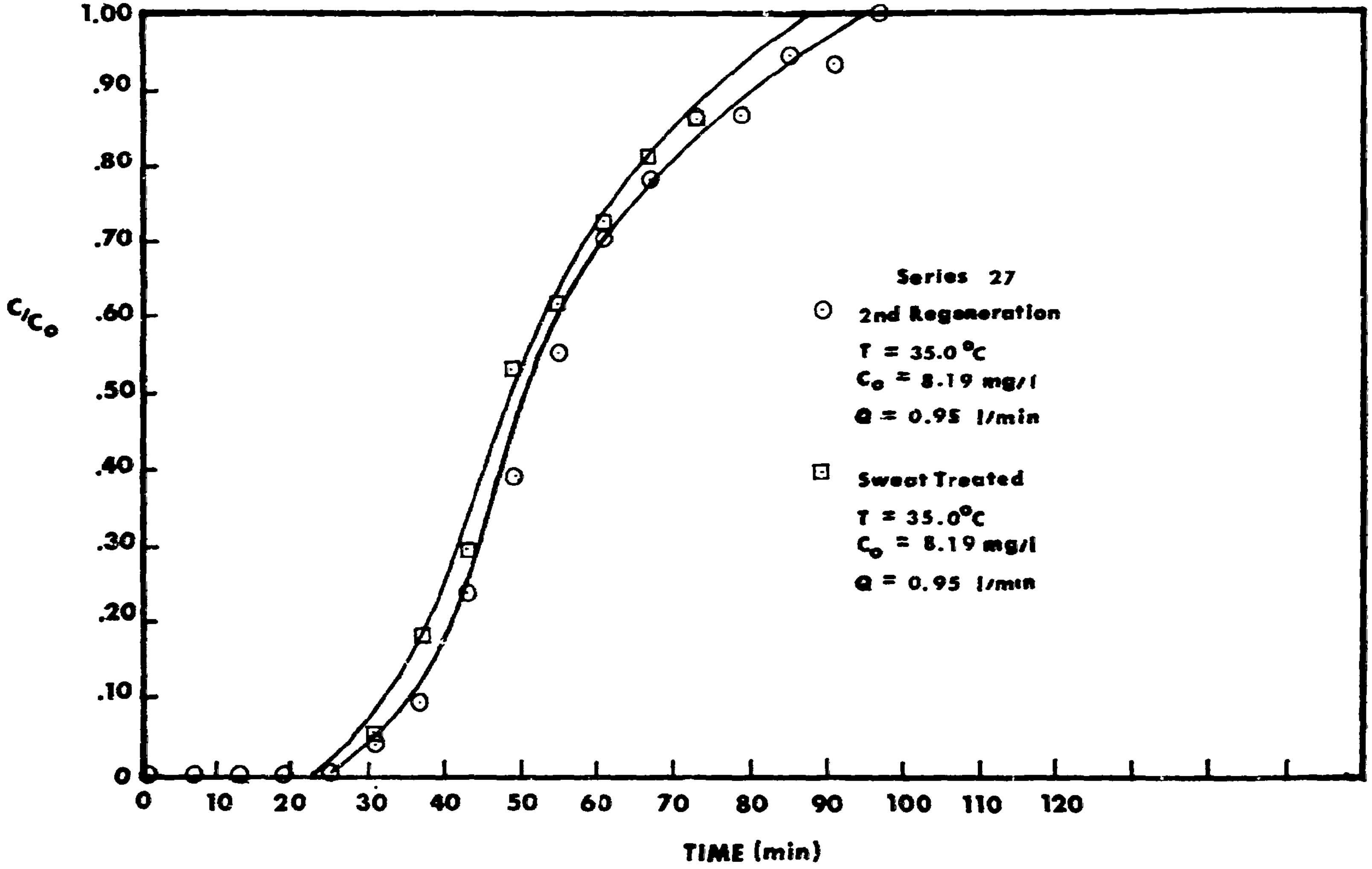


Figure 3. Effect of Sweat on DCEE Adsorption-Series 27

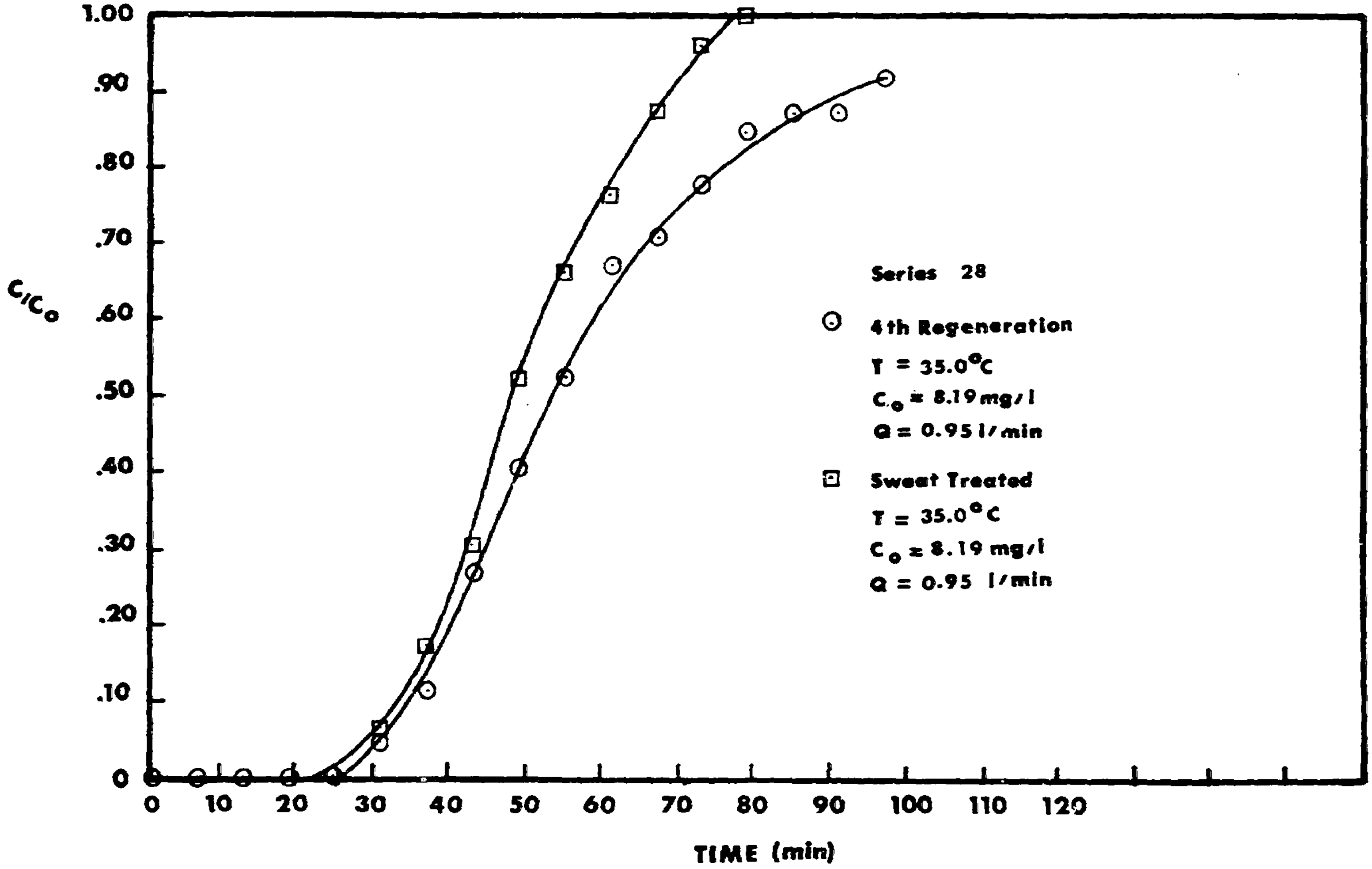


Figure 4. Effect of Sweat on DCEE Adsorption-Series 28

DCEE Equilibrium Isotherms

Experiments were performed at 35.0°C on the McBain balance to determine adsorption isotherms for DCEE. The data from these experiments are plotted in Figure 5 and show that DCEE adsorption on carbon-impregnated foam follows a Type I isotherm. The scatter in the data is believed to be caused by variability in the foam samples; the active carbon fraction varies from one sample to another.

Although the DCEE concentrations in the dynamic adsorption runs were in the same range as that used in the CCl_4 runs, there was a substantial difference in activities — defined as the ratio of partial pressure to vapor pressure (p/p_s). Experiments on CCl_4 were conducted with $p/p_s < 0.1$ which corresponded to a range of activities over which the isotherm was linear. Linearity of the isotherm was an assumption in developing the overall coefficient model (Reference 1) used to describe adsorption on carbon-impregnated foam. On the other hand, experiments on DCEE have been conducted with $p/p_s \approx 0.5$. As can be seen in Figure 5, operating at this ratio of partial pressure to vapor pressure means that the adsorption process included a nonlinear portion of the isotherm. There may, therefore, be some difficulty in using the overall coefficient model to describe this system.

Also shown in Figure 5 is an adsorption isotherm for DCEE on carbon-free foam material. These data show that roughly 20% of the capacity of the carbon-impregnated foam is in the foam itself. This is approximately the same relative capacity exhibited by the foam for CCl_4.

Figure 6 shows data obtained for an adsorption-desorption set of experiments. Removal of all adsorbed DCEE from activated carbon was found to be extremely difficult.

