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Studies on Some Failure Modes in Latex Barrier Films

Charles M. Guttman
Gregory B. McKenna
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National Institute of Standards and Technology
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Annual Report
Contract No. FDA 224-79-5023, Mod 18
L. Schroeder, Contract Officer

Prepared for:
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National Bureau of Standards became the National Institute of Standards and Technology on August 23, 1988, when the Omnibus Trade and Competitiveness Act was signed. NIST retains all NBS functions. Its new programs will encourage improved use of technology by U.S. industry.

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U.S. DEPARTMENT OF COMMERCE
Robert Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Raymond G. Kammer, Acting Director

ABSTRACT

This report covers work on a 1988 contract with FDA to study failure modes of latex barrier films in their use as condoms or medical gloves. Two areas have been studied in this reporting period: The change in the failure of latex barrier films as a result of swelling in body fluid simulants and the cross-link density variations on the .1 mm scale.

I. Effect of Fluid Environment on the Swelling and Mechanical Properties of Natural Rubber Latex Condoms

Gregory B. McKenna and Kathleen M. Flynn
National Institute of Standards and Technology
Polymers Division

I-A. Introduction.

It is well known[1] that the tensile strength of crosslinked polymers is adversely affected by swelling in organic solvents. As depicted in Figure 1, even small amounts of swelling can dramatically reduce the resistance of rubbers to failure. Similar losses of mechanical properties can be expected for natural rubber latex condoms when subjected to appropriate environments and for sufficient lengths of time. In use, however, the environment seen by the condom is not that of an organic solvent (in fact the reason that petroleum jelly based lubricants are not used or recommended as synthetic lubricants with natural rubber condoms is the fact that such lubricants adversely affect the performance of the condoms), rather, the environment on both the vagina and penile sides is primarily a buffered saline environment with small amounts of fatty acids, proteins and other organics. Furthermore, condoms are not expected to be exposed to such environments for inordinate lengths of time.

Because vaginal fluids and seminal fluids were not readily available to us in sufficient quantities, we examined the response of the condoms in water, a buffered saline "pseudo-extra-cellular-fluid" (PECF)[2] and in calf serum. Normal decane, a good solvent for natural rubber, was used as a control. In what follows we describe the techniques used to evaluate the effects of these environments on the tensile strength and elongation at break of natural rubber latex condoms after exposure to water or normal decane and the simulated body fluids. We further examined the mass uptake by condoms immersed in the fluids for up to several days. Based on the results which we obtained, we can conclude that upon exposure to water, PECF or calf serum, the condoms do not change in strength relative to dry control samples. Exposure to n-decane causes a dramatic decrease in the tensile strength and elongation to failure of the condoms. With the exception of the normal decane, the rubber condom samples exhibited extremely low degrees of absorption of fluid in all of the fluids even after immersion for times of up to 11 days. The normalized mass uptake was always less than 1.15 (corresponding to a mass increase of 15%) thus indicating that it is likely that the fluid environment has little effect on response of the condoms which can be interpreted as adversely affecting their performance.

1-B. Experimental Methods

1. Materials

The condoms used in this study were natural rubber condoms (Trojans[3] Latex Condoms, plain rounded end, corresponding to Style I per ASTM D 3492-83[4]) purchased at a local drug store. These condoms were selected because they came without any lubricant. Upon examination, however, they all had a white powder on the surface. This was probably talc which is used as an antisticking agent in the manufacture and handling of natural rubber latex products. In addition, a sample of natural rubber compounded with 1 part dicumyl peroxide per hundred parts rubber was prepared. This sample was prepared by milling the peroxide into the rubber at 55 °C and molding into sheets approximately 0.084 in in thickness and curing in a steam heated press at 149 °C for two hours.

The fluids used in the study were distilled water, pseudo-extra-cellular-fluid (PECF)[2], bovine calf serum and normal decane. The composition of the PECF is given in Table 1. The bovine calf serum was a γ-irradiated product from Sigma Chemical Co. Ltd.[3,5]. The chemical analysis of the serum given by the manufacturer is summarized in Tables 2 and 3. The normal decane was reagent grade obtained from Aldrich Chemical Company[3].

2. Mechanical Testing

Mechanical testing of the condoms was performed using rings of material cut from the condom and following ASTM D-412[6]. The width of the cutting die was 0.786 in, the rollers were lubricated with a silicone fluid during the tests. The tests were run on a Tinius Olson[3] mechanically driven test machine at a crosshead displacement rate of 5 inches/min. Elongation at failure and stress at failure were calculated for each sample. Dry samples were used as controls. Samples were immersed in the test fluids for 4 hours prior to removal and mechanical testing. Five ring samples were cut from each condom and either four or five condoms were used per test fluid.

3. Swelling

Measurement of the swelling of the latex condoms in the different test fluids was found to be extremely difficult to do accurately because of the large surface area of the condom(they are extremely thin films) which made drying of the condoms prior to weighing difficult. In order to reduce the magnitude of this effect a special set of apparatuses was constructed which allowed reasonably reproducible drying of the condoms after immersion and prior to weighing. A typical apparatus is described as follows: a rigid tube of

polyvinyl chloride, approximately 1 inch in diameter was cut to a length of 10 inches. The ends of the tube were sanded to a good degree of smoothness so that the rigid polymer would not damage the test condoms. At one end of the tube, holes were drilled to accomodate a wire so that the tube could be suspended from the top of a beaker. For testing the swelling degree of the condoms, the test condom was taken and the tube was inserted to a length of approximately 8-9 inches. The tube with condom on it was then suspended from the top of the test beaker so that the condom was immersed in the test fluid for a length of 7.5-8.5 inches. Each time that a measurement was made of the amount of fluid uptake, the tube and condom were removed from the test fluid, the condom carefully patted dry with a tissue, the condom carefully removed from the tube and the condom weighed. Any evidence of pinholes in the condom resulted in ceasing the test on the condom in question. The most obvious sign of pinholes was the presence of fluid on the inside of the condom.

Mass uptake was measured at 5, 10, 15, 20, 25, 30, 60, 120, and 240 minutes. Several systems were tested for longer times and these results will be reported as well. All tests were carried out at a room temperature of 24 ± 1 °C.

I-C. Results and Discussion

1. Tensile Strength and Elongation at Break of Condoms

We found that the tensile strength and elongation at break of the condoms were not significantly affected by immersion in the test fluids for up to 4 hours. The only exception was the normal decane, in which fluid there was a very important loss in both tensile strength and elongation at break. The results are depicted in the bar graphs of Figures 2 and 3. We note that the error bars represent one standard deviation about the mean value of the tests. Tables 4-9 summarize the statistics of the tensile test results. The lack of influence of the "relevant" test fluids on the tensile properties of the condoms is perhaps not surprising given the low amount of swelling observed with these fluids. This is discussed in the next section.

Besides the important observation that the relevant test fluids do not significantly alter the tensile properties of the natural rubber latex condoms, the results reported here point up a significant variability in the strength of the condoms. Whether this is due to pinholes or some other effect is unknown and warrents further investigation by the FDA.

2. Swelling or Fluid Uptake

The results of immersion of the condoms in the test fluids is depicted in Figures 4-6. The results are presented as M/M_0 vs logarithm of immersion time, where M is the mass of the sample after immersion and M_0 is the mass of the dry sample(condom). In Figure 7 swelling of the 1 phr peroxide crosslinked rubber in the PECF is also depicted. In all cases the amount of mass uptake is small, being less than 15% ($M/M_0 \leq 1.15$) even in the longest time experiments. Interestingly, the fluid which is apparently most easily absorbed is the distilled water. The PECF and calf serum appear to be absorbed less by the condoms than is the distilled water. The relative mass uptake for the peroxide crosslinked rubber was even less than for the condoms. This is probably due to the increased crosslink density, but may be due to differences in crosslinking agent and the difference between latex and molded rubber products. Finally, there is considerable variability in the data. This is due to the large surface area of the condoms which, as noted above makes them difficult to dry. However, the results show that, in the short times of interest in condom performance. there is little uptake of simulated body fluids by natural rubber latex condoms.

I-D. Conclusions

Natural rubber condoms were tested for resistance to the presence of potentially hostile environments which simulated the in use environment. Distilled water, pseudo-extra-cellular-fluid (PECF), and bovine calf serum did not significantly alter the tensile strength or elongation at break of condoms which had been immersed in these fluids for 4 h at 24 °C. These fluids did not greatly swell (were not greatly absorbed by) the condoms either. Normal decane, a good solvent for natural rubber was found to greatly decrease the strength and elongation at failure of the condoms.

Table I-1. Composition of Pseudo-Extra-Cellular-Fluid (PECF)[4].

Ingredient	Quantity
Distilled Water	4.01 l
NaCl	27.36 g
KCl	0.30 g
$NaHCO_3$	10.08 g
K_2HPO_4	1.352 g

Table I-2. Chemical Composition of Calf Bovine Serum[5].

Chemical	Amount
Glucose	88 mg%
Sodium	144 mEq/l
Potassium	4.8 mEq/l
Chloride	100 mEq/l
CO_2	19 mEq/l
Blood Urea Nitrogen(BUN)	8 mg%
Creatinine	1.0 mg%
Uric Acid	0.4 mg%
Calcium	10.6 mg%
Phosphorous	9.1 mg%
Total Protein	6.7 g%
Albumin	4.1 g%
Alkaline Phosphatase	226 mU/ml
Total Bilirubin	0.2 mg%
SGOT	44 mU/ml
Gamma GT	29 mU/ml
Lactate Dehydrogenase(LDH)	527 mU/ml
Cholesterol	158 mg%
Triglycerides	14 mg%
Total Iron	153 µg%
Ionized Calcium	4.8 mg%
Protein Electrophoresis	
Serum Total Protein	6.7 g%
Serum Albumin	2.7 g%
Globulins	
Alpha 1	0.0 g%
Alpha 2	2.5 g%
Beta	1.5 g%
Gamma	0.0 g%

Table I-3. Amino Acid Analysis of Calf Bovine Serum[5].

Free Amino Acid	Assayed Value μmoles/ml	Free Amino Acid	Assayed Value μmoles/ml
Alanine	0.44	Leucine	0.18
Arginine	0.19	Lysine	0.11
Aspargine	-	Methionine	<0.1
Aspartic Acid	-	Phenylalanine	0.07
Cystine	-	Proline	*
Glutamine	*	Serine	*
Glutamic Acid	*	Threonine	-
Glycine	0.51	Tryptophan	-
Histidine	0.07	Tyrosine	0.05
Isoleucine	0.1	Valine	0.20

*Formed Inseparable Peaks.

Table I-4. Failure Statistics for Natural Rubber Latex Condom Ring Tests: Dry, T=24 °C.

	Tensile Strength	Elongation at Failure
Number of Samples	25	23
Mean Value	2815.4 psi	7.51
Maximum Value	4062.0	8.11
Minimum Value	1699.0	6.67
Standard Deviation	623.8	0.38

Table I-5. Failure Statistics for Natural Rubber Latex Condom Ring Tests: After immersion in distilled water for four hours. T=24 °C.

	Tensile Strength	Elongation at Failure
Number of Samples	20	20
Mean Value	2423.6 psi	7.43
Maximum Value	3368.0	8.08
Minimum Value	1411.0	6.91
Standard Deviation	525.6	0.32

Table I-6. Failure Statistics for Natural Rubber Latex Condom Ring Tests: After immersion in PECF[4] for four hours. T=24 °C.

