OPTIMIZING COLLAGEN FIBERS FOR USE IN A COLLAGEN ENGINE

by

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ABSTRACT

Surgical collagen sutre fibers were cross-linked in an effort to optimize those fiber parameters which govern the mechanical behavior necessary for the operation of a collagen engine. This was accomplished by exposing three types of sutre material to various concentrations of formaldehyde for varying amounts of time. The test conducted yielded force versus time data for a constrained fiber as it was exposed to saturated LiBr, and for the same fiber as it relaxed in water. Such critical parameters as time required for the fiber to develop a tension of 40 grams (t_{40}), equilibrium force attained (f_{max}), and time required for the fiber relaxing in water to decrease its tension by 40 grams (t'_{40}) were analyzed. Of the samples tested, the optimum parameters were attained from an Ethicon chromic 000 sutre treated with LiBr for 20 hours before cross-linking with 0.01M HCHO for 300 seconds. This sample had a t_{40} of 27 seconds as compared with 4 seconds for collagen tape. This sample could theoretically operate the collagen engine at 6 r.p.m. if 2.7 feet of it were immersed in the LiBr bath of the engine at any given time.

INTRODUCTION

Collagen is a protein fiber found abundantly in the body where it functions primarily as tendon, ligament, and connective tissue. Its most dramatic property is the "melting" or contraction it exhibits when immersed in certain aqueous solutions such as lithium bromide and urea. The reverse of that reaction, the expansion from its contracted state and recrystallization occurs when the fiber is washed in water or in a dilute solution. An investigation which studied these mechanical properties of reconstituted collagen tape[1] was undertaken in May 1968 by Thomas Turai and myself. A direct result of this study was the design, construction and successful operation of a collagen engine. Although the design was originally conceived, it was similar to one of the designs proposed by Professor A. Katchalsky and his colleagues of the Weizman Institute, published in Nature.[2] This engine operating between two LiBr concentration levels, had a rotary motion output of about 20 r.p.m. and a theoretical torque of 95 cm.-gm.[3] (See Figure 1).

A detailed study of the engine performance was planned, but the scarcity of the collagen tape was an impediment. Thus the present study was conceived. Surgical sutre, unlike the tape is easily available on the market and is composed of collagen. An attempt was made to run the engine using such sutre fibers and although in some cases slight rotary motion was detectable, in general these attempts failed. Thus it was decided to study

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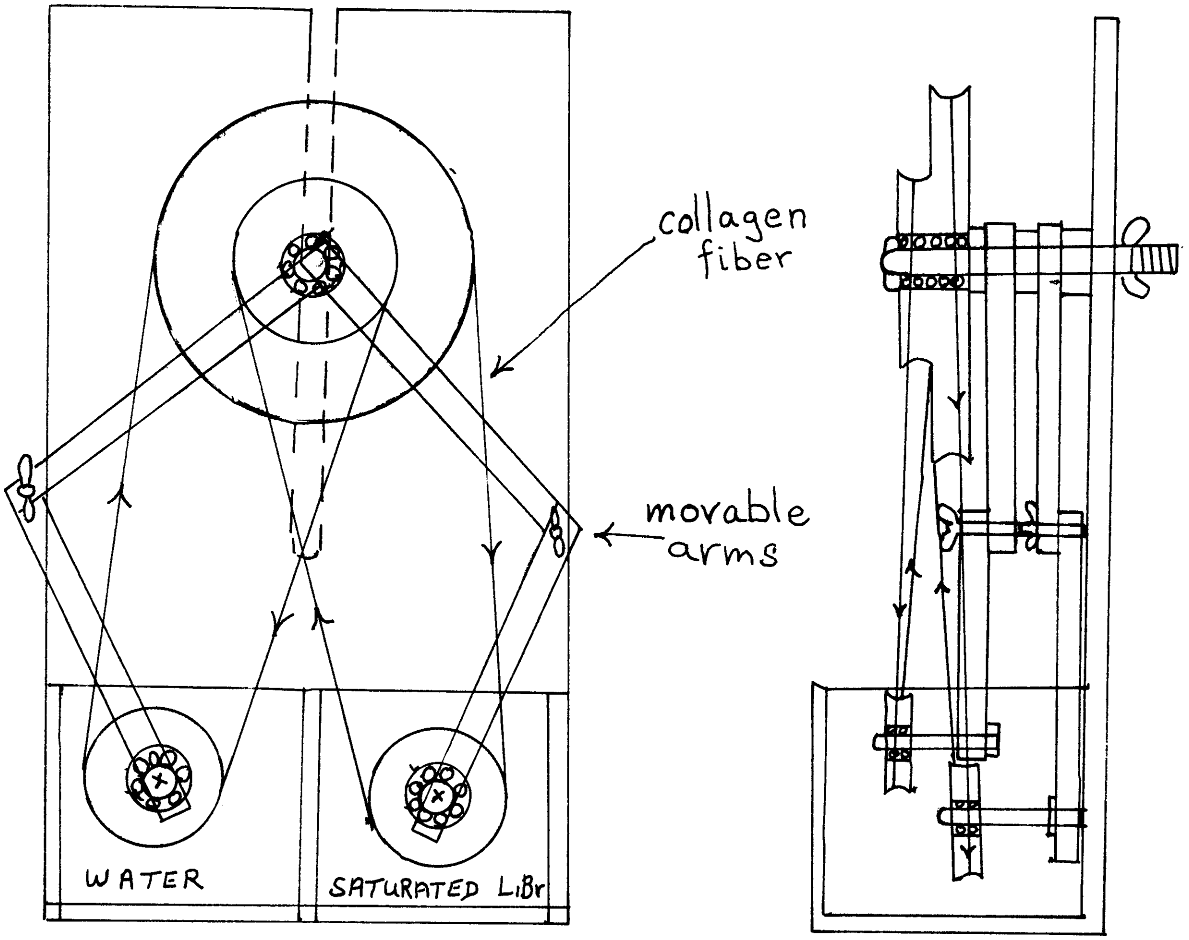
[1] Supplied by Ethicon Inc. of New Jersey