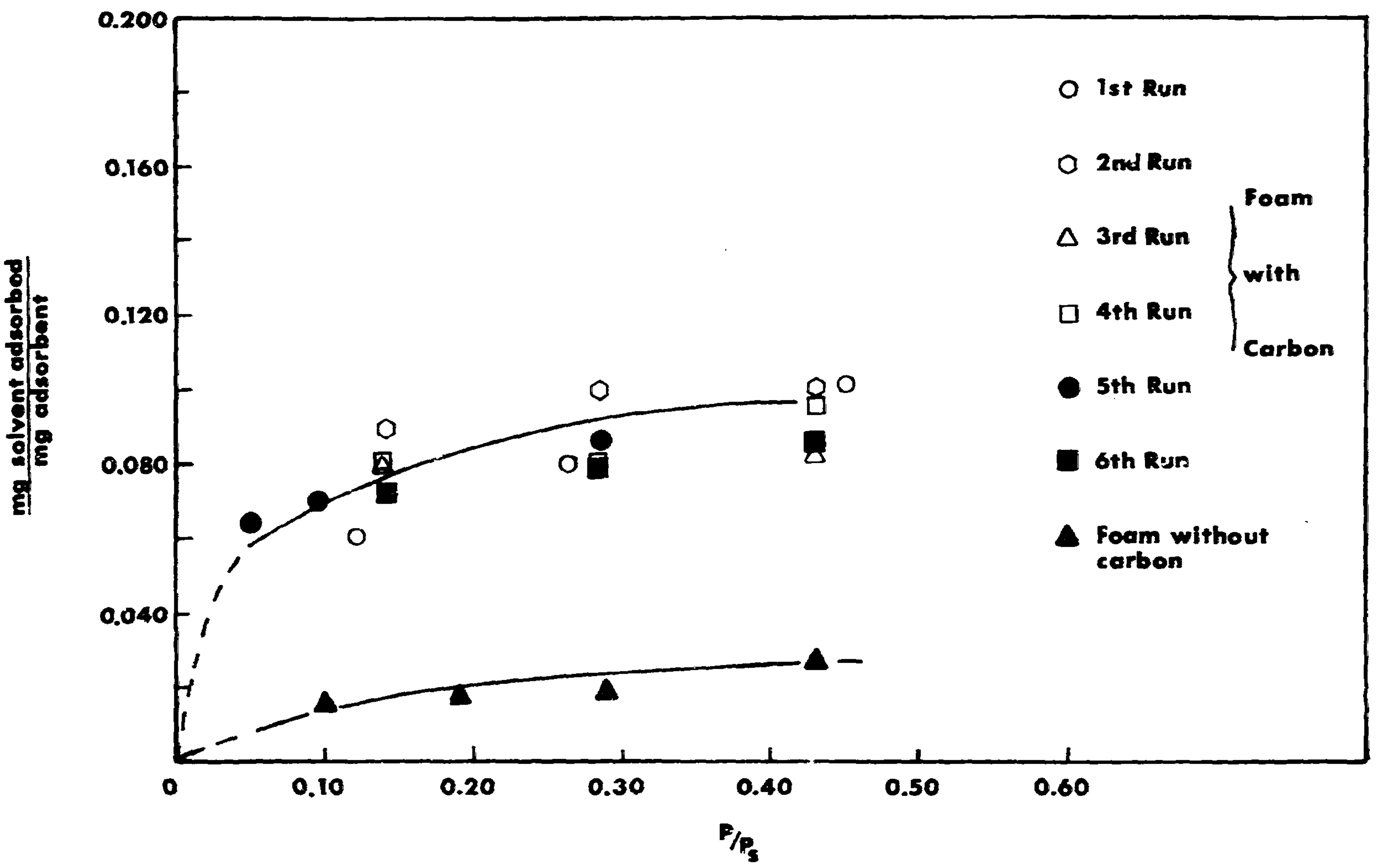


Figure 5. DCEE Adsorption Isotherms.

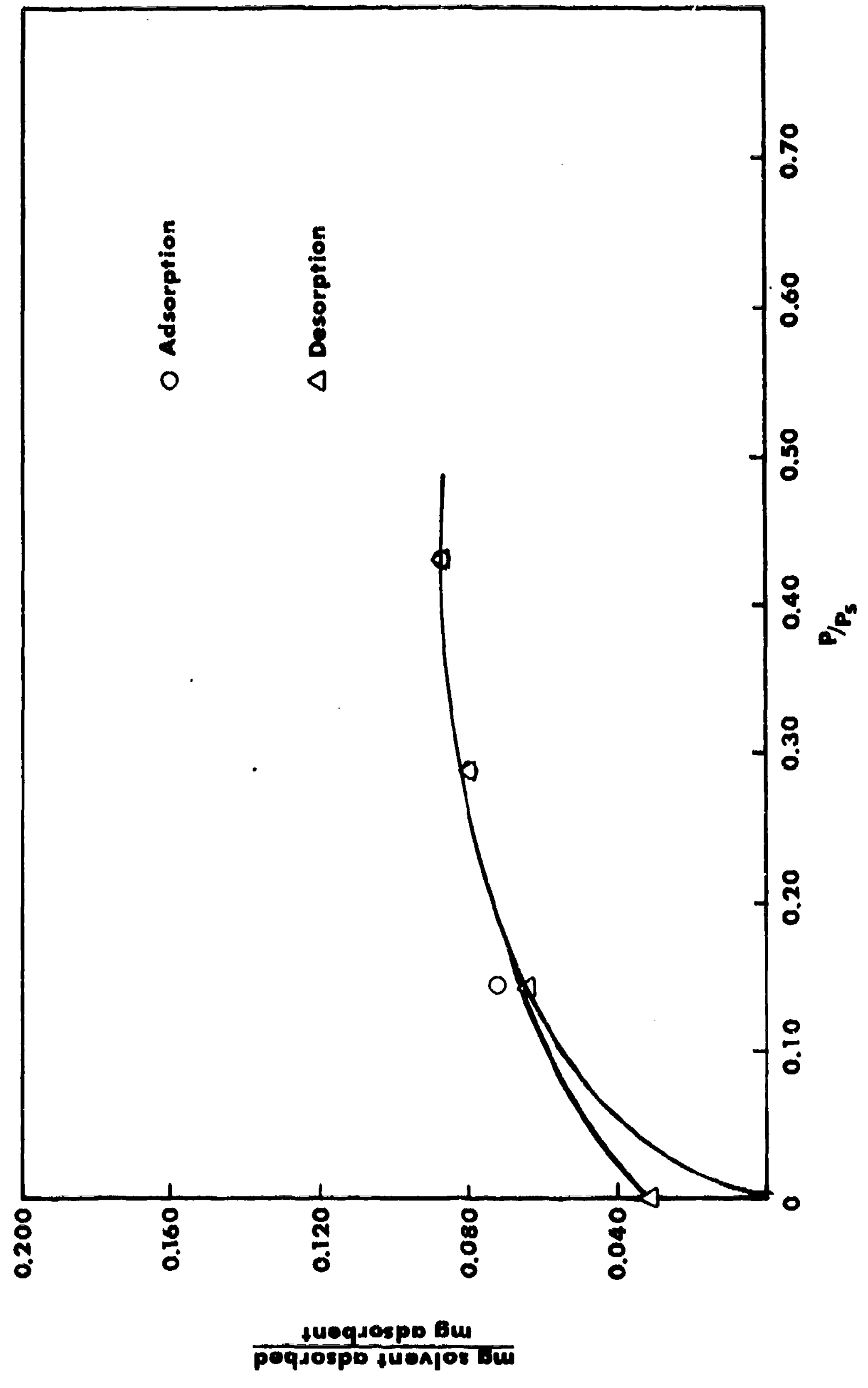


Figure 6. Adsorption-Desorption of DCEE on Carbon Impregnated Foam.

MODIFICATION OF COTTON UNDERGARMENT

One of the primary objectives of this research project has been to investigate methods of modifying cotton undergarment fabric which, when worn beneath a protective overgarment, results in a reduction in sweat poisoning of the overgarment. Data were presented in Reference 1 which indicated that grafting anion exchange substituents to the cellulose substrate of the undergarment fabric reduced the deleterious effects of sweat poisoning. Experiments along these lines have been continued and expanded to consider other synthesis procedures, and the effects of other types of modifications.

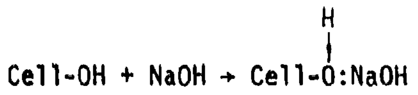
Grafting Amine Substituents to Cellulose

As illustrated in Reference 1, lactic acid is dominant among sweat constituents in reducing the adsorptive capacity of carbon impregnated foam. Since lactic acid may be exchanged on an anion exchange resin by the reaction

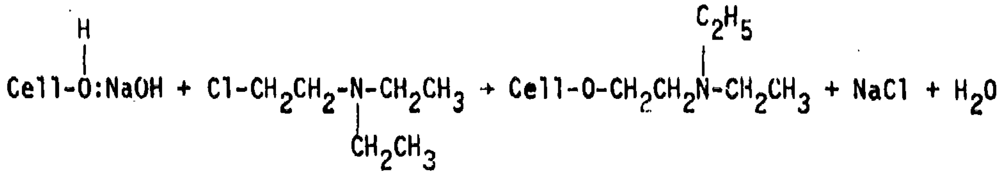
$$R_1\,COOH + R_2^+\,X^- \rightarrow R_1.COOR_2^+ + HX \qquad (1)$$

experiments were conducted which imparted this exchange capability to the cellulose substrate of the cotton undergarment fabric.