	Tensile Strength	Elongation at Failure
Number of Samples	20	20
Mean Value	2524.1 psi	7.59
Maximum Value	3602.0	8.38
Minimum Value	1488.0	6.98
Standard Deviation	575.0	0.35

Table I-7. Failure Statistics for Natural Rubber Latex Condom Ring Tests: After immersion in Calf Bovine Serum[5] for four hours. T=24 °C.

	Tensile Strength	Elongation at Failure
Number of Samples	25	25
Mean Value	2524.1 psi	7.26
Maximum Value	3275.0	7.69
Minimum Value	1733.0	6.70
Standard Deviation	429.8	0.23

Figure Captions

I-1. Elongation at break vs volume fraction of rubber for swollen natural rubber(open circles) and styrene butadiene rubber(filled circles). [After Greensmith, et. al.[1]].

I-2. Tensile Strength of Natural Rubber Condoms in Different Fluids. Exposure time: 4 h. T= 24 °C.

I-3. Elongation at Break of Natural Rubber Condoms in Different Fluids. Exposure time: 4 h. T=24 °C.

I-4. Fluid Uptake vs Time by Natural Rubber Condoms in Water at 24 °C.

I-5. Fluid Uptake vs Time by Natural Rubber Condoms in PECF at 24 °C.

I-6. Fluid Uptake vs Time by Natural Rubber Condoms in Bovine Calf Serum at 24 °C.

I-7. Fluid Uptake vs Time by Dicumyl Peroxide Crosslinked Natural Rubber in Bovine Calf Serum at 24 °C.

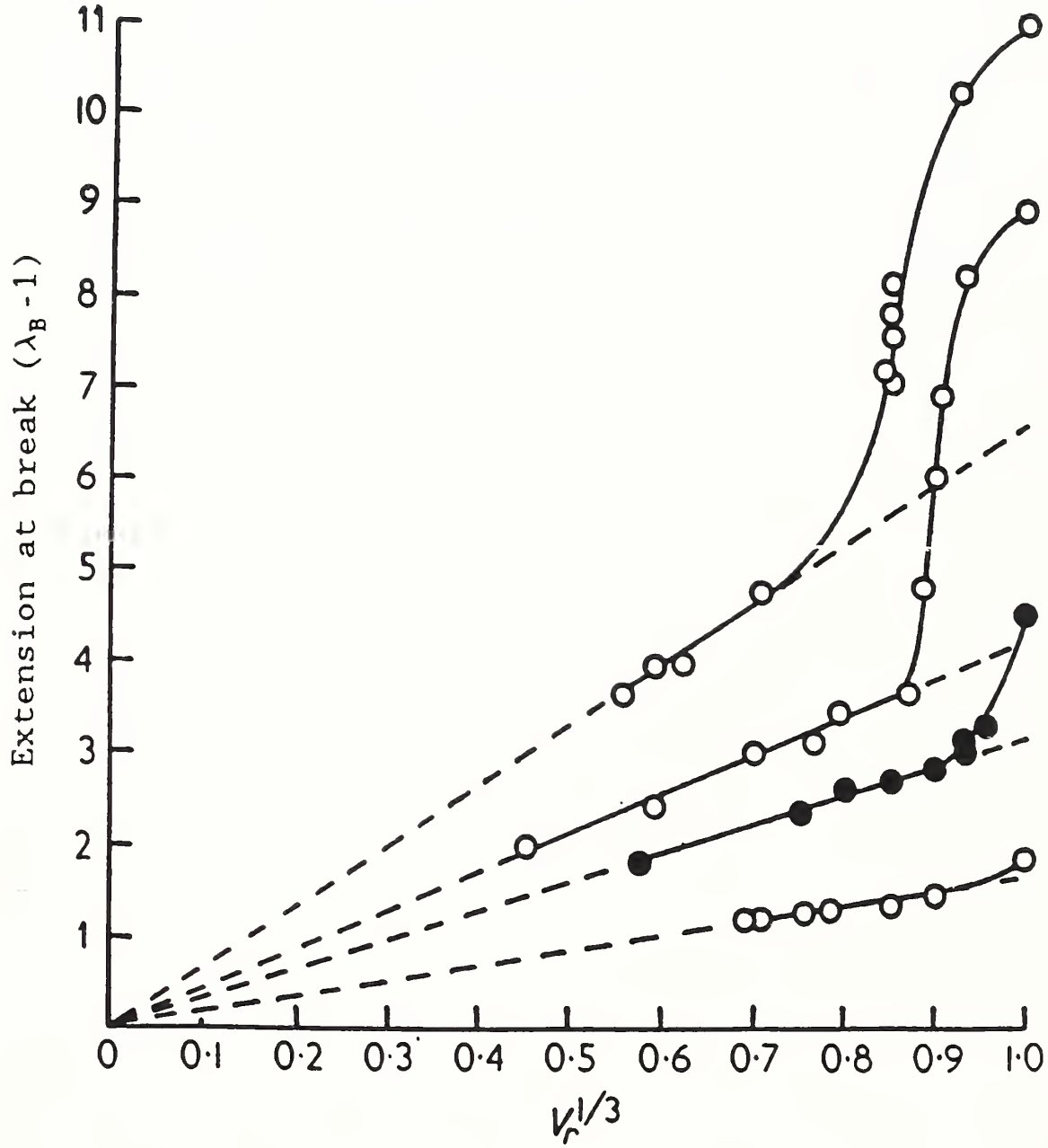
Extension at break (λ_B -1)
11
10
9
8
7
6
5
4
3
2
1
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
$V_r^{1/3}$

Fig. I-1

TENSILE STRENGTH OF NATURAL RUBBER CONDOMS IN DIFFERENT FLUIDS.
EXPOSURE TIME: 4 H. T=24°C.