[2] Steinberg, Dr. I. Z., Oplatka, Dr. A., Katchalsky, Prof. A., Nature, Vol. 210, 1966, p. 568

[3] Turai, Thomas and Mark, Dan, "The Design and Operation of a Collagen Engine", (unpublished report submitted for course 2.671, M.I.T., May 1968) p. 2



Collagen Engine

figure 1

the critical fiber parameters, those that govern the mechanical behavior necessary for engine operation. Since it was already obvious that the untested sutre would not be suitable, attempts were undertaken to improve the sutre properties by cross-linking it with formaldehyde.

The test chosen for this purpose was one which yielded force versus time data for a constrained fiber sample as it was exposed to saturated LiBr. When the force developing in the constrained fiber reached equilibrium, the LiBr was removed and water replaced it. Similar data for the ensuing relaxation process was recorded. This test was employed because it yielded the information needed for evaluating the fiber's applicability to the engine design. Of greatest importance is the parameter t_{40}, the time required for the constrained fiber to develop a force of 40 grams. The previous investigation showed that the collagen tape developed such a force while running the engine at the optimal rate of 20 r.p.m. (See analysis in Appendix). Thus it was desirable to approach the t_{40} of collagen tape with sutre fibers. Another parameter, t'_{40}, the time required for the fiber relaxing in water to decrease its tension by 40 grams was also essential. In the case of collagen tape, the two parameters were almost identical and of the order of 5 seconds. A fiber with a t_{40} close to its t'_{40} was essential because of constraints imposed by the engine design. If, for example, t'_{40} were much larger than t_{40}, the duration of the fiber's presence in the water bath of the engine would have to be increased accordingly or else complete relaxation would not take place, the fiber would tighten and engine motion would come to a stop. Another important parameter is f_{max}, the equilibrium force developed in the constrained fiber. This force would have to exceed a threshold of about 40 grams, otherwise static frictional forces would not be overcome and no motion would occur. A high f_{max}, on the other hand, may indicate better design possibilities but may also indicate new friction problems due to the increased normal force applied to the bearings. The last parameter to be studied is τ, the time constant for the tightening process. This parameter is useful in studying the viscoelastic behavior of the fiber. If we use the Voight Model in analyzing the behavior of the fiber, we can relate the time constant to the Young's Modulus E and the normal viscosity component, by means of the equation $\tau = \eta/E$.

The aqueous solution utilized in these procedures was saturated LiBr, for the aforementioned investigation indicated that to be the optimal solution of all those tested.