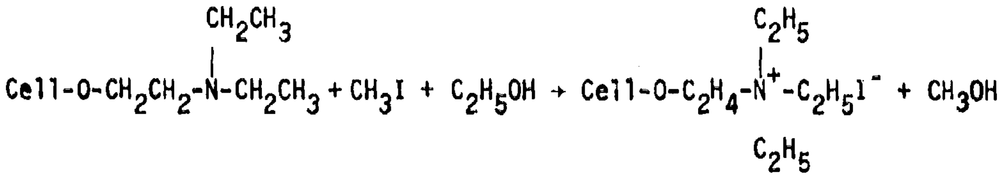
Initial experiments concentrated on producing a quarternized ammonium substituent because it was believed that a strongly basic anion exchange group would have advantages over weakly basic groups. The strongly basic triethyl aminoethyl (TEAE) cellulose was synthesized by the following series of reactions:



$$\mathrm{Cell\text{-}OH + NaOH \rightarrow Cell\text{-}\overset{H}{O}{:}NaOH} \qquad (2)$$



$$\mathrm{Cell\text{-}\overset{H}{O}{:}NaOH + Cl\text{-}CH_2CH_2\text{-}\underset{CH_2CH_3}{N}\text{-}CH_2CH_3 \rightarrow Cell\text{-}O\text{-}CH_2CH_2\overset{C_2H_5}{N}\text{-}CH_2CH_3 + NaCl + H_2O} \qquad (3)$$



$$\mathrm{Cell\text{-}O\text{-}CH_2CH_2\text{-}\overset{CH_2CH_3}{N}\text{-}CH_2CH_3 + CH_3I + C_2H_5OH \rightarrow Cell\text{-}O\text{-}C_2H_4\text{-}\overset{C_2H_5}{\underset{C_2H_5}{N^+}}\text{-}C_2H_5I^- + CH_3OH} \qquad (4)$$

Reactions 2 and 3 produce diethyl aminoethyl (DEAE) cellulose,a weakly basic cellulose derivative. Quaternizing the amine groups of DEAE cellulose by reaction 4 produces a strongly basic quaternary ammonium complex — triethyl aminoethyl (TEAE) cellulose. There are, therefore, two important steps in the synthesis procedure: grafting the amine groups to the cellulose substrate and quaternizing the attached amines. Degree of substitution (D.S.) is the number of amine groups per monomer unit and degree of quaternization is the fraction of these amine groups which have been quaternized.

A grafting procedure described in Reference 1 was used with limited success in the early part of this study to synthesize DEAE cellulose. Degrees of substitution of 0.08 to 0.12 were obtained but the product fabric was obviously non-uniform and unsuitable for use as an undergarment material. A procedure suggested by Kimura[3] was used in later runs; product fabric from these tests was uniform and had a D.S. of 0.05 to 0.09. This procedure called for immersing the cotton fabric in 6N sodium hydroxide for 30 minutes, washing the excess

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[3] M., Kimura, Bull. Natl. Inst. Health (Kawaraki, Japan), 2, 48 (1959).

sodium hydroxide from the material and allowing it to air-dry overnight. The fabric sample was then placed in a resin kettle containing about 1.5 liters of a solution of 2-chlorotriethylamine hydrochloride, dissolved in a minimal amount of water, and 2N sodium hydroxide. The solution had been prepared immediately before its use and cooled to 4°C. After the fabric was in the solution the contents of the resin kettle were hand stirred briefly, then allowed to stand at 4°C for 30 minutes. A stirrer was then connected and the mixture was stirred at 30°C for 8 hours. Two molar sodium chloride was then added before the fabric was placed in 1N sodium hydroxide for 15 minutes, then in 1N HCl for 15 minutes and finally overnight in 0.1N sodium hydroxide. The fabric was then washed with distilled water until the washings were neutral, as determined with a phenolphthalein indicator solution, and dried at room conditions.

The degree of substitution of the amine group onto the substrate to form DEAE cellulose was determined by a simple acid titration procedure, described in Appendix A. This relatively simple analytical procedure was checked by the more time-consuming Kjeldahl analysis for nitrogen described in Appendix B. Duplicate analyses on a single grafted material gave a degree of substitution of 0.085 when determined by the acid titration procedure and 0.087 when determined from the Kjeldahl procedure. These results show that the simple titration procedure can be used to determine degree of substitution. A simple determination of weight gain by the fabric can be used for a quick estimate for D.S., but this is not as accurate as the titration method.

Two procedures were used to quaternize DEAE cellulose to TEAE cellulose. These involved refluxing the DEAE cellulose in either 10% or 20% ethanolic solutions of methyl iodide. By using the 20% methyl iodide solutions, the degree of quaternization was increased from 0.15 to 0.59.

The ion exchange capacity of the product fabrics is defined as the equivalents of acid exchanged per unit mass of fabric. This quantity can be determined from the acid titration procedure described in Appendix A. The ion exchange capacity gives an indication of the total number of sites on the fabric that can exchange anions; the sites may be quaternary or tertiary amine groups. Unless the fabric has a reasonable anion exchange capacity,it will not be useful in reducing sweat poisoning caused by lactic acid transmission.

The ion exchange capacity of the modified fabric from the preparative procedure described above was 0.55 meq/gram fabric. In other words, a one-gram sample of the modified cloth could theoretically remove all of the lactic acid from 28 ml of simulated sweat. The actual effectiveness of these materials in reducing sweat poisoning will be shown in a later section.

Mercerization

Cotton undergarment fabric was treated, with stirring, overnight at room temperature in 20% sodium hydroxide. It was then washed free of excess sodium hydroxide, as determined with a phenolphthalein indicator solution and dried at room conditions. This material was used to compare fabric which had amine substituents attached to the cellulose substrate to material which had been through identical caustic treatment. Mercerization did not provide as much protection against sweat poisoning as did amine cellulose derivatives.

Increasing the Water Absorbency of Cotton Fabric

Samples of the cotton undergarment material were modified by grafting acrylic acid monomer to the cellulose substrate. The procedure is described in Appendix C. It was believed that the attachment of these substituents would cause the undergarment to retain a greater quantity of sweat thereby lengthening the useful lifetime of protective overgarment material.

This method provided more protection against sweat poisoning than did mercerization, but was less effective than the amine cellulose derivatives.

REDUCTION IN SWEAT POISONING

The results of tests reported in Reference 1 showed that forming the TEAE cellulose derivative on cotton undergarment fabric produced a material which reduced the deleterious effects of sweat poisoning. Those and subsequent experiments were conducted using a procedure described in detail in Reference 1. This procedure called for repeating breakthrough runs on a sample of carbon-impregnated foam until successive runs produced identical breakthrough curves. The sample was then removed from its holder and placed on the sweat applicator with a piece of the test undergarment between the applicator and the foam. A fixed volume (20 ml) of sweat was forced through the undergarment material and into the foam. The foam was then placed in a desiccator over P_2O_5 and dried to constant weight. It was then returned to the sample holder and an adsorption run made under conditions identical to the reference runs.

With the procedure described above a comparison could be made of the effects of sweat poisoning with no undergarment, unmodified undergarment, or modified undergarment placed between the sweat applicator and foam. A visual comparison of breakthrough curves and/or a determination of percentage changes in key variables were used to make this comparison. The variables considered most important were breakthrough time t_b (when the ratio $C/C_o = 0.05$) and total amount of vapor adsorbed, M_t. The changes evaluated were determined as follows:

$$\Delta t_b = \frac{t_b \text{ (sweat treated)} - t_b \text{ (as received)}}{t_b \text{(as received)}} \times 100\% \qquad (5)$$

$$\Delta M_t = \frac{M_t \text{ (sweat treated)} - M_t \text{ (as received)}}{M_t \text{ (as received)}} \times 100\% \qquad (6)$$

Early experiments in the period covered by this report were unsatisfactory because of nonuniformity of the modified cotton fabric and variability of the carbon-impregnated foam. These difficulties were solved by simplifying the synthesis procedure of the modified fabric and by using foam samples which had more uniform adsorption capacities.

The procedure for quaternizing DEAE cellulose to TEAE cellulose was recommended by McKelvey and Benerito (4), and requires refluxing the reaction mass for two hours. There has been disagreement in the literature over the effectiveness of the quaternization step, particularly as to whether or not the quaternization actually takes place as shown in Equation 4, or if this step actually results in degradation of the fabric. Because of these factors, it was decided to try to use the DEAE cellulose fabric as the anion exchange undergarment material. The fabric should still remove lactic acid from solution since the substituent amine groups, as Lewis bases, will react with carboxylic acids.

As a second change in experimental procedure, it was decided to use a simulated sweat containing twice the solids concentration used in previous runs. This should more vividly demonstrate the effects of sweat poisoning on the adsorptive process. The composition of the "double strength" sweat is given in Table 2.

Four sets of carbon-impregnated foam samples were conditioned and dried before reference curves were prepared for CCl_4 adsorption on each; the samples were then exposed to the simulated poisoning process described above. The only variation among the samples was the nature of the fabric placed between the sweat source and the carbon impregnated foam: run CDSTH had no

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[4] J. B. McKelvey, and R. R. Benerito, J. Appl. Sci., 2, 1693 (1967).