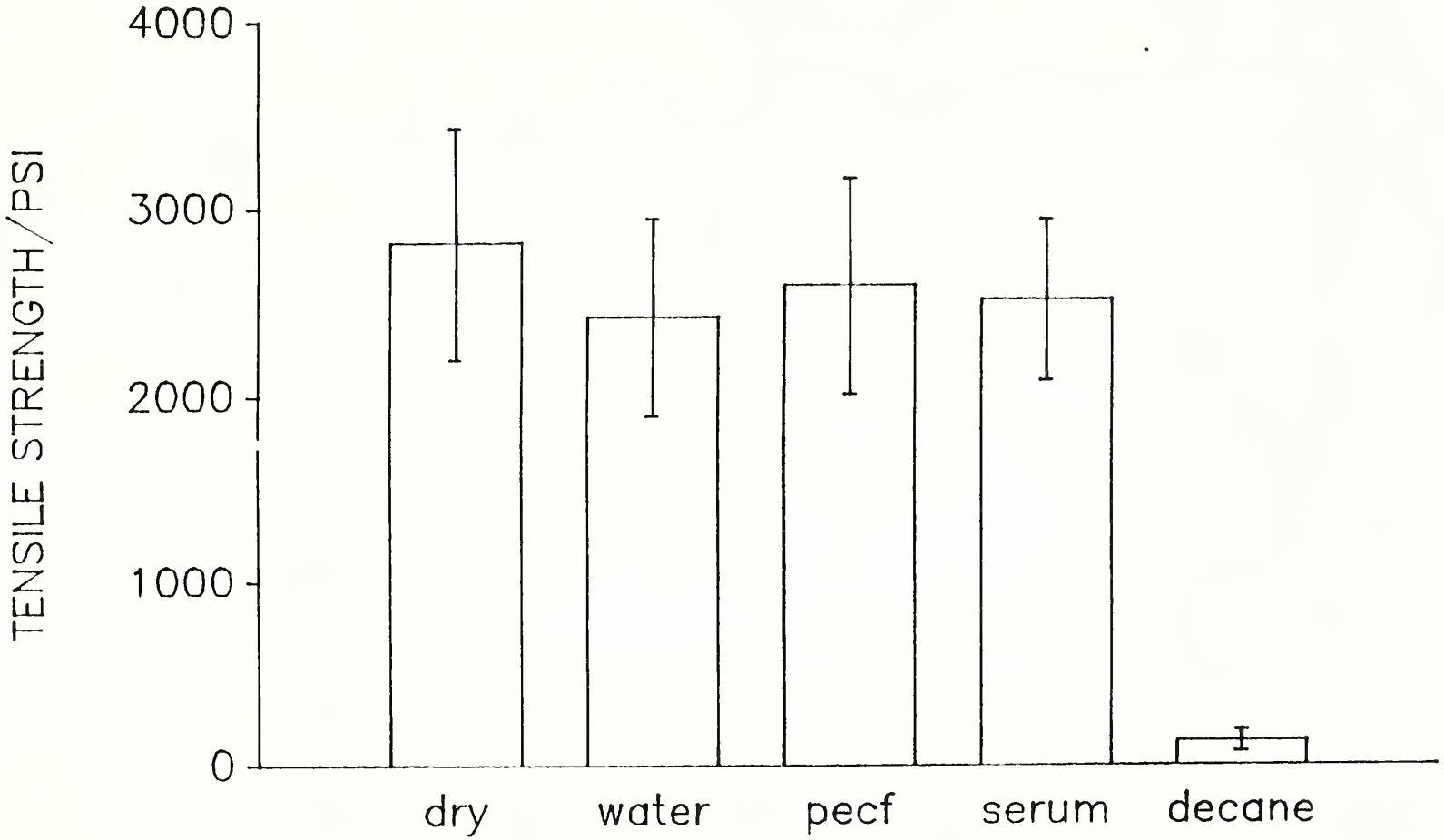

Fig. I-2

ELONGATION AT BREAK OF NATURAL RUBBER CONDOMS IN VARIOUS FLUIDS
EXPOSURE TIME 4 H. T=24°C

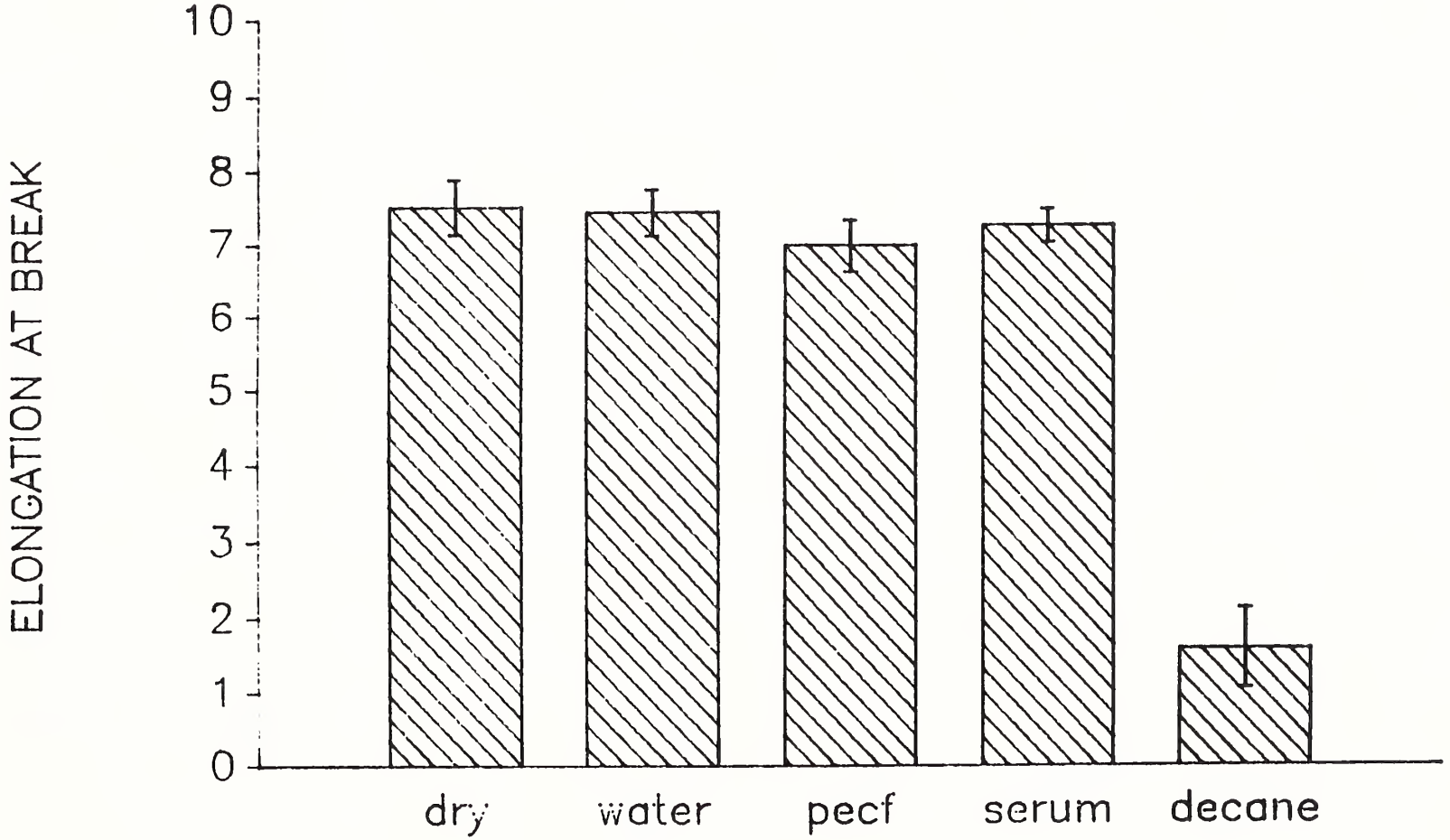

Fig. I-3

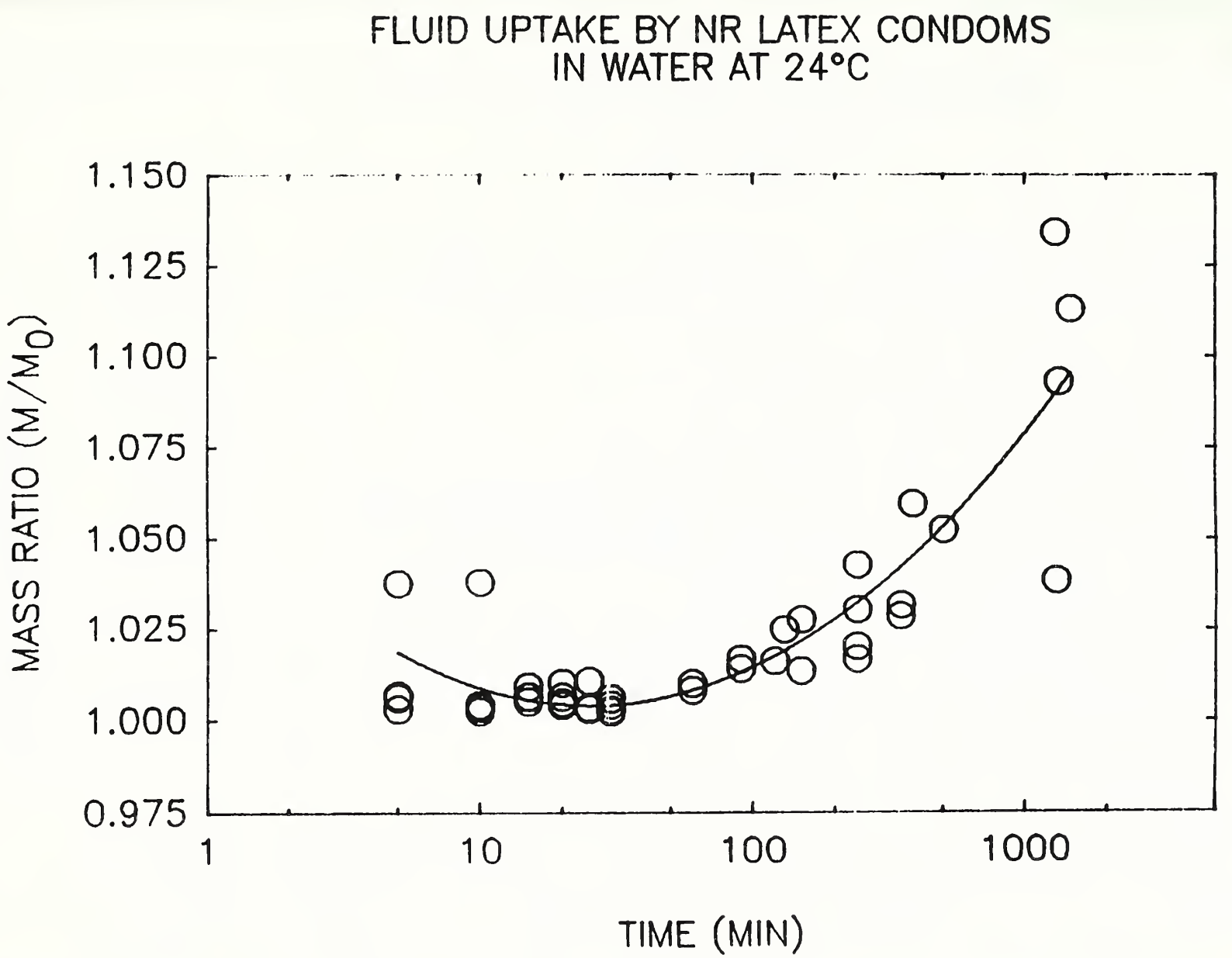
FLUID UPTAKE BY NR LATEX CONDOMS
IN WATER AT 24°C
MASS RATIO (M/M0)
1.150
1.125
1.100
1.075
1.050
1.025
1.000
0.975
1
10
100
1000
TIME (MIN)

Fig. I-4

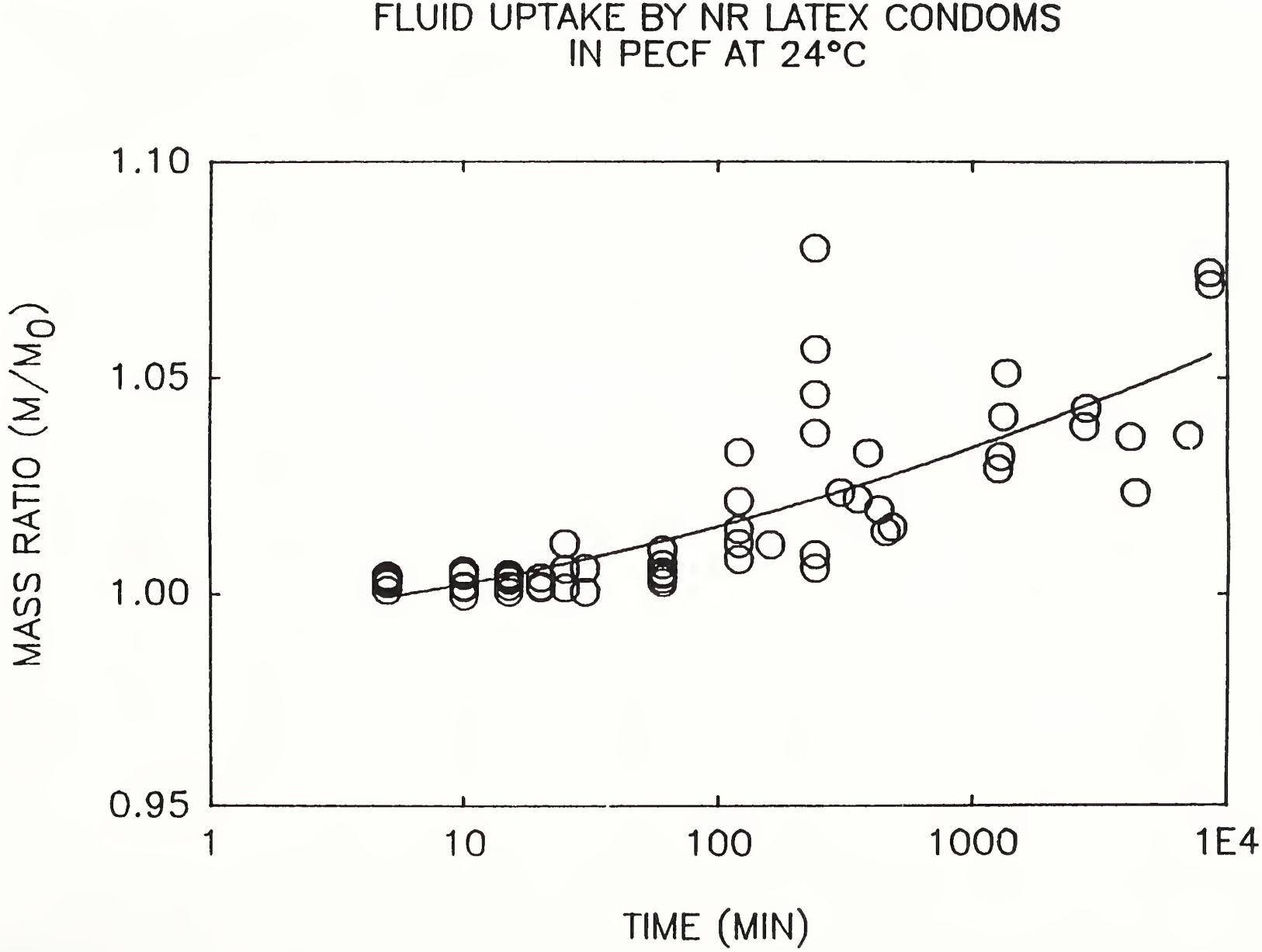
FLUID UPTAKE BY NR LATEX CONDOMS
IN PECF AT 24°C
1.10
1.05
1.00
0.95
MASS RATIO (M/M0)
1
10
100
1000
1E4
TIME (MIN)