Thus this investigation will attempt to discover a sutre material, optimally cross-linked with HCHO to be used in operating the collagen engine. If this cannot be done, information will be gathered which will enable the designing of a new engine to be operated by a sutre fiber.

PROCEDURE

Three different types of sutre were tested. These were: Davis and Geck chromic C medium which had a cross-sectional area of 3.14×10^{-4} in.^{2};[4] Ethicon chromic COOO with a cross-sectional area of 9.45×10^{-5} in.^{2}; and Ethicon plain OOO which also had a cross-sectional area of 9.45×10^{-5} in.^{2}. The reconstituted collagen tape specially made by Ethicon was tested alongside the sutre. The tape had a cross-sectional area of 10^{-4} in.^{2}. The

[4] All figures for cross-sectional areas are for unswollen samples

plain sutre is collagen taken from the wall of animal gut. The chromic sutre is similar collagen but is treated with chromic acid to retard its absorption by the body. The difference in absorption rates between these fibers is a factor of 3 or 4.[5] All samples were 4½ in. long and were immersed in water of 65-75°F for 24 hours before testing. Shortly after the testing began, it became apparent that the cross-linking with HCHO was not very effective if the samples were not exposed to LiBr for some time before the cross-linking. (See Appendix Table 1). Thus all samples, except some checks, after their exposure to water, were exposed to 100 minutes of LiBr at 75°F.

Each of the two ends of the fiber was squeezed between two metal plates measuring 3/4 in. x 1/8 in. x 1/16 in. The plates were tightened with screws. The ends of the fiber were wrapped in paper to protect them from the metallic edges. The plates were then placed into separate metallic sockets. One socket was fixed to a metallic plate which constituted the base of a plexiglass tube. This tubing stand fits tightly into the base of the plexiglass stand. (See Figure 2). The other socket was connected to a vertical wire which was attached directly to the load cell. A one-pound Bytrex load cell model BC-1 was firmly attached at the top of the plexiglass stand and was powered by a 22½ volt Burgess "B" battery, It was connected to a Model 2D-2 Moseley x-y recorder. The recorder was calibrated to read grams force in the vertical direction and time in seconds in the horizontal. The initial tension in the fiber, a critical factor for this test, was held constant at 5±3 grams. Dow Corning vacuum grease was effectively used to seal the tube at its base.

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[5] Dr. Lele, Department of Mechanical Engineering, M.I.T., from a conversation, June 1969.