Table 2. Composition of "Double-Strength" Simulated Sweat.

Compound	Concentration (g/ℓ)
Sodium Chloride	10.0
Potassium Sulfate	1.0
Sodium Sulfate	0.2
Magnesium Sulfate	2.04
Calcium Chloride	0.08
Urea	1.0
Glucose	0.30
Lactic Acid	2.0
Pyruvic Acid	0.06

The pH was corrected to 7.5 with ammonium hydroxide, and deionized water was used as the solvent.

fabric, run CDSUE had "as received" fabric, run CDSMF had fabric which had been mercerized (treated with sodium hydroxide only), run CDSDG had DEAE cellulose fabric, and run CDSSL had cotton fabric treated to increase its water absorbency by grafting acrylic acid monomer to the cellulose.

After sweat poisoning, carbon tetrachloride adsorption runs were made on each foam sample. Results of these runs and their corresponding reference runs are shown in Figures 7 through 11. Percent changes in amount of CCl_4 adsorbed to breakthrough time M_b and in total amount of CCl_4 adsorbed caused by the sweat treatment process are shown in Table 3. These quantities on a per unit mass of foam basis M_b^* and M_t^* are also given in Table 3.

Figure 7 shows that the breakthrough time of CCl_4 is reduced by ∿ 60% due to sweat poisoning. Figure 8 shows that by forcing the simulated sweat to pass through an untreated undergarment placed between the sweat source and the protective foam,the sweat causes a 56.25% reduction in breakthrough time. As shown in Figure 9, mercerization of the undergarment material extends the breakthrough time further, but the introduction of the ion exchange groups in DEAE cellulose causes the breakthrough time for the reference runs to be essentially identical to that of the sweat-treated run (see Figure 10). Figure 11 shows that the modification to the cotton fabric to increase its water absorbency increases breakthrough time slightly more than mercerization. The increase in water absorbency was not measured quantitatively.

The results of these experiments prove that the effects of sweat poisoning are reduced slightly by simply placing a cotton undergarment between the sweat source and the protective overgarment. However, if the cotton fabric has been modified to give it ion exchange characteristics, as described in this report, the amount of CCl_4 that can be adsorbed before breakthrough is increased by more than 35%.

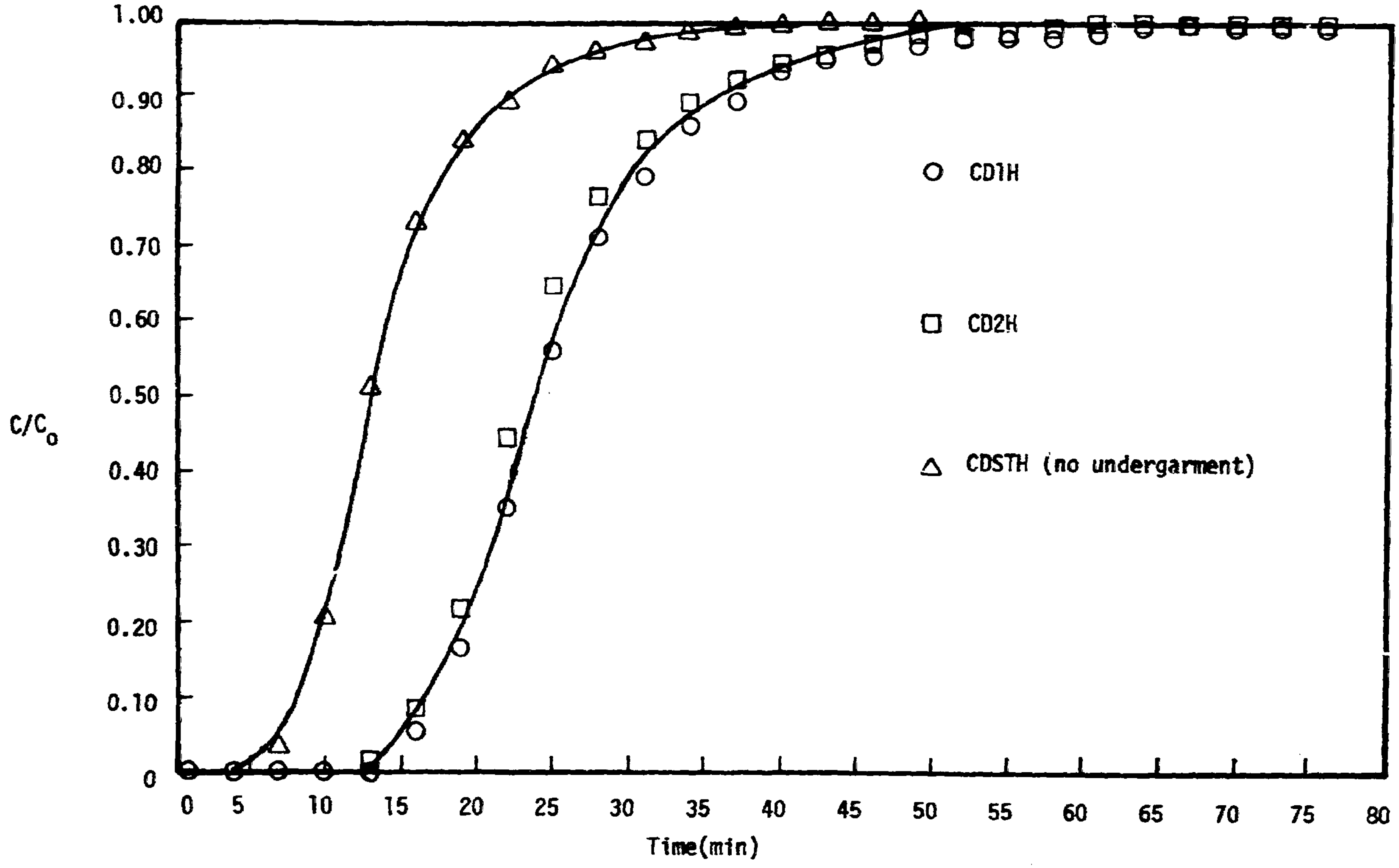

Figure 7. The Effect of Double-Strength Sweat on CCl_4 Adsorption (No Undergarment).

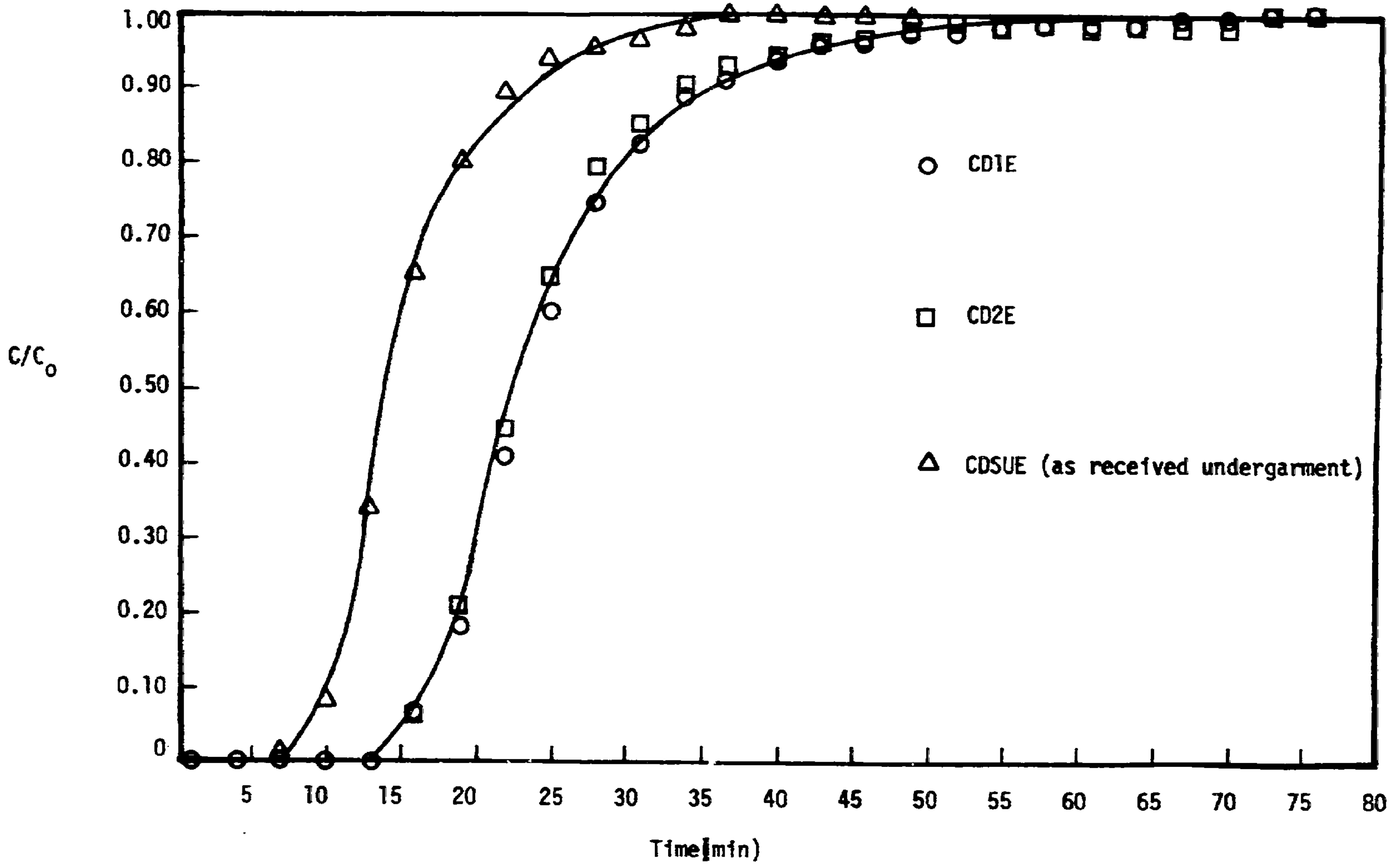

Figure 8. The Effect of Double-Strength Sweat on CCl_4 Adsorption (As-Received Undergarment)