Fig. I-5

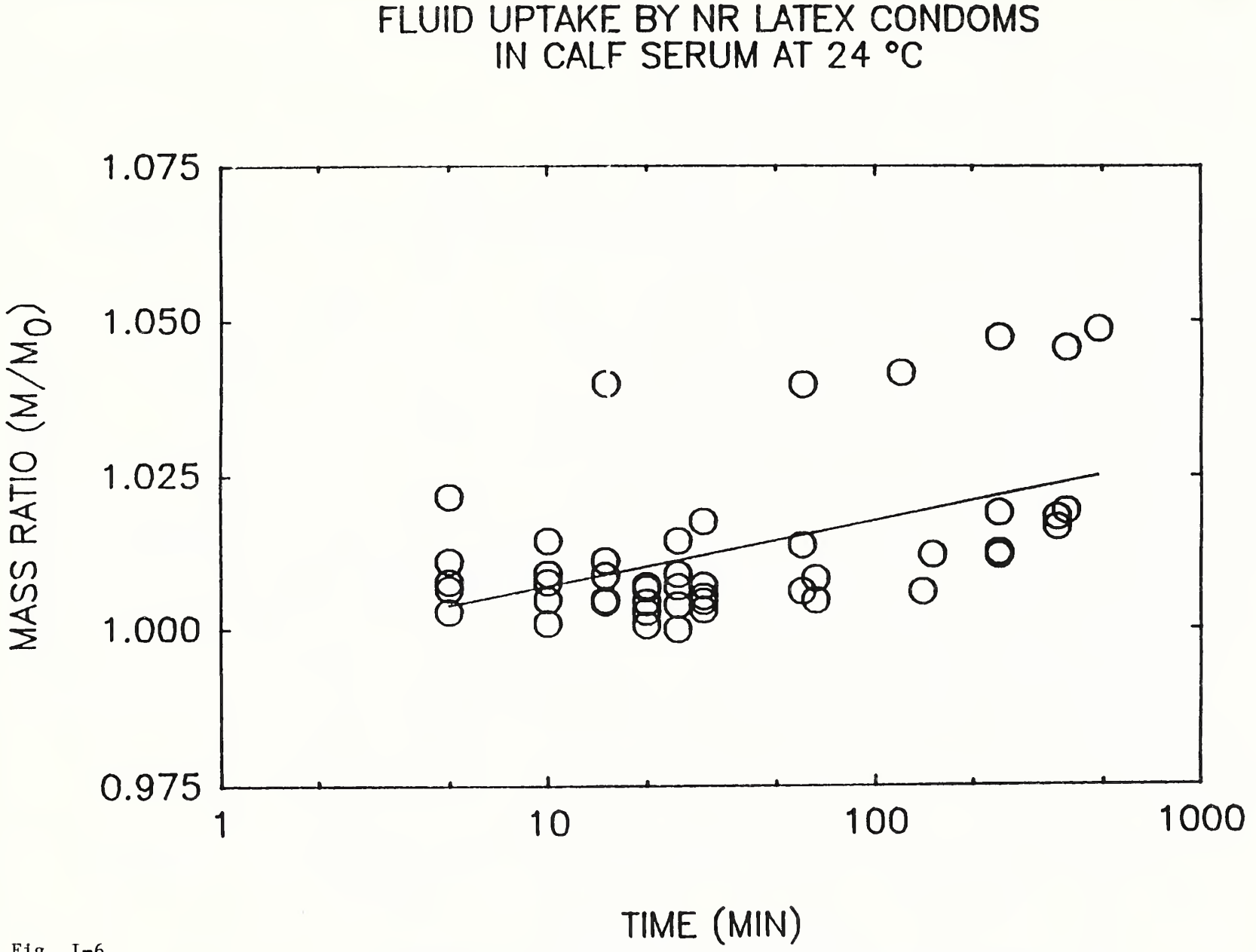
FLUID UPTAKE BY NR LATEX CONDOMS
IN CALF SERUM AT 24 °C
MASS RATIO (M/M0)
1.075
1.050
1.025
1.000
0.975
1
10
100
1000
TIME (MIN)

Fig. I-6

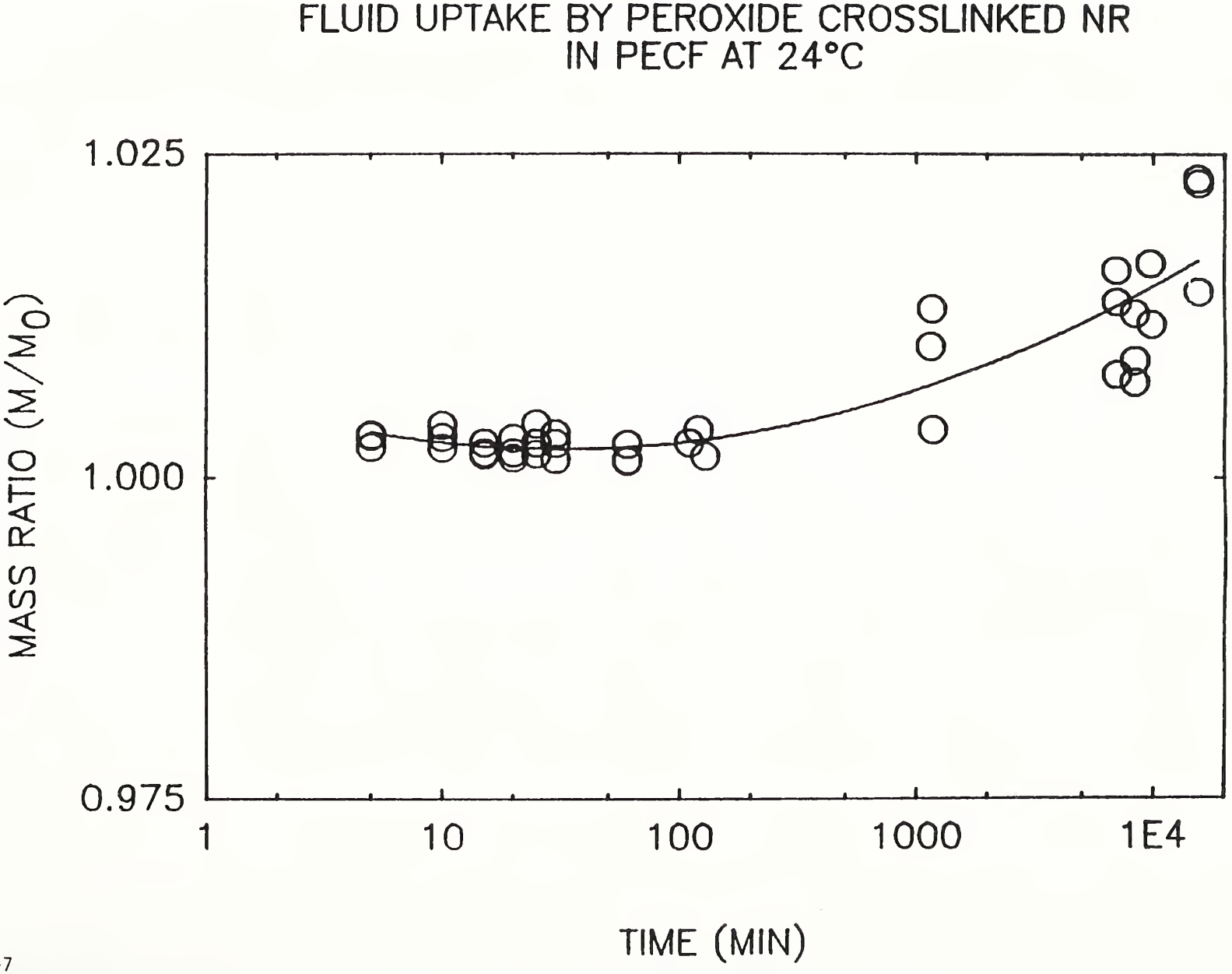
FLUID UPTAKE BY PEROXIDE CROSSLINKED NR
IN PECF AT 24°C
1.025
1.000
0.975
MASS RATIO (M/M0)
1
10
100
1000
1E4
TIME (MIN)

Fig. I-7

II. A Method to Estimate Cross-link Density Variation on the 100 Micron Scale in Latex Barrier Films

C. M. Guttman and T. K. Trout
National Institute of Standards and Technology
Polymers Division

II-A. Introduction

Most condoms and surgical gloves are made of lightly cross-linked latex films. For such lightly cross-linked latex films, the tear strength decreases as the cross-link density decreases (see Fig. II-1).[8]

The overall cross-link density of thin latex films is measurable with some care from swelling measurements on the whole or large pieces of a condom (see report by McKenna in this annual report). However the variation of cross-link density from region to region on the scale of 0.1mm or less can not be measured by conventional swelling methods. Yet weaknesses in regions of this size may allow for tear initiation. This report discusses the theory and some experiments aimed at developing a method to determine cross-link density variation on the 0.1mm scale or less.

The method discussed in this report depends on the fact that regions of high cross-link density will swell less than regions of low cross-link density. The regions of high swelling have a lower polymer concentration ([p]) and a higher solvent concentration ([s]).

In the experiments reported here, we estimate the concentration of solvent by using a fluorescent dye which is soluble in the solvent. It is assumed that the ratio of dye to swelling solvent for the polymer is independent of polymer concentration in solution.

A Zeiss fluorescent microscope[3] is used to determine local variation in fluorescence dye concentration and thus to estimate the variation in ratio [p]:[s]. This microscope can look at regions as small as a cross-section of 40 micron radius to one of 150 micron radius. We expect that a choice of optics will allow one to look either at a fixed volume in the film or a region throughout the film.

In the next section of this report, we describe the general methodology and give a theoretical development for the method. This is followed by a section in which experimental details are given. In the final sections some conclusions and suggestions for further work are given.

II-B. General Development of Methodology

In the development given here we assume that the experimental method to determine the fluorescence from the swollen latex films samples a volume which is fixed and independent of the original or swollen thickness of the latex film. We shall develop the equations for this method under this assumption in this report. In our next report we shall give the development when the method does not look at a fixed volume.

We first give a description of the method. Consider the measurement of fluorescence from a fixed volume in a latex film. In that fixed volume of swollen film we have polymer, solvent and fluorescence dye. If we assume that the ratio of dye to solvent is fixed by the solution preparation (i.e. we have no special interaction of the dye with the polymer) then the amount of fluorescent dye in the measurement volume is always proportional to the solvent concentration. For a fixed measurement volume, the fluorescent dye then also measures the polymer concentration. In a swollen media, the polymer concentration is related to the cross-link density through the Flory [8] rubber elasticity equations. These equations suggest that there is an inverse relationship between the cross-link density of a polymer and the extent of swelling the polymer displays when exposed to a suitable solvent. Therefore, the greater the cross-link density of a polymer, the smaller the resulting [p]:[s] ratio after swelling. The detailed theory for the method is given below.

Theoretical development for the method

Let us consider the total measurement volume v_T in a local region of polymer and solvent.

$$v_T = (N_{solv}\, v_{solv})_i + (N_p v_p)_i \qquad \text{(II-1)}$$

where

v_{solv} = volume/solvent molecule

v_p = volume/monomer of polymer

N_p = number of monomers in volume v_T at point i

N_{solv}=number of solvent molecules in volume v_T at point i

We assume v_T is independent of i.

The ratio of a linear dimension of a swollen polymer to the unswollen polymer at a local region indexed by i is

$$\lambda_i = x_i/x_o = y_i/y_o = z_i/z_o \qquad \text{(II-2)}$$

where x_i is the swollen dimension in the x direction in region i, x_{oi} is the unswollen dimension in the x direction in region i etc.

Now $(N_p v_p)_i = x_{oi} y_{oi} z_{oi}$ and we let ν_{2i}, the volume fraction of polymer be defined as

$$1/\nu_{2i} = \lambda_i^3 = v_T/(N_p v_p)_i = v_T/(v_T - (N_{solv} v_{solv})_i) \qquad \text{(II-3)}$$

Let us assume the concentration of fluorescent molecules in solvent when the solvent swells the polymer to be the same as when it does not swell the polymer (i.e. there is little or no partitioning of the fluorescent molecule between the solvent when it swells the polymer and the solvent outside the polymer). Thus the signal, S_i, from the microscope in the local region i is proportional to the volume of solvent molecules. That is

$$S_i = k(N_{solv} v_{solv})_i \qquad \text{(II-4)}$$

By our previous equations

$$(N_{solv} v_{solv})_i = v_T - v_T/\lambda^3{}_i = v_T(1-\nu_{2i}) \qquad \text{(II-5)}$$

Thus the signal at a point i is proportional to

$$S_i = k(v_T - v_T/\lambda^3{}_i) = k\, v_T\, (1-\nu_{2i}) \qquad \text{(II-6)}$$

And our signal is proportional to swelling. Let us say we make measurements at n points and in doing so correctly sample the entire film. We have then for the average signal <S>

$$\langle S \rangle = \frac{1}{n} \sum_{i=1}^{n} S_i = \frac{k v_T}{n} \sum_{i=1}^{n} (1-\nu_{2i}) \qquad \text{(II-7)}$$

and we have

$$\langle S \rangle = k\, v_T\, (1 \frac{1}{n} - \sum_{i=1}^{n} \nu_{2i}) = k\, v_T\, (1-\langle \nu_2 \rangle) \qquad \text{(II-8)}$$

where $\langle \nu_2 \rangle$ is the measured swelling over the whole film. Then the average signal, <S> over the whole film can be related to the average swelling over the

whole film, $\langle \nu_2 \rangle$. From Eq. 6 and 7 we have

$$\frac{S_i}{\langle S \rangle} = \frac{1-\nu_{2i}}{1-\langle \nu_2 \rangle} \qquad \text{(II-9)}$$

Then $$\frac{S_i - \langle S \rangle}{\langle S \rangle} = \frac{\langle \nu_2 \rangle - \nu_{2i}}{1-\langle \nu_2 \rangle} \qquad \text{(II-10)}$$

For now we assume $\langle \nu_2 \rangle = \nu_2$ where ν_2 is a swelling change obtained by a more conventional macroscopic swelling method on the whole film. Under this assumption Eq. (10) allows us to obtain ν_{2i} without knowing k. Of course with this assumption Eq.8 is an excellent test of the method.