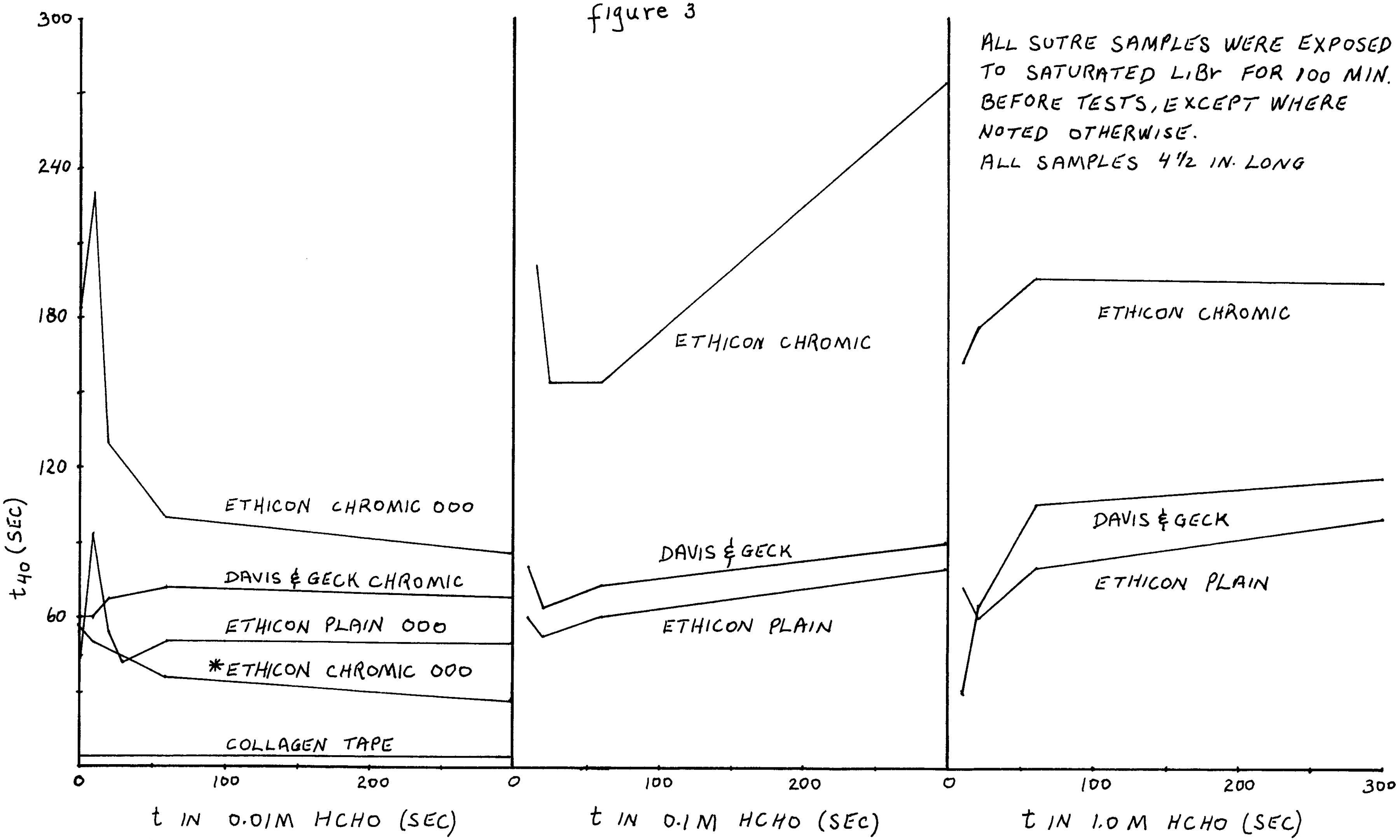
figure 2

Each run consisted of mounting a sample in the apparatus, pouring in the LiBr ($T=70\pm5^{\circ}F$), and recording force versus time till force equilibrium was attained. Then the LiBr would be emptied through a small opening near the base of the tube by removing a tiny cork, water would be poured into the tube and again force versus time to equilibrium would be recorded. Equilibrium was considered an increase of no more than 3 grams per 750 seconds. The tape and each sutre were tested totally untreated (except for initial water bath), with a LiBr exposure of 100 minutes and finally with varying HCHO treatments in addition to the LiBr treatment. These HCHO treatments consisted of three different concentration levels: 0.01M, 0.1M, and 1.0M solutions. To each of these concentrations, the fibers were exposed for about 4 or 5 ~~minutes~~ different periods ranging from 10 sec. to 5 min. After about 5 minutes the effects of cross-linking seemed to have leveled off. All the initial tests in each of the three concentration groupings, and all the tests on the untreated samples were carried out three times each. Subsequent tests were only conducted once each. These procedures seem justified since the deviation was only of the order of 10%. The curves in the appendix are mean composites of the three actual runs conducted for each test. As the importance of LiBr exposures became apparent, a few miscellaneous runs were made testing its effects.

RESULTS AND DISCUSSION

Of all the sutre samples exposed to 100 minutes of LiBr before testing, the Davis and Geck chromic sutre proved most promising with a t_{40} of only 30 seconds at an HCHO treatment of 10 seconds in a 1M bath. (See Figure 3). This t_{40} was still much higher than that of the collagen tape which was only

figure 3



ALL SUTRE SAMPLES WERE EXPOSED TO SATURATED LiBr FOR 100 MIN. BEFORE TESTS, EXCEPT WHERE NOTED OTHERWISE.
ALL SAMPLES 4 1/2 IN. LONG

* LiBr PRE-EXPOSURE OF 20 HRS.

4 seconds. On the other hand, the sample of Ethicon chromic which was exposed to 20 hours of LiBr before testing proved even more promising. At a 0.01M HCHO treatment of 300 seconds it had a t_{40} of only 27 seconds, as compared with 90 seconds for a similar chromic sutre with only 100 minutes of LiBr exposure previous to the HCHO treatment. This may indicate that a similar treatment of Davis and Geck chromic or Ethicon plain may decrease their t_{40} to a level comparable with that of the collagen tape. Perhaps an even longer, or a shorter exposure to LiBr will yield the best results.

In general, the initial LiBr bath brought the t_{40} for all sutre down dramatically from what it was in the untreated samples. (See Figure 4).