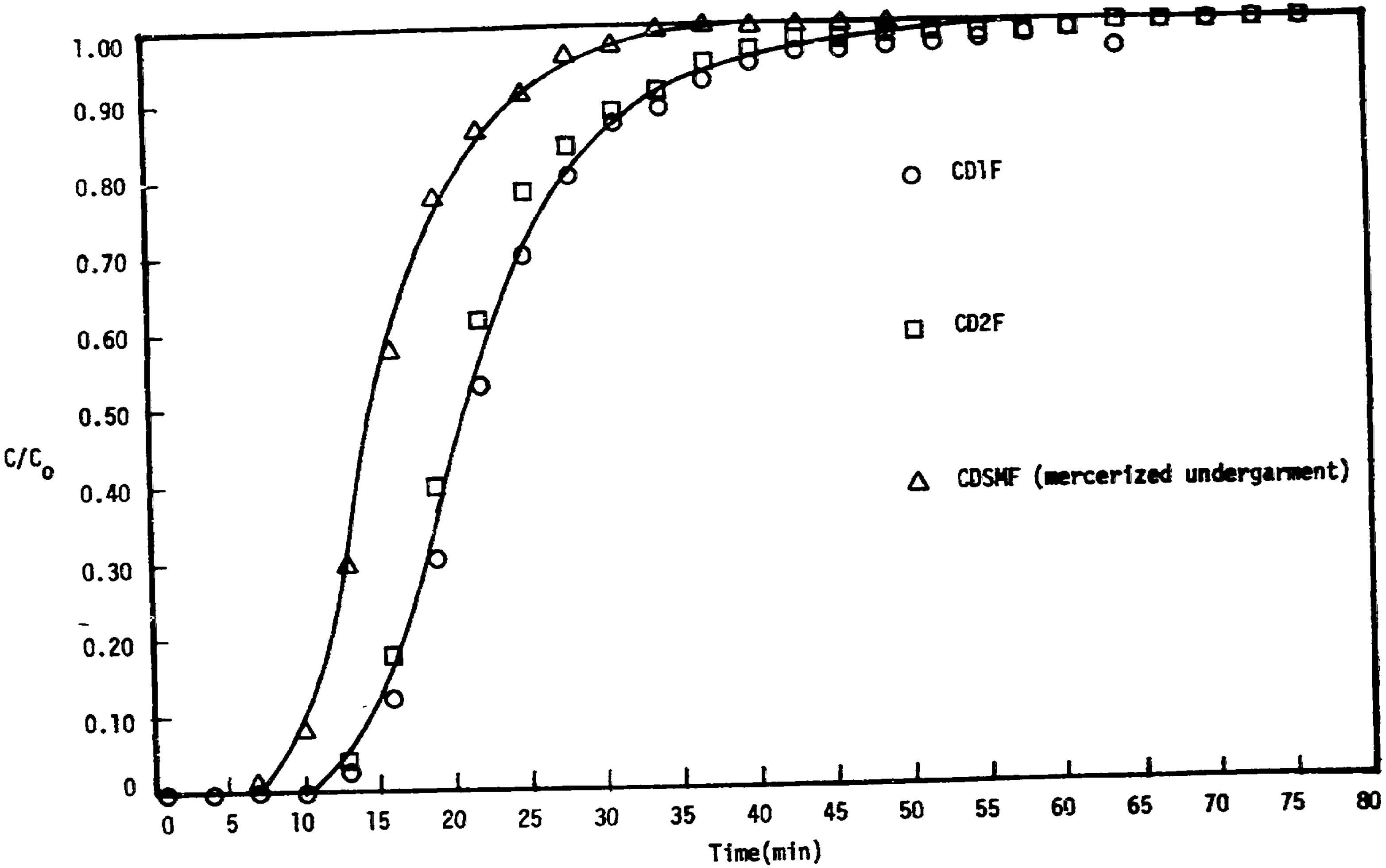

Figure 9. The Effect of Double-Strength Sweat on CCl_4 Adsorption (Mercerized Undergarment).

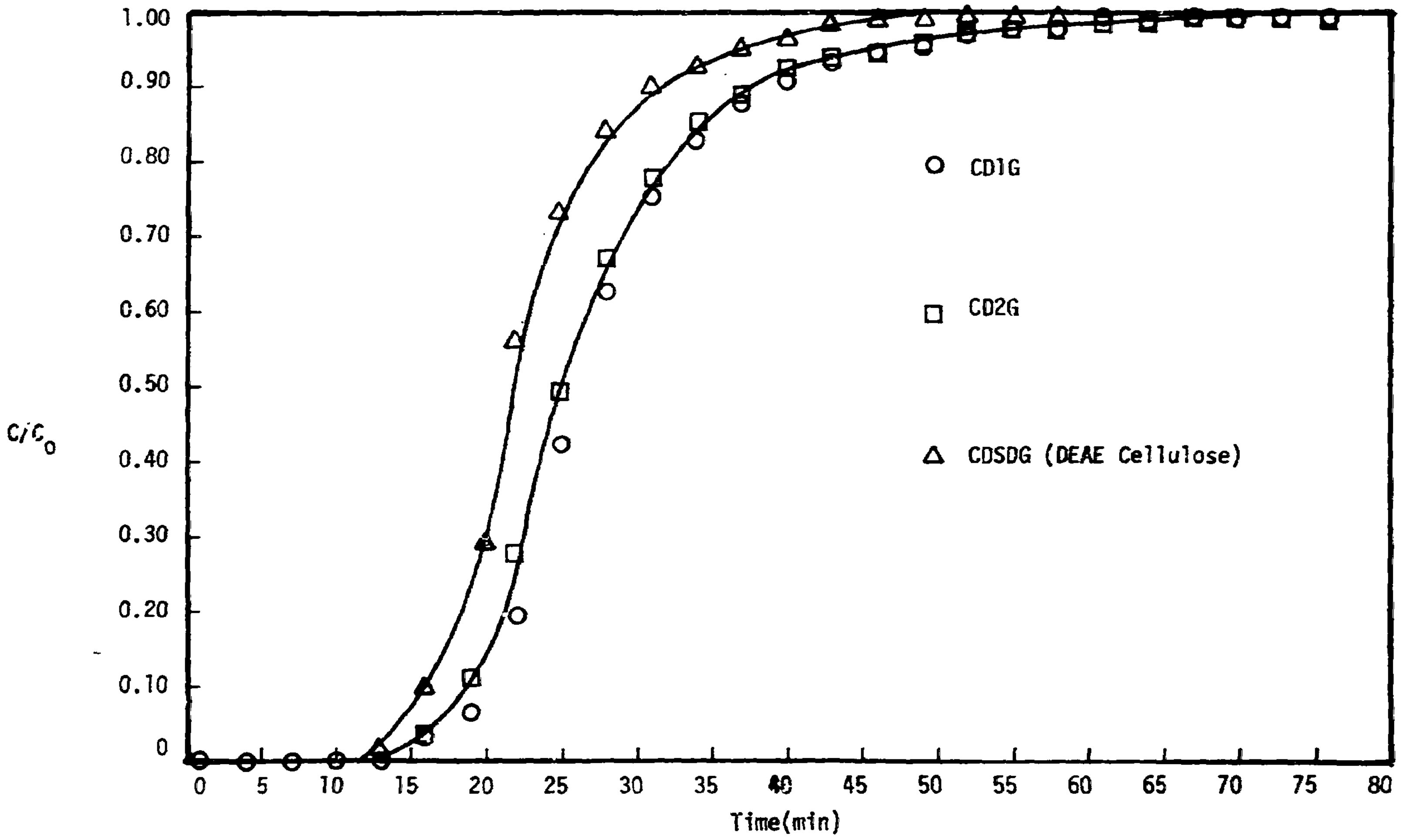

Figure 10. The Effect of Double-Strength Sweat on CCL_4 Adsorption (DEAE Cellulose)