We can relate our results to crosslink density. By Flory theory [2]

$$\ell n(1-\nu_2) + \nu_2 + \chi(\nu_2)^2 + \frac{\rho V_1}{M_c} (\nu_2^{1/3} - \nu_2/2) = 0 \qquad \text{(II-11)}$$

where

χ is the Flory interaction parameter
ρ is the rubber density
V_1 is the molar volume of the swelling fluid
M_c is the chain length between crosslinks

$1/M_c$ is related to the crosslink density in the rubber as seen in Figure 1 of this report.

II-C. Experimental

Chemicals. All experiments were performed with analytical-reagent grade chemicals and solvents. No further purifications were performed.

A stock solution of 9,10 dimethylanthracene (DMA) (Aldrich Chemical Co., Milwaukee, WI)[3] in toluene (Aldrich) was prepared by placing 0.08744 g of DMA into 30 mLs of toluene. This stock solution was diluted prior to experimentation by combining 0.871 g of the stock solution with 16.86 g of hexadecane. The dilute DMA/hexadecane solutior was used as the swelling solution for all condom samples that were to contain the DMA chromophore. Hexadecane was chosen as the swelling solvent due to its low vapor pressure. For samples that were to serve as controls, i.e. samples that were swollen but contained no chromophore, neat hexadecane was used as the swelling solvent.

Condom Samples. Condoms were obtained from local drug stores and FDA sources[1] and are designated A,B,C and D. Prior to experimentation all of the samples were washed with deionized water and were patted dry. This removed any powders or lubricants that were applied to the condom by the manufacturer.

Equipment. All fluorescence emission measurements were made on a Zeiss Universal epifluorescence microscope[3]. The excitation and emission monochromators, microscope optics and photomultiplier assemblies that comprise the apparatus were specially designed for NIST by Carl Zeiss, German Federal Republic. Data acquisition is based on proprietary Zeiss software packages λ-Scan and MPP. Excitation radiation is provided by an Osram HBO 100 Super Pressure mercury lamp[3]. The mercury line located at approximately 368 nm was used as the excitation wavelength, while emission was monitored at the emission maximum for DMA, 429 nm. The excitation and emission bandwidths were 10 nm and 3 nm, respectively. A barrier filter was inserted between the mercury lamp and the sample to eliminate stray radiation over 400 nm wavelength.

Depending upon experimental requirements, either a 63x or 40x objective was used to image the samples. The different magnifications and apertures of the two objectives result in different working distances, sizes of field of view, and different imaging volumes within the translucent condom samples. The epifluorescence microscopy imaging (EMI) system allows the operator to adjust an emission slit so as to restrict the field of view that the photomultiplier tube measures. In this study, the slit was kept at a constant size so that the field of view was a circle with a diameter of 41 μm for the 63x objective. Using the 40x objective the circular field had a 69 μm diameter.

An additional feature of the microscope is a calibrated fine-adjustment focus control that guaranteed the position of the focal plane was within ± 2 μm of any targeted surface. It permitted precise movement of the microscope stage, which allowed evaluation of the fluorescence contribution to the total measured fluorescence intensity of the sample from every depth of a translucent sample, such as a doped condom.

Absorption/scattering measurements were made with a Perkin Elmer Model 330 UV-VIS spectrometer[1].

Procedure. The washed condoms were cut into strips of approximately uniform dimension (2.7 cm x 0.8 cm). The masses of the strips were measured using a model B6 Mettler balance[3]. The strips were then placed into either neat hexadecane or DMA/hexadecane solution (see Chemicals section). The condom strips remained in the swelling solutions for 46 hours. After swelling, the samples were patted dry, and their masses were again recorded.

The samples were analyzed for UV-VIS absorption and scattering. The absorption/scattering measurements were obtained from condom samples by placing the swollen samples against an empty quartz cuvette so as to uniformly cover the sample holder. The spectra obtained represent the transmissibility of light as a function of wavelength as it passes through the swollen condom; the light that was not transmitted by the condom was either absorbed or scattered by the sample.

Swollen condom samples doped with DMA were analyzed for variation in fluorescence emission intensity (429 nm) at different (x,y) positions of the condom surface. The focal plane was maintained at the surface of the condoms during acquisition of fluorescence intensities through the use of a tungsten white-light source that was located below the condom. Before each fluorescence measurement was made, the focus of the sample was checked by using the white-light and was adjusted if necessary. This position in the z-axis was not the focal plane depth at which measured fluorescence intensities were a maximum (see above). Relative intensity measurements were made as the operator moved the microscope stage in one-dimension, field by field. Thus, the emission intensities were taken from a continuum along the condom sample, with a data point being recorded at every 41 μm or 69 μm along the continuum, depending upon the objective employed. Each relative fluorescence intensity measurement represented the average of 50 photomultiplier tube (PMT) readings.

In order to evaluate the contribution that each unique plane of fluorescent species makes to the total fluorescence measured by the PMT, a fluorescent ink smear was placed onto a glass slide. This marker smear, after drying, had a thickness of $\leq$ 1 μm. This served as a model of a monolayer of luminescent material. By initially focusing on the surface of the smear, recording the PMT response, moving the microscope stage up or down a few microns in the z-direction and again recording the PMT response, we could determine to what extent the optics of the EMI system limited the contributions from each "monolayer" of chromophore contained within the doped condom.

II-D. Results

Table II-1 displays the measured effect that swelling the condom samples had on the masses of the condoms. Data presented here, along with other data we have collected clearly show that the mass increase seen with condoms swollen with hexadecane is a very reproducible quantity. It also appears that the percent increase in mass is approximately the same regardless of the manufacturer of the condom. This implies that the cross-link density of the four brands is approximately the same for each manufacturer. Condoms placed in deionized water swell only about one tenth as much as those placed in organic solvents such as hexadecane.

Figure II-2 shows an emission spectrum acquired from a condom sample that was swollen with the DMA/hexadecane solution. The peaks of the spectrum match those characteristic of DMA emission. The emission intensity at 429 nm of a DMA doped condom is about twenty times stronger than the emission of a condom swollen with neat hexadecane. Figure II-3 shows a plot of measured emission intensities at 429 nm of a fixed (x,y) coordinate on the surface of a doped condom as a function of time. The slope of the line is approximately zero, indicating that DMA is a stable chromophore within the polymer matrix throughout the duration of time required to make an intensity measurement.

Figures II-4 and II-5 are plots representative of the data collected by measuring fluorescence emission intensities at 429 nm for each of the four condom brands as a function of location on the condom surface. Data were collected using both the 63x and 40x objectives. Tables II-2 and II-3 give a statistical interpretation of all of the data obtained. The standard deviations seen for each data set are measures of the uniformity of the emission intensities. If non-uniform cross-link density exists within the polymer matrix, this may result in non-uniform swelling on the microscopic scale which could result in varying numbers of chromophores within the image volume of the EMI system. It must be stressed that trends seen in Figures II-4 and II-5 with a given objective will not correspond to trends seen with the other objective because the analyses were not carried out at the same location on the condom surface.

E. Experimental Estimation of Depth of Measurement

As indicated in the theory section the interpretation of the results depends on the depth of penetration of the fluorescence microscope measurements. The experiments discussed below describe our efforts to

estimate this depth. We expect to improve this approach in future work.

The absorption data on the swollen doped condom described here coupled with the ink smear experiments permit estimation of the contribution that each monolayer of chromophore makes to the readout displayed by the PMT. A simplified model of this system suggests that the magnitude of the emitted light that originates from any given layer is directly proportional to the number of chromophores located in that plane and the intensity (flux) of the excitation beam at that level. The intensity of the excitation beam at any given level is determined by two factors. The intensity of the light exciting the fluorescence at any level will depend upon the intensity of the excitation beam prior to entering the sample, minus the fraction of this intensity that is lost due to absorption and scatter of the sample as it travels to the depth of the sample from which emission originates. Since the exciting light comes from the microscope, the flux of the beam will vary along the z-axis due to the optics of the microscope. The excitation beam approaches a sample in the shape of a cone. As the excitation beam approaches the "focal point", the diameter of the beam becomes smaller. As this occurs, the flux increases. After reaching the focal point, the excitation beam diverges away from the focal point, and the flux diminishes.

In the fluorescence experiment on the condom the excitation beam was 368 nm ± 5 nm and the measured emission energy was 429 nm ± 1.5 nm. By measuring the UV-VIS spectra of these samples and knowing the approximate thicknesses of the samples, we can calculate absorption/scatter coefficients for the samples that are analogous to extinction coefficients of analytical solutions. This data will permit calculation of the intensity (I_1) that will reach any given monolayer in the condom sample as compared to the intensity of the 368 nm excitation beam prior to entering the sample (I_0). From this point forward, the absorption/scatter data will simply be referred to as absorption spectra.

The absorption spectra generated from the condom samples were very reproducible, both in terms of spectral shape and absorption magnitude. Since the swollen polymer is translucent one can focus on the top and bottom of the condom permitting measurement of the approximate thicknesses of the condom samples. The average measured thickness of the eight swelled condoms measured this way (two trials of each of the four brands) was 81.2 μm ± 10.4 μm. For simplification, we shall assume that the thickness of all of the condoms were of z_o uniform thickness, where z_o = 81.2 μm.

Figure II-6 shows our model of the absorption of light in this system. We shall call the intensity of the incident light I_0. At a given depth, z, this light will have been attenuated by sample absorption to a reduced intensity, referred to as $I_1(z)$.

$$I_1(z) = \kappa_1 \exp(-A(368)\ z/z_o) \qquad \text{(II-12)}$$

where A(368) is the measured absorption/scattering coefficient at 368nm across the thickness of the condom, z is the depth below the focal plane from which we are getting light, and z_o is the average thickness of the condom.

If the DMA chromophore absorbs the excitation energy at this depth level, the light will be re-emitted from this level at intensity I_2. The completeness of the conversion of light from I_1 to I_2 depends upon the quantum efficiency of DMA, Q. The quantum efficiency for conversion of 368 nm light to 429 nm light by DMA will be assumed to be constant throughout the condom. From a given layer z, a fraction of the light emitted, f(z), travels towards the photomultiplier tube of the microscope. Of this, some additional fraction is lost by reabsorption in the condom at the fluorescence wave length. The reabsorption can be estimated using Beers law at the wavelength of emitted light, 429 nm. Thus the intensity at the photomultiplier, $I_{pm}^{(z)}$, from a layer in the condom at z is

$$I_{pm}(z) = K_2 \exp\ (-A(429)\ z/z_o)\ f(z)\ Q\ I_1(z) \qquad \text{(II-13)}$$

where z_0 is about 80 microns and z is the depth in microns, below condom surface and A(429) is the absorption/scattering coefficient at 429 nm.

In order to estimate the signal of the photomultiplier tube at each different monolayer depth, f(z), we monitored the emission of a magic marker smear as a function of the position of the focal plane of the microscope relative to the plane of the sample. Data are presented in Figure II-7. In Figure II-7, the z-coordinate represents the distance in microns from the focal plane to the ink smear. A negative value for the z-coordinate indicates that the focal plane is above the chromophore plane. A positive value of the z-coordinate indicates that the focal plane is below the chromophore plane. We shall use this data from the 40x objective for f(z) in the following discussion.

Figure II-8 shows the combined effects of Eq. (II-13) of absorption, emission and the depth effect seen in f(z).

The total intensity, G, across the condom is given by the integral of $I_{pm}(z)$ for a given excitation wave length and emission wave length

$$G(-z) = \int_{-z}^{o} du\ I_{pm}\ (u) \qquad \text{(II-14)}$$

In general one must do an integral over all the excitation wave length and emission wave lengths. For this report we shall only look at the central excitation and emission wave length.

Of more interest, from the point of view of the condom measurement, is the fraction of fluorescence signal which comes from the bottom half of the film. If little signal comes from the bottom half of the condom then the measurement can be thought of as essentially independent of thickness. Since the optics of the microscope determine the area of the condom observable, thickness independence implies the volume of measurement is thickness independent. Under these conditions, the theoretical development in section II-B is then valid.

For a film 80 microns thick, quantities like G(-40)/G(-80) and G(-70)/G(-80) are of interest. If G(-40)/G(-80) is about equal to G(-70)/G(-80) and near 1.0, then we may consider the measurement to be thickness independent. We define

$$H(z)=G(z)/G(-80) \qquad \text{(II-15)}$$

If Figure 10 we plot H(z) versus z. We see that for z less than -50, H(z) is near 1 and unsensitive to z indicating the flourescence measurement is nearly depth independent.

F. Conclusions

From the above data we may judge that the technique can sense differences in the florescence properties of the swollen doped condoms. Data in figure II-3 on the brand C condom shows a significant fluorescence variation. If we use equation 10 and assume that the average $\langle \nu_2 \rangle$ for the condom is about .4 as is suggested by the data from table II-1, the data would suggest that the local ν on that condom increased by nearly 100% . This result suggests that we would see a significant change in the local properties of that particular condom.

In this report we have described the development a fluorescence microscope technique to obtain an estimate of local cross-linked density variations in condoms. This technique permits determination of the change in local cross-linked density by estimate of the change in local swelling. In future work on this contract we shall direct our efforts at making the method more quantitative.

To make the method more quantitative and confirm the original evidence of changes of florescence intensity resulting from changes in cross-link density we shall determine optimum focusing point for measurement and determine volume of measurement from theoretical calculations and experimental measurements on the florescence microscope system. In addition, we shall attempt to produce a set of polymer standards that will approximate condom films both in terms of cross-link density and thickness. This will permit us to directly relate our fluorescence measurements to polymer cross-link density.

Upon successful development of the micro-spectroscopic technique described above, we shall use it to:

a. look at a number of different brands of condoms

b. look at how reproducible the method is by making the measurement over the same region a number of times on the same sample with varying step size.

c. try to set up the method on an automatic stage to allow automatic sampling of a larger area of the condom

d. try to isolate regions of condoms and gloves that might be expected to show the largest deviations in cross-link density, for example, fingers, tips, ribbing etc.

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2. C. A. Homsy, J. Biomed. Mater. Res., 4, 341 (1970).

3. Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

4. ASTM D-3492-83, American Society for Testing and Materials, 1916 Race St. Philadelphia, Pennsylvania.

5. Sigma Chemical Co. Ltd, Catalog #C-5155, γ-irradiated Bovine Calf Serum, Lot # 87F-0562. Technical Bulletin issued December, 1987.

6. ASTM D-412, American Society for Testing and Materials, 1916 Race St., Philadelphia, Pennsylvania.

8. Treloar, L. R. G.; The Physics of Rubber Elasticity, Clarendon Press, Oxford, 1975

Cable II-1. Effect of exposure to an excess of hexadecane on the mass of commercial condoms

Sample	% Mass Increase†
A Control	156.8
A Doped(trial 1)	153.8
A Doped(trial 2)	155.8
A Doped(trial 3)	156.5
A Doped(trial 4)	155.3
B Control	164.5
B Doped	185.1
C Control	155.1
C Doped	163.0
D Control	158.7
D Doped	174.3

†The percent change in mass is defined by:
% = [(final mass) - (initial mass)]/(initial mass)

Table II-2. Measured emission intensities at 429 nm of DMA doped condoms as a function of position on the sample surface. 40x objective used.

Sample	Largest measured intensity	Smallest measured intensity	Average ± S.D.
A Doped	19.97	17.97	18.92 ± 0.54
B Doped	20.82	19.21	20.14 ± 0.40
C Doped	26.09	15.21	17.31 ± 2.86
D Doped	23.14	21.61	22.32 ± 0.37

Table II-3. Measured emission intensities at 429 nm of DMA doped condoms as a function of position on the sample surface. 63x objective used (emission intensities are not relative to the 40x data)

Sample	Largest measured intensity	Smallest measured intensity	Average ± S.D.
A Doped	54.08	46.00	50.10 ± 2.35
B Doped	61.74	55.05	58.38 ± 1.90
C Doped	60.09	54.99	58.37 ± 1.43
D Doped	66.51	57.97	61.69 ± 1.98

Captions

Fig II-1. Tensile strength of natural rubber versus degree of crosslinking ($1/M_c$)

Fig II-2. The emission spectrum of a condom sample swollen with DMA/hexadecane solution.

Fig II-3. The emission intensity at 429 nm at a fixed spot on the surface of a dope condom as a function of time.

Fig II-4. Emission intensity at 429 nm for four different condoms as a function of location on the condom surface using a 40x objective .

Fig II-5. Emission intensity at 429 nm for four different condoms as a function of location on the condom surface using a 63x objective .

Fig II-6. Crude model of path of excited light from microscope and of emitted light back into the microscope and to the photomultiplier.

Fig II-7. Emission intensity from a glass slide covered with a thin ink smear as a function of the distance above or below the focal plane of the smear. In this data the focal plane is a z=0.

Fig II-8. Effect of absorption and reemission on the intensity at the photomultiplier from a layer of depth z in the condom.

Fig II-9. Fraction of total fluorescence light which comes from a film of thickness - tau microns compared to the light which comes from a film of thickness 80 microns.

Fig. II-1

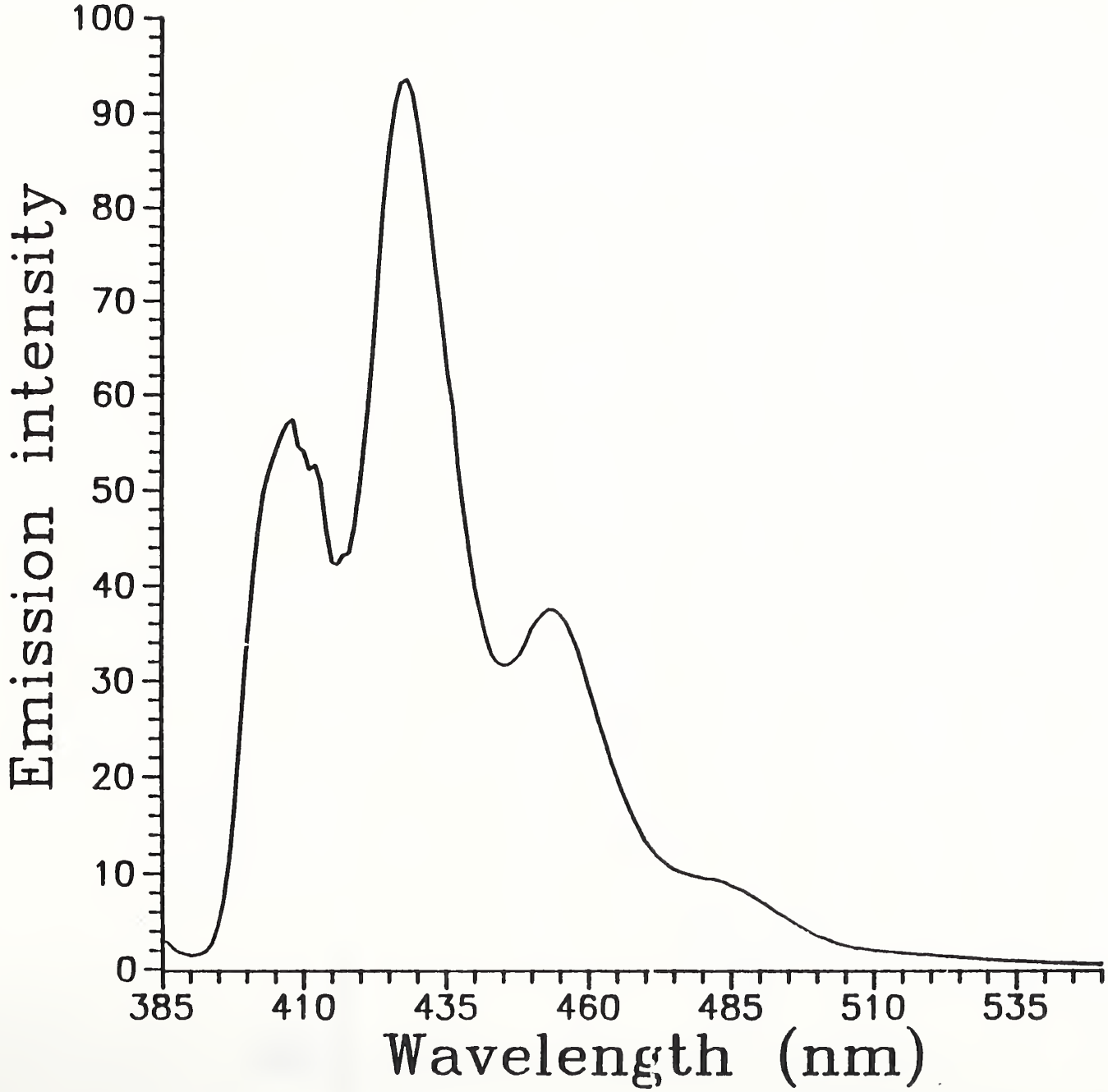
Emission intensity
100
90
80
70
60
50
40
30
20
10
0
385
410
435
460
485
510
535
Wavelength (nm)

Fig.II-2

Emission intensity
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
Time (s)