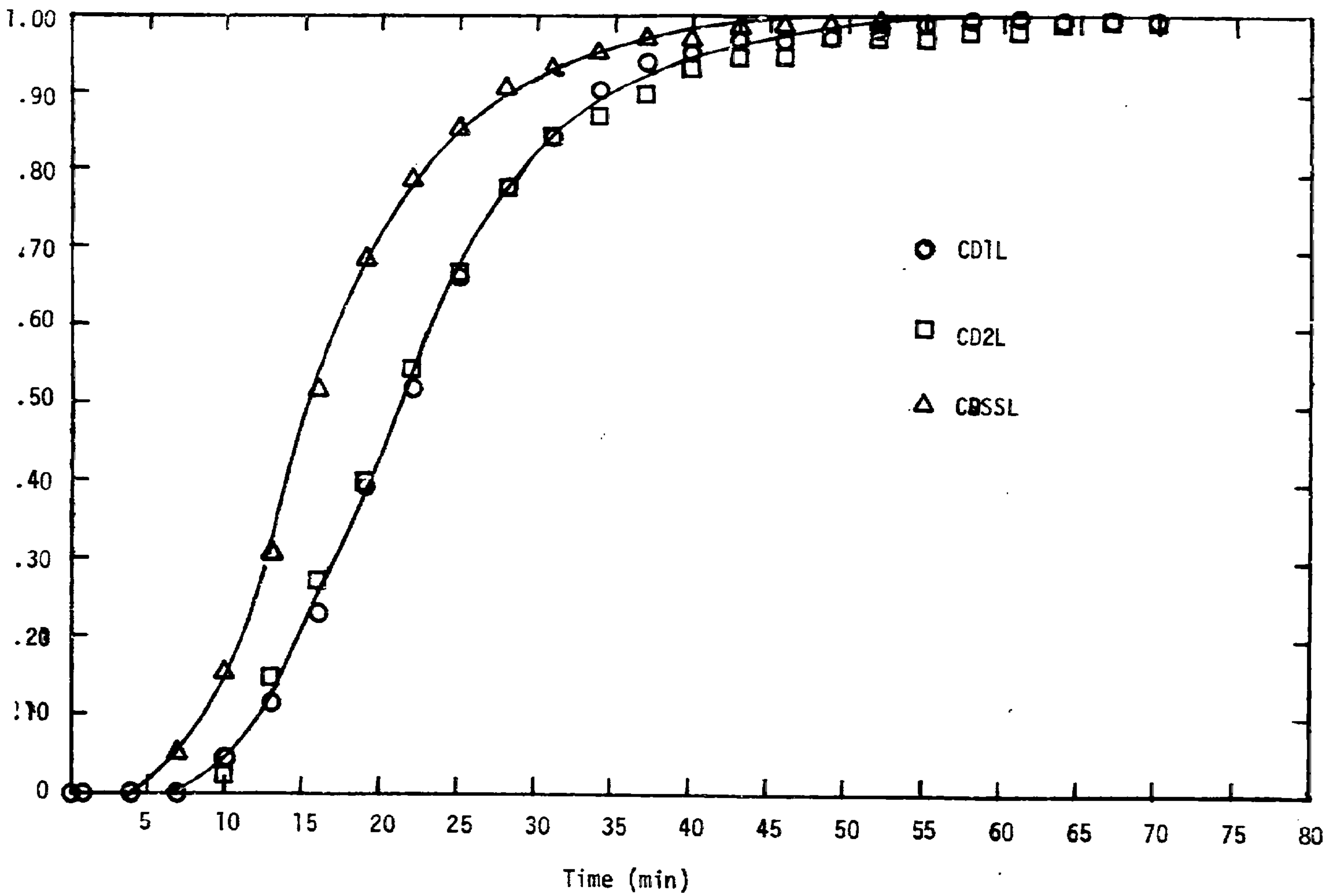

Figure 11. The Effect of Double-Strength Sweat on CCl_4 Adsorption (cellulose modified to increase water absorbency).

Table 3. Percent Changes in M_b, M_b*, M_t, M_t* Due to Sweat Treatment.

Run Sequence	Fabric	ΔM_b(%)	ΔM_b*(%)	ΔM_t(%)	ΔM_t*(%)
CDSTU	none	-56.25	-56.07	-44.29	-44.33
CDSUE	as received cotton tee shirt	-56.25	-56.25	-38.16	-38.16
CDSMF	mercerized cotton tee shirt	-46.15	-45.83	-29.85	-29.88
CDSDG	DEAE modified cotton tee shirt	-18.75	-18.80	-18.02	-18.16
CDSSL	cellulose modified to increase water absorbency	-30.0	-29.89	-25.86	-25.84

A COMPARISON OF LIQUID AND VAPOR SWEAT POISONING

The following experimental procedure was used to determine the effects of liquid sweat and sweat vapors on the adsorptive properties of carbon-impregnated foam:

Carbon tetrachloride adsorption runs were made on foam samples in the dynamic adsorption apparatus until successive breakthrough curves (a plot of C/C_0 vs. time) were identical.

The samples to be treated with liquid sweat were placed on the sweat applicator (see Reference 1) and allowed to absorb simulated sweat until further wetting of the foam was impossible. Approximately 20 ml of sweat were absorbed by each sample layer. The sweat-treated foam was then removed from the applicator and dried to constant weight in a dessicator. A dynamic adsorption run on the sample gave a comparison between the as-received foam and the liquid sweat-treated foam.

With one exception, a similar procedure was followed for samples which underwent treatment with sweat vapors. Rather than being soaked with liquid sweat, the foam samples were hung in an atmosphere of simulated sweat at 38°C. After coming to equilibrium absorption in this atmosphere, the sample was dried to constant weight and run in the dynamic adsorption apparatus.

Results of these experiments are summarized in Table 4. Application of liquid sweat in the quantities described has a significant effect on the CCl_4 breakthrough time and the total amount of CCl_4 adsorbed. Sweat vapors had no influence on these properties. These data show, then, that sweat poisoning is due entirely to contact of the protective overgarment with liquid sweat.

Table 4. Comparisons Between As-Received and Sweat-Treated Carbon Impregnated Foam Material (Bolt 4) at 35°C and 1.0 liter/min.

Run No.	No. of Layers	t_b(min)	M_t^*(mg/g)	Foam Condition
2-B_4AR	1	4	24.49	as received
2-B_4SS	1	1	21.39	liquid sweat treated
4-B_4AR	2	10	27.82	as received
4-B_4SS	2	7	24.92	liquid sweat treated
6-B_4AR	2	13	30.63	as received
6-B_4SS	2	10	25.28	liquid sweat treated
8-B_4AR	2	10	27.42	as received
8-B_4SS	2	7	24.58	liquid sweat treated
5-B_4AR	2	10	28.04	as received
5-B_4SSH	2	10	28.94	vapor sweat treated
7-B_4AR	2	13	33.77	as received
7-B_4SSH	2	13	35.87	vapor sweat treated

PROTECTIVE LIFE CALCULATIONS

The purpose of this section is to present results of calculations predicting, from CCl_4 data and a mathematical model, the protective life (t_b) of all materials studied at N. C. State University, when exposed to mustard vapor. Calculations were made using the following formula supplied by the U. S. Army Natick R&D Command

$$t_b(HD) = 165\ t_b(CCl_4) + 752 \qquad (7)$$

The materials studied under Grant No. DAAG17-72-G-0004 are listed in Table 5. Complete data on these materials are given in Reference 1.

The materials listed as Bolts 1, 2, 3, and 4 are all carbon impregnated, foam materials supplied by Natick at different times during the project, and are all different in their adsorption characteristics. All materials discussed below were conditioned as described in Reference 1.

Bolt 1 material was used for preliminary and exploratory work and no useful data were taken on this material.

For Bolt 2 and Bolt 3 material, sufficient data were taken on conditioned material to determine a good statistical equation for the breakthrough time for CCl_4 adsorption. This analysis is described in detail in Reference 1.

These equations are, for Bolt 2,

$$t_b = -\ 5.87 + 1192\ \frac{Z}{nC_oQ} \qquad (8)$$

and for Bolt 3,

$$t_b = -\ 12.18 + \frac{Z}{nC_oQ} \qquad (9)$$

Table 5. Adsorbent Materials Studied Under Previous Contract.

Material	Description	Utility
Bolt 1	carbon impregnated foam material	initial investigation
Bolt 2	carbon impregnated foam material	central composite statistical design of experiments used in modeling
Bolt 3	carbon impregnated foam material	investigation of sweat poisoning
Bolt 4	carbon impregnated foam material	control of sweat poisoning
VEE 3280	Nomex-cotton-carbon composite	
VEE 3279	carbon-Nomex-weftamatic	
VEE 3219	carbon-Nomex fabric	
Pluton B-1	woven carbon fabric	
VEE 3098	quilted fabric	
A46C54	British cloth (woven carbon fabric)	
P99	British cloth (woven carbon fabric)	

The range of applicability of these equations, for t_b in minutes, is

C_o - 5 to 12 mg/ℓ
Q - 0.5 to 1.5 ℓ/min
z - 1 to 3 layers, where layer thicknesses are given in Table 6.

In the above equation n is a sample weight normalizing factor and is the average sample weight divided by the individual weight. For predicting t_b, where n is not known, it should be taken as 1. It is believed that Equations 8 and 9 give better values for t_b than any individual run since they represent the results of a statistical analysis.

Equations 8 and 9 may be combined with Equation 7 to give equations for the protective life, t_b(HD) for distilled mustard.

For Bolt 2,

$$t_b(\text{HD}) = -217 + 196680 \frac{z}{C_o Q} \tag{10}$$

and for Bolt 3,

$$t_b(\text{HD}) = -1258 + 468435 \frac{z}{C_o Q} \tag{11}$$

In using Equations 10 and 11 the values of z, C_o, and Q must be within the limits noted above and are for CCl_4.

For all experiments reported in Reference 1, the calculated values of t_b(HD) are presented in Table 7.

Table 6. Physical Properties of the Adsorbent Material.

Cloth Type	Cloth Thickness(cm)	Porosity(α)
Bolt 2	0.172	0.846
Bolt 3	0.183	0.813
Bolt 4	0.174	0.860
Pluton B-1	0.062	0.440
British Cloth A46C54	0.060	0.865
British Cloth P99	0.066	0.880

Table 7a. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Comparison Runs to Determine Effect of Foam Material Treatment, Third Bolt of Foam Material Material.

Run No.	L^*	W_t^*	T^*	Q^*	C_o^*	t_b^*	$t_b(HD)^*$
Sweat Treated							
3-6-ST	1	5.071	32.5	1.0	7.87	40	7352
3-7-ST	3	15.1282	32.5	1.0	7.75	164	27812
3-8-ST	1	4.8895	37	1.3	10.43	20	4052
3-9-ST	3	14.8746	37	1.3	10.47	93	16097
3-12-ST	1	4.6564	28	1.29	10.47	20	4052
As Received							
3-21-AR	1	5.1273	32.5	0.99	7.94	44	8012
3-22-AR	3	15.4468	32.5	1.0	7.87	157	26657
3-10-AR	1	5.1598	37	1.3	10.47	26	5042
3-20-AR	3	15.3595	37	1.3	10.60	92	15932
Conditioned							
3-13-WT	1	5.0624	32.5	0.99	7.87	41	7517
3-17-WT	3	14.7066	32.5	0.99	7.87	174	29452
3-3-WT	1	4.7749	37	1.3	10.30	26	5042
3-1-WT	3	15.3932	37	1.3	10.45	116	19892
Dried in Desiccator							
3-15-D	1	5.1941	32.5	0.99	7.87	48	8672
3-14-D	3	15.3120	32.5	0.99	7.86	178	30122
3-19-D	1	4.9722	37	1.3	10.47	29	5537
3-18-D	3	14.6848	37	1.3	10.47	102	17582

NOTE:

* L=Number of Layers, W_t=Sample Weight (g), T=Temperature (°C), Q=Flow Rate Through Sample l/min), C_o=Vapor Concentration in Inlet Stream (mg/l), t_b-Breakthrough time (min) for CCl_4, $t_b(HD)$=Breakthrough Time (min) for Distilled Mustard.

Table 7b. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Effect of Poisoning by Sweat and Sweat Components on Carbon Impregnated Foam Material

Run No.	L	W_t	T	Q	C_o	t_b	t_b(HD)
Lactic Acid Treated (1 g/ℓ)							
3-27-LA	1	4.5865	32.5	0.99	7.86	34	6362
3-30-LA	3	14.7712	32.5	0.99	7.86	154	27152
3-35-LA	1	4.8503	37	1.3	10.43	29	5537
3-29-LA	3	14.1418	37	1.3	10.43	92	15932
Urea treated (0.5g/ℓ)							
3-33-U	1	4.8542	32.5	0.99	7.86	46	8342
3-32-U	3	14.2229	32.5	0.99	7.86	160	27152
3-31-U	1	4.8503	37	1.3	10.43	29	5537
3-34-U	3	14.1418	37	1.3	10.43	92	15932
Charcoal impregnated foam material - treated with solution of 5g/ℓ lactic acid							
3-37-LA	1	4.6030	32.5	0.99	7.81	31	5867
3-36-LA	1	5.0117	37.5	1.3	10.39	20	4052
3-41-LA-D**	1	4.9988	37.0	1.3	10.39	20	4052
Charcoal impregnated foam material - treated with solution of 2.5 g/ℓ urea							
3-38-U	1	4.9346	32.5	0.99	7.86	40	7352
3-39-U	1	4.8564	37	1.3	10.43	21	4217
3-40-UD**	1	4.9314	37	1.3	10.39	22	4382
Charcoal impregnated foam material - treated with real sweat							
3-42-RST	1	5.0100	32.5	0.99	7.76	34	6362
3-43-RST	1	5.0441	37	1.3	10.39	18	3722

**Sample placed in desiccator for two days after treating and before being run.

Table 7c. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Fourth Bolt of Carbon Impregnated Foam Material

Fourth bolt of cloth, as received

Run No.	L	W_t	T	Q	C_o	t_b	t_b(HD)
11-3-AR	1	3.8463	32.5	0.99	7.82	4	1412
11-8-AR	3	11.4988	32.5	0.99	7.82	20	4052
11-1-AR	1	4.1937	37	1.3	10.39	4	1412
11-2-AR	1	3.8225	37	1.3	10.39	4	1412
11-9-AR	3	11.6264	37	1.3	10.39	13	2897
Fourth bolt of cloth, conditioned							
11-4-WT	1	3.7481	32.5	0.99	7.81	4	1412
11-7-WT	3	11.4435	32.5	0.99	7.86	29	5537
11-5-WT	1	3.8522	37	1.3	10.39	4	1412
11-6-WT	3	11.4106	37	1.3	10.39	20	4052
Fourth bolt of cloth conditioned and dried							
12-8-CD	1	3.2939	32.5	1.0	7.76	10	2402
Fourth bolt of cloth sweat treated on the applicator with air blowing over it for 3 1/2 hours							
12-10-ST	1	4.1980	32.5	1.0	7.76	4	1412
Fourth bolt of cloth sweat treated on the applicator with air blowing over it for 7 hours							
12-11-ST	1	3.8035	32.5	1.0	7.76	4	1412

(Both 11 and 12 designations refer to Bolt-4.)

Table 7d. Calculated Breakthrough Time (Protective Life) for HD
Through Various Materials
Comparison Between New and Old Sample Holders

Run No.	L	W_t	T	Q	C_o	t_b	t_b(HD)
Old Sample Holder							
12-13-WT	1	3.4610	32.5	1.0	7.76	8.0	2072
12-14-WT	1	3.4952				10.0	2402
12-16-WT	1	3.4610				10.0	2402
New Sample Holder							
12-340-WT	1	3.7623	32.5	1.0	7.76	7.0	1907
12-346-WT	1	3.7456				7.0	1907
12-347-WT	1	3.6213				7.0	1907

Table 7e. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Effect of Cobalt-60 Radiation on Carbon Impregnated Foam

Run No.	W_t	t_b	Time of Irradiation (Hrs.)	t_b(HD)
12-16-WT	3.4610	9.0		2237
12-37-I	3.4931	9.5	12	2155
12-48-I	3.5423	10.7	24	2518
12-54-I	3.8504	8.4	72	2138

Table 7f. Calculated Breakthrough Time (Protective Life) for HD
Through Various Materials
Study of Poisoning Phenomena for 1-Layer Runs

Run No.	W_t	T	Q	C_o	t_b	Nature of Treatment	t_b(HD)
12-16-WT	3.4610	32.5	1.0	7.76	9.0	conditioned	2237
12-23-LA	3.5321				7.0	no undergarment	1907
12-328-LA	3.6600				7.0	unmodified undergarment	1907
12-335-LA	3.7345				9.2	modified undergarment	2270
12-31-ST	3.6000				5.0	no undergarment	1577
12-336-ST	3.4822				4.0	unmodified undergarment	1412
12-341-ST	3.9721				7.5	modified undergarment	1990

Table 7g. Calculated Breakthrough Time (Protective Life) for HD
Through Various Materials
Study of Poisoning Phenomena for 2-Layer Runs

Run No.	W_t	T	Q	C_o	t_b	Nature of Treatment	t_b(HD)
12-63-WT	7.9600	32.5	1.0	7.76	31.5	conditioned	5950
12-58-LA	7.7071				22.5	no undergarment	4465
12-333-LA	7.3037				24.2	unmodified undergarment	4745
12-332-LA	7.6678				27.0	modified undergarment	7207
12-52-ST	7.2668				15.8	no undergarment	3359
12-339-ST	7.5417				14.5	unmodified undergarment	3145
12-343-ST	7.9755				21.0	modified undergarment	4217

Table 7h. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Evaluation of Sweat Poisoning for 2-Layer Runs Each With its Own Independent Reference

Run No.	W_t	T	Q	C_o	t_b	Nature of Modification	t_b(HD)
12-351-WT3	6.9030	32.5	1.0	7.76	13.0		2897
12-351-LA	6.8030				8.0	No undergarment	2072
12-353-WT3	6.9853				14.5		3145
12-353-LA	6.9853				12.0	unmodified undergarment	2732
12-355-WT3	7.6474				16.0		3392
12-355-LA	7.6474				15.0	modified undergarment	3227
12-357-WT3	7.0268				19.0		3887
12-357-ST	7.0268				11.0	no undergarment	2567
12-350-WT3	7.7084				18.5		3805
12-350-ST	7.7084				13.0	unmodified undergarment	2897
12-359-WT3	6.8855				16.0		3392
12-359-ST	6.8855				14.5	modified undergarment	3145

Table 71. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Adsorption of CCl_4 by Various Conditioned Fabrics