Fig.II-3

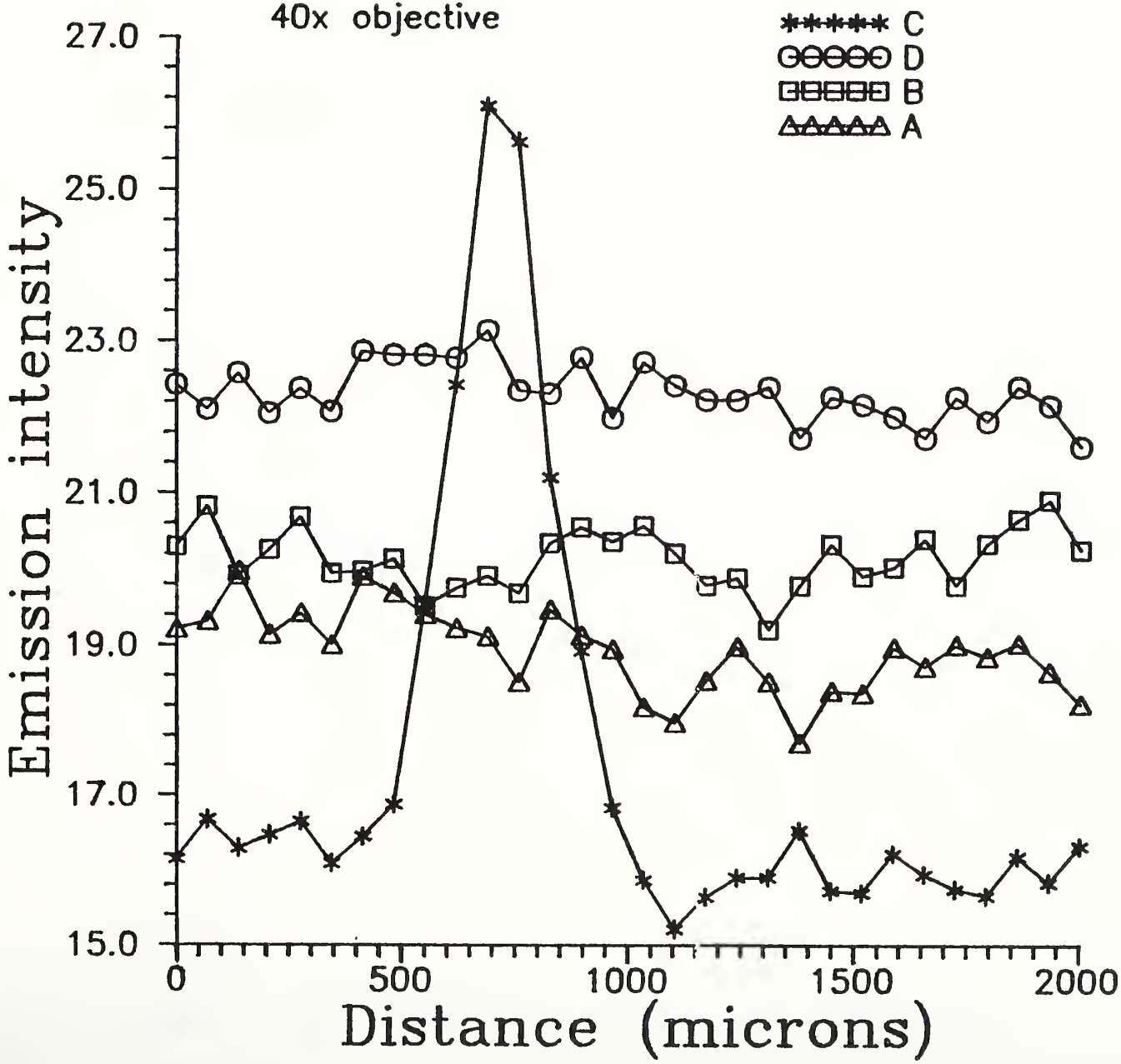
40x objective
C
D
B
A
Emission intensity
27.0
25.0
23.0
21.0
19.0
17.0
15.0
0
500
1000
1500
2000
Distance (microns)

Fig. II-4

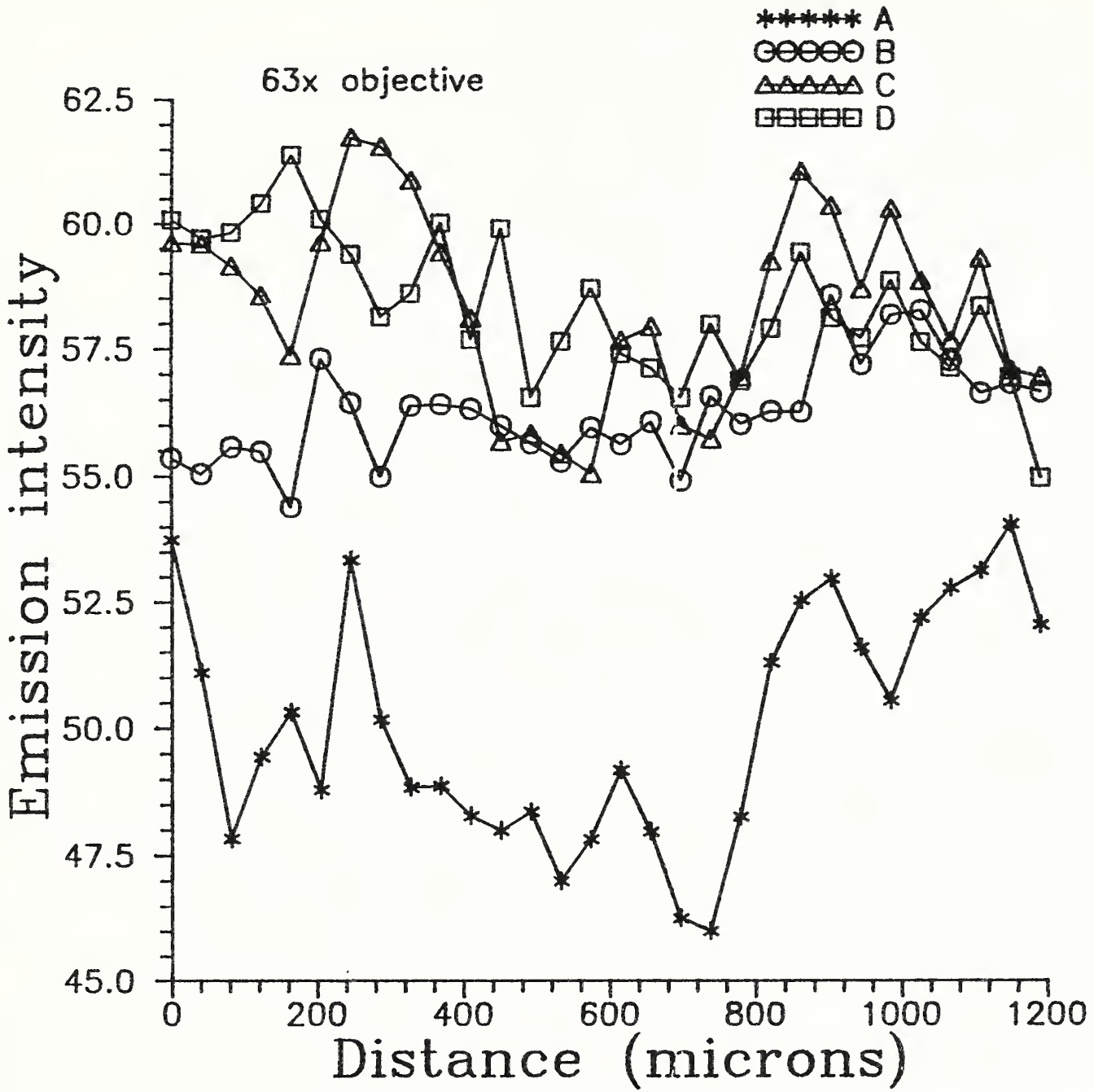
63x objective
A
B
C
D
Emission intensity
62.5
60.0
57.5
55.0
52.5
50.0
47.5
45.0
0
200
400
600
800
1000
1200
Distance (microns)

Fig. II-5

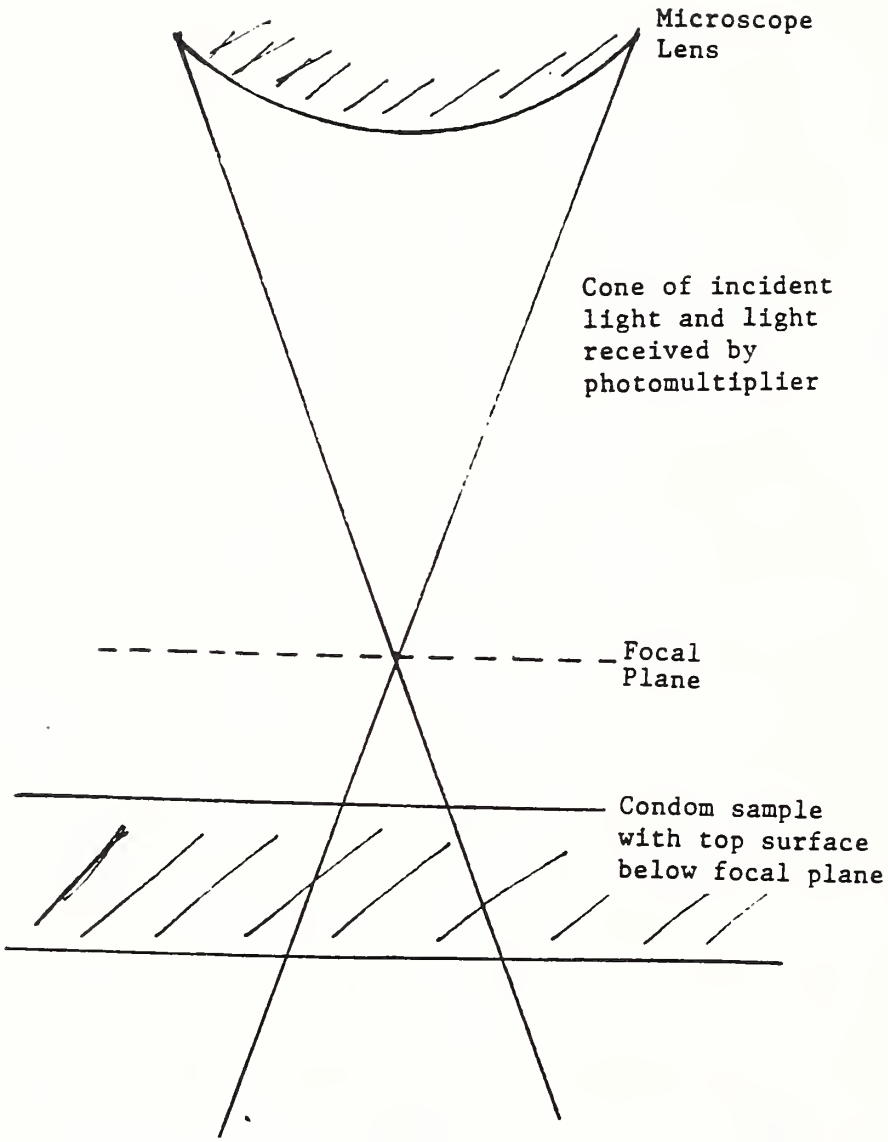
Microscope
Lens
Cone of incident
light and light
received by
photomultiplier
Focal
Plane
Condom sample
with top surface
below focal plane

Fig. II-6

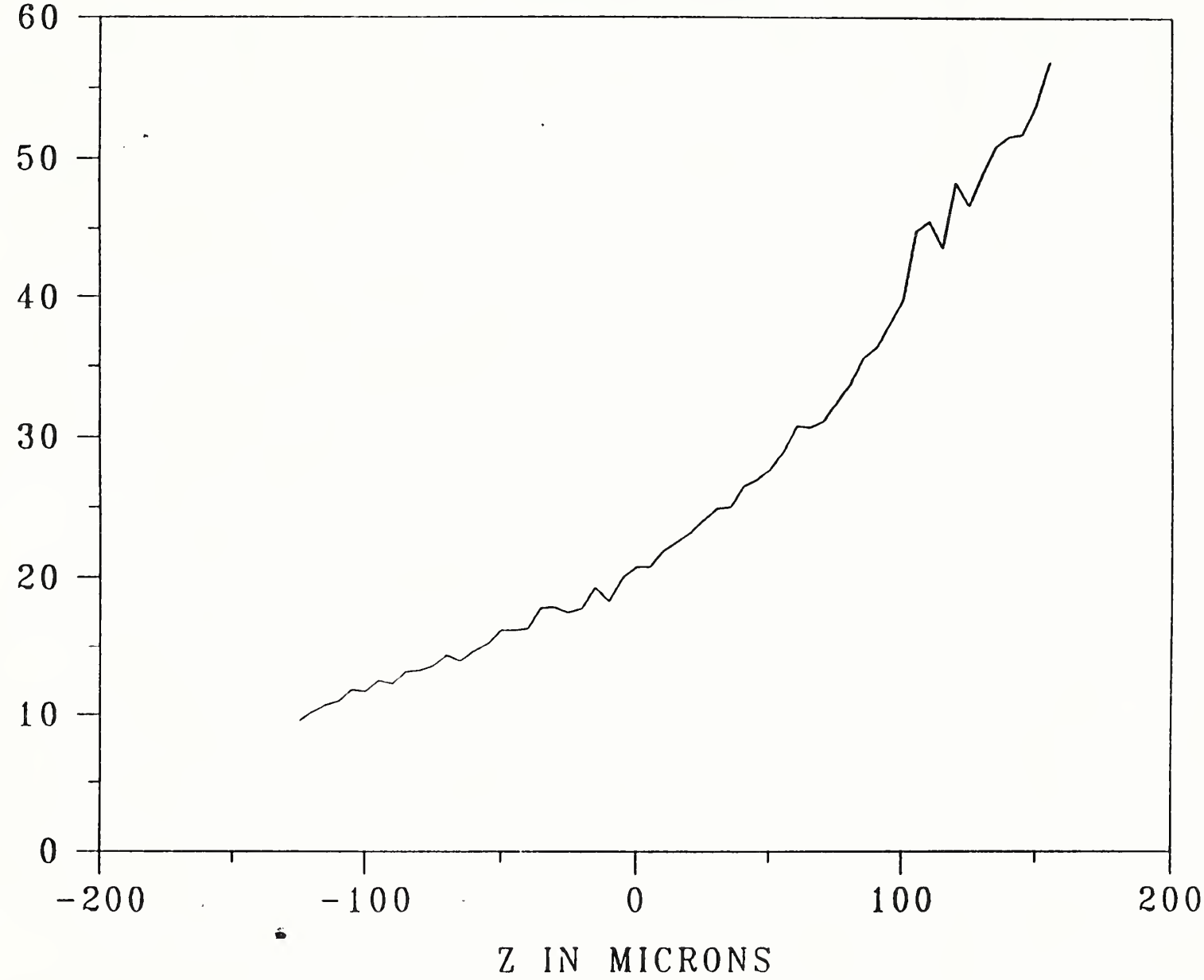
SIGNAL FROM Z LAYER
60
50
40
30
20
10
0
F(Z)
-200
-100
0
100
200
Z IN MICRONS

Fig. II-7

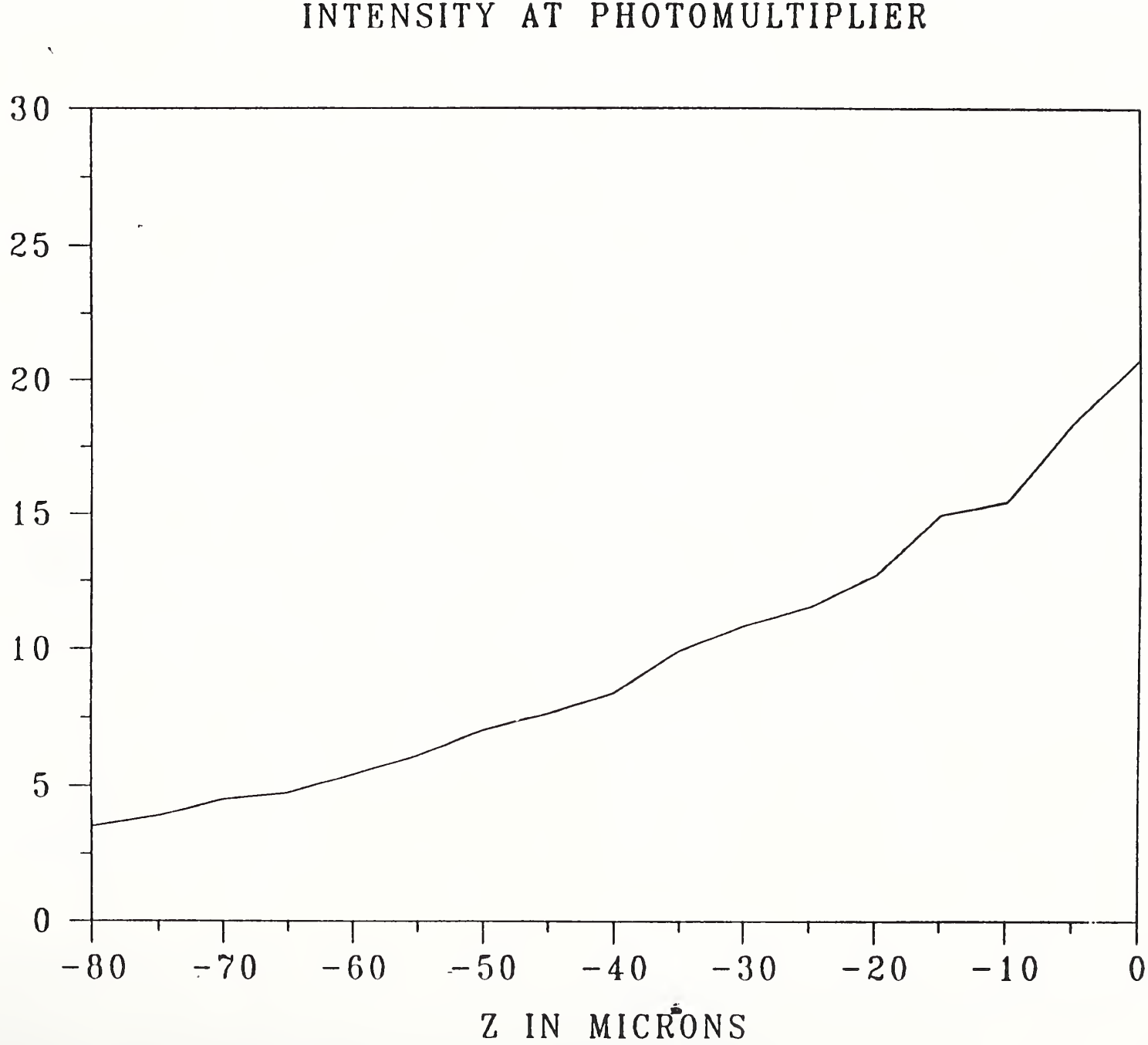
INTENSITY AT PHOTOMULTIPLIER
30
25
20
15
10
5
0
I_{PM}
-80
-70
-60
-50
-40
-30
-20
-10
0
Z IN MICRONS

Fig. II-8

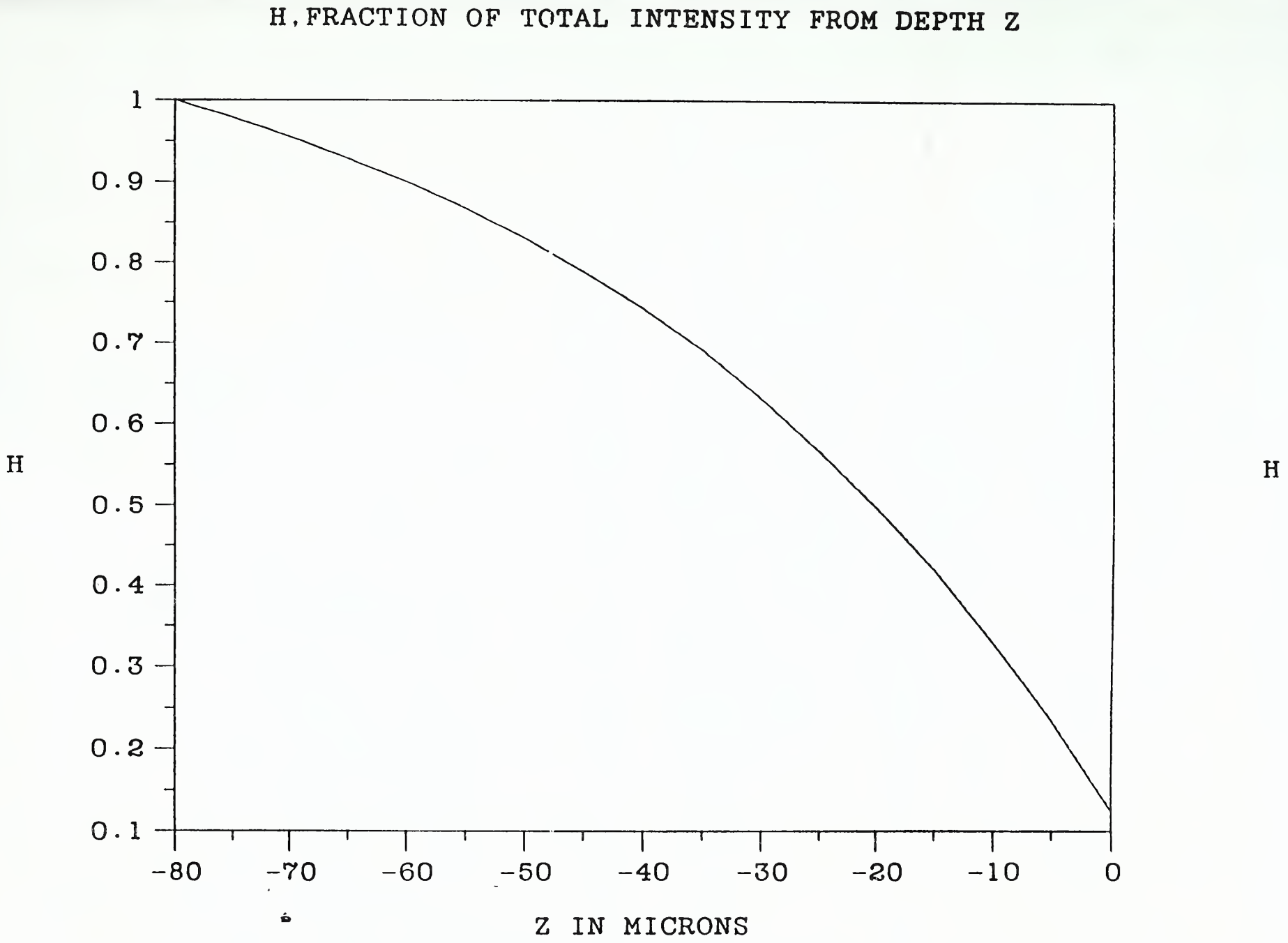
H, FRACTION OF TOTAL INTENSITY FROM DEPTH Z
H
H
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-80
-70
-60
-50
-40
-30
-20
-10
0
Z IN MICRONS

Fig. II-9

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This report covers work on a 1988 contract with FDA to study failure modes of latex barrier films in their use as condoms or medical gloves. Two areas have been studied in this reporting period: The change in the failure of latex barrier films as a result of swelling in body fluid simulants and the cross-link density variation in condoms on the .1 mm scale.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Latex barrier films, condoms, medical gloves, crosslink, swelling, body fluids, rubber, natural rubber

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