Run No.	L	W_t	T	Q	C_o	t_b	t_b(HD)
Nomex-Cotton-Carbon Composite VEE 3280							
4-1-WT	1	5.9240	32.5	0.99	7.81	3	1247
4-4-WT	3	17.0421	32.5	0.99	7.81	16	3392
4-2-WT	1	5.5275	37	1.30	10.39	2	1082
4-3-WT	3	16.9686	37	1.30	10.39	9	2237
Carbon-Nomex-Weftamatic VEE 3279							
5-2-WT	1	5.1352	32.5	0.99	7.76	1**	-
6-4-WT	3	15.7943	32.5	0.99	7.87	4	1412
5-1-WT	1	5.2652	37	1.30	10.39	1**	-
5-3-WT	3	15.7679	37	1.3	10.43	11	2567
Carbon-Nomex Fabric VEE 3219							
6-1-WT	1	4.7278	32.5	0.99	7.81	1**	-
6-4-WT	3	13.6253	32.5	0.99	7.86	7	1907
6-2-WT	1	4.6463	37	1.3	10.43	2**	-
6-3-WT	3	15.1309	37	1.3	10.43	5	1577
Pluton B-1							
7-3-WT	1	3.2482	32.5	0.99	7.81	1	-
7-4-WT	3	10.0671	32.5	0.99	7.81	34	6362
7-2-WT	1	3.3583	37	1.3	10.39	2	1082
7-1-WT	3	9.9462	37	1.3	10.39	21	4217

Quilted Fabric VEE 3098

8-1,2,3,4 immediate breakthrough, very little adsorption of CCl_4

Table 7i. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Adsorption of CCl_4 by Various Conditioned Fabrics

British Cloth A46C54							
9-1-WT	1	2.5581	32.5	0.99	7.82	26	5042
9-4-WT	3	7.4954	32.5	0.99	7.86	132	22532
9-2-WT	1	2.5441	37	1.3	10.45	14	3062
9-3-WT	3	7.6294	37	1.3	10.43	84	14612
British Cloth P99							
10-1-WT	1	1.8610	32.5	0.99	7.81	7	1907
10-3-WT	3	6.8461	32.5	0.99	7.86	160	27152
10-2-WT	1	2.2071	37	1.3	10.43	10	2402
10-4-WT	3	5.6492	37	1.3	10.43	67	11807

**Cl_4 peak appeared at first sampling

Table 7j. Calculated Breakthrough Time (Protective Life) for HD Through Various Materials

Reproducibility Data on Two-Layer Runs

Run No.	W_t	T	Q	C_o	t_b	t_b(HD)
12-351-WT	6.9030	32.5	1.0	7.76	16	3392
12-351-WT2					13	2897
12-351-WT3					13	2897
12-353-WT1	6.9853				16	3392
12-353-WT2					14.5	3145
12-353-WT3					14.5	3145
12-355-WT1	7.6474				19	3887
12-355-WT2					16	3392
12-355-WT3					16	3392
12-357-WT1	7.0268				20.5	4135
12-357-WT2					19	3887
12-357-WT3					19	3887
12-350-WT1	7.7084				20	4052
12-350-WT2					18.5	3805
12-350-WT3					18.5	3805
12-359-WT1	6.8855				18.0	3722
12-359-WT2					16.0	3392
12-349-WT3					16.0	3392

WT1, WT2 and WT3 refer to first, second and third runs on the same sample.

NOMENCLATURE

C	vapor concentration (mg/ℓ) in exit stream from sample
C_o	vapor concentration (mg/ℓ) in inlet stream to sample
M_b	mass of vapor adsorbed up to the breakthrough time (mg)
$M_b{}^*$	mass of vapor adsorbed up to the breakthrough time per unit mass of foam (mg/g)
M_t	total mass of vapor adsorbed during a run (mg)
$M_t{}^*$	total mass of vapor adsorbed per unit mass of foam (mg/g)
p	partial pressure of vapor
p_s	vapor pressure of vapor
t_b	breakthrough time (min)
Q	flow through sample (L/min)
z	thickness of sample (cm)

APPENDICES

A Acid-Base Procedure for Determination of the Degree of Substitution and Ion Exchange Capacity

B Kjeldahl Method for Determining Nitrogen Content

C Procedure for Increasing the Water Absorbency of Cotton Tee Shirt Material

Appendix A. Acid-Base Procedure for Determination of the Degree of Substitution and Ion Exchange Capacity.

1. After preparing the sample fabric, wash well with deionized water until the washings are neutral to phenolphthalein indicator solution.
2. Dry the fabric for forty-eight hours under room conditions.
3. Place a known amount ($\sim$ 1 g) of the fabric in a flask with 50.00 ml of 1N NaCl.
4. Add 50.00 ml of 0.1 N HCl.
5. Flush the flask with N_2 and allow twenty-four hours for equilibration.
6. Remove a 50.00 ml aliquot of the supernatant liquid and titrate with 0.1 N NaOH to a phenolphthalein endpoint.
7. Calculate the equivalents of acid consumed per gram of material and the degree of substitution.

Example Calculation

1. Fabric weight = 1.0897 g

   $N_{HCl} = 0.1022$; $N_{NaOH} = 0.0859$

2. Equivalents of HCl added:

   $(0.050\ \ell)(0.1022\ eq/\ell) = 5.11 \times 10^{-3}$ eq

3. HCl Concentration:

   5.11×10^{-3} eq/100 ml = 5.11×10^{-5} eq/ml

4. HCl in aliquot

   (50 ml)(5.11×10^{-5} eq/ml) = 2.555×10^{-3} eq

5. 26.40 ml of 0.0859 normal NaOH is required to neutralize aliquot to phenolphthalein end point.

6. HCl remaining in aliquot:

$$(0.02640\ \ell)(0.0859\ \text{eq}/\ell) = 2.268 \times 10^{-3}\ \text{eq}$$

7. HCl, in 50 ml aliquot, consumed by fabric:

$$(2.555 - 2.268) \times 10^{-3}\ \text{eq} = 2.87 \times 10^{-4}\ \text{eq}$$

8. Ion exchange capacity:

$$(2.87 \times 10^{-4}\ \text{eq/50 ml})(100\ \text{ml})/1.0897\ \text{g fabric}$$

$$= 5.27 \times 10^{-4}\ \text{eq/g fabric} - 0.527\ \text{meq/g fabric}$$

9. Mass of amine on fabric

$$(5.27 \times 10^{-4}\ \text{eq/g fabric})(100\ \text{g amine/eq}) = 5.27 \times 10^{-2}\ \text{g/g fabric}$$

10. Degree of substitition

$$\frac{5.27 \times 10^{-2}\ \text{g amine}}{(1-5.27 \times 10^{-2})\ \text{g cellulose}} \Bigg| \frac{1\ \text{g-mole amine}}{100\ \text{g amine}} \Bigg| \frac{162\ \text{g cellulose}}{1\ \text{g-mole cellulose}} = 0.090$$

Appendix B. Kjeldahl Method For Determination of Nitrogen Content.

1. After preparing the sample fabric, wash well with deionized water until the washings are neutral to phenolphthalein indicator solution.
2. Dry this material for forty-eight hours under room conditions.
3. Cut the material into pieces about 1/8 inch on a side.
4. Transfer a known amount (~ 1 g) to an 800 ml Kjeldahl flask containing 7 to 10 g of K_2SO_4 and 0.6 to 0.8 g of mercury.
5. Add 30 ml concentrated H_2SO_4 (sp. gr. 1.84) and swirl the flask to insure wetting of the sample.
6. Digest, insuring the H_2SO_4 vapors condense no more than half-way up the neck of the flask, until the solution in the flask is colorless.
7. Allow to cool, and add 300 ml cold deionized water, allow to cool again.
8. Pipet 20.00 ml of 0.2 N H_2SO_4 into a 240 ml Erlenmeyer flask. Attach a glass connecting tube to the discharge end of a condensor and incline the Erlenmeyer flask at a suitable angle so that the glass connecting tube is immersed to the maximum depth in the acid.
9. Add 1 to 2 g of granular zinc to the mixture in the Kjeldahl flask and 100 ml of an alkali solution prepared by dissolving 8.0 g of potassium sulfide, and 500 g sodium hydroxide in deionized water and diluting to 1 liter. Insure that the alkali solution forms a distinct layer under the acid solution in the Kjeldahl flask.
10. Connect the flask to the distilling condensor through the Kjeldahl connecting bulb and swirl the contents of the flask to mix.
11. Distill the ammonia over into the acid solution in the Erlenmeyer flask, and continue the distillation until about 150 ml of distillate have been collected.

12. Back-titrate the acid in the Erlenmeyer flask with 0.2 N NaOH to determine the amount of ammonia formed from the sample and the degree of substitution.

Appendix C. Procedure for Increasing the Water Absorbency of Cotton Tee Shirt Material.

1. Purification of the cellulose.

The cellulose was washed with methanol, at its boiling point, for six (6) hours, then dried in a vacuum oven for six hours at a temperature of 60°C.

2. Deoxygenation.

The above material was then deoxygenized in a vacuum line for 24 hours.

3. Preirradiation.

The material from step 2 was irradiated by a Co-60 γ-ray source, receiving a total dose of 10 kgy (1 Mrad) at a rate of 3.1 kgy (0.31 Mrads)/hr.

4. Preparation of Monomer Solution.

The monomer solution used was 75% (vol.) acrylic acid. The acrylic acid was purified by passing an acrylic acid solution through a column packed with Amberlyst. This step was repeated ten times. Then, the purified solution was degassed in a vacuum line by freezing, degassing, and melting. This cycle was repeated four times.

5. Grafting.

The degassed monomer solution and the deoxygenized, irradiated cellulose were combined together and placed in a temperature controlling bath at 45°C for 24 hours.

6. Decrystallization.

The grafted samples were placed in a 70% $ZnCl_2$ solution for 45 minutes, then washed with 2% HCl, then water, then 2% NaOH, then a final rinse with water.