The cross-linking with HCHO brought t_{40} down to an even lower minimum and then, an increase in the cross-linking by increasing the exposure time, by increasing HCHO concentration or both, would bring t_{40} back up again. (See Figure 3).

The collagen tape was virtually unaffected by exposures to 0.01M HCHO. Exposures to higher concentrations of HCHO decreased the tape's f_{max} below 40 grams and thus t_{40} was not measurable. On the other hand, the τ for the tape remained unchanged at 4 seconds even at these higher concentrations.

For the sutre, the behavior of τ was generally similar to that of t_{40}. The lowest τ, 38 seconds, was again attained by the Ethicon chromic which was pre-exposed to LiBr for 20 hours, and then treated with 0.01M HCHO for 300 seconds. (See Figure 5).

The relaxation parameter t'_{40} remained at a relatively constant level for all runs, varying from 4 seconds to 27 seconds over the entire range of tests. (See Table 1).

figure 4

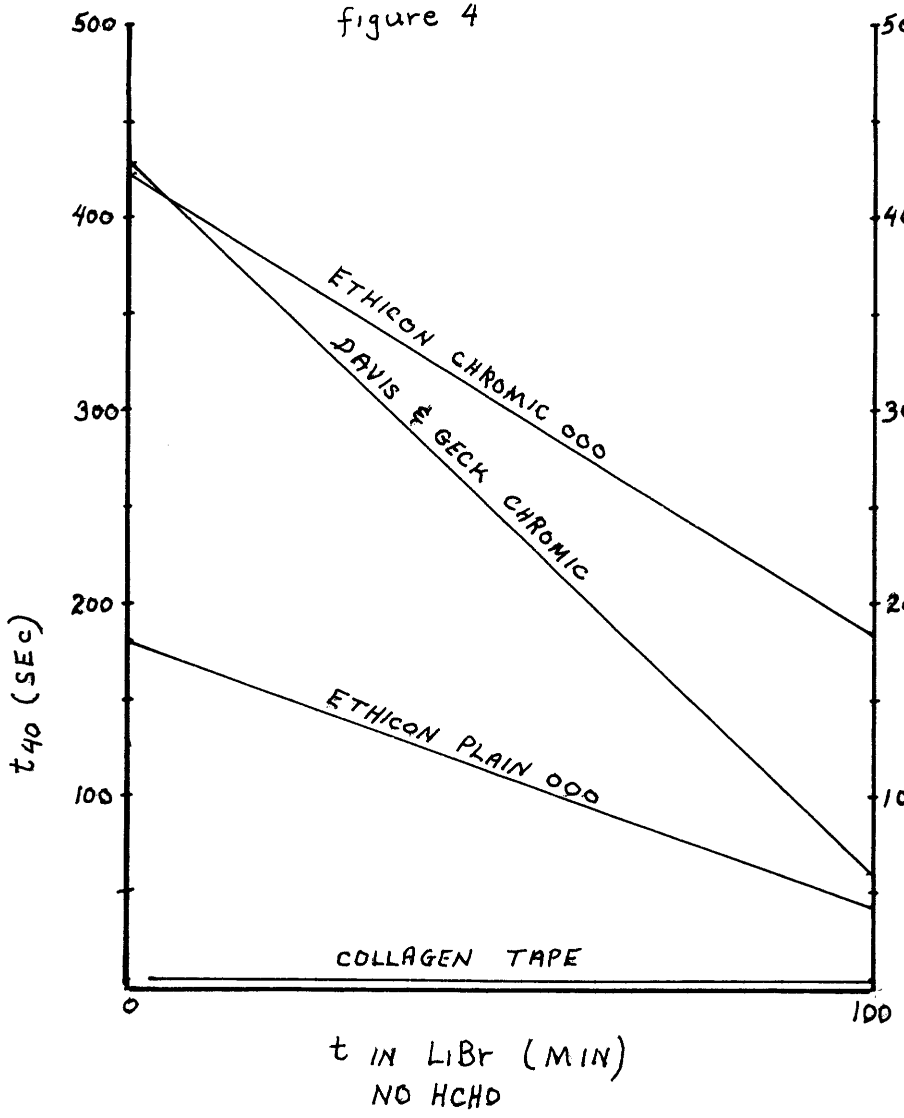


figure 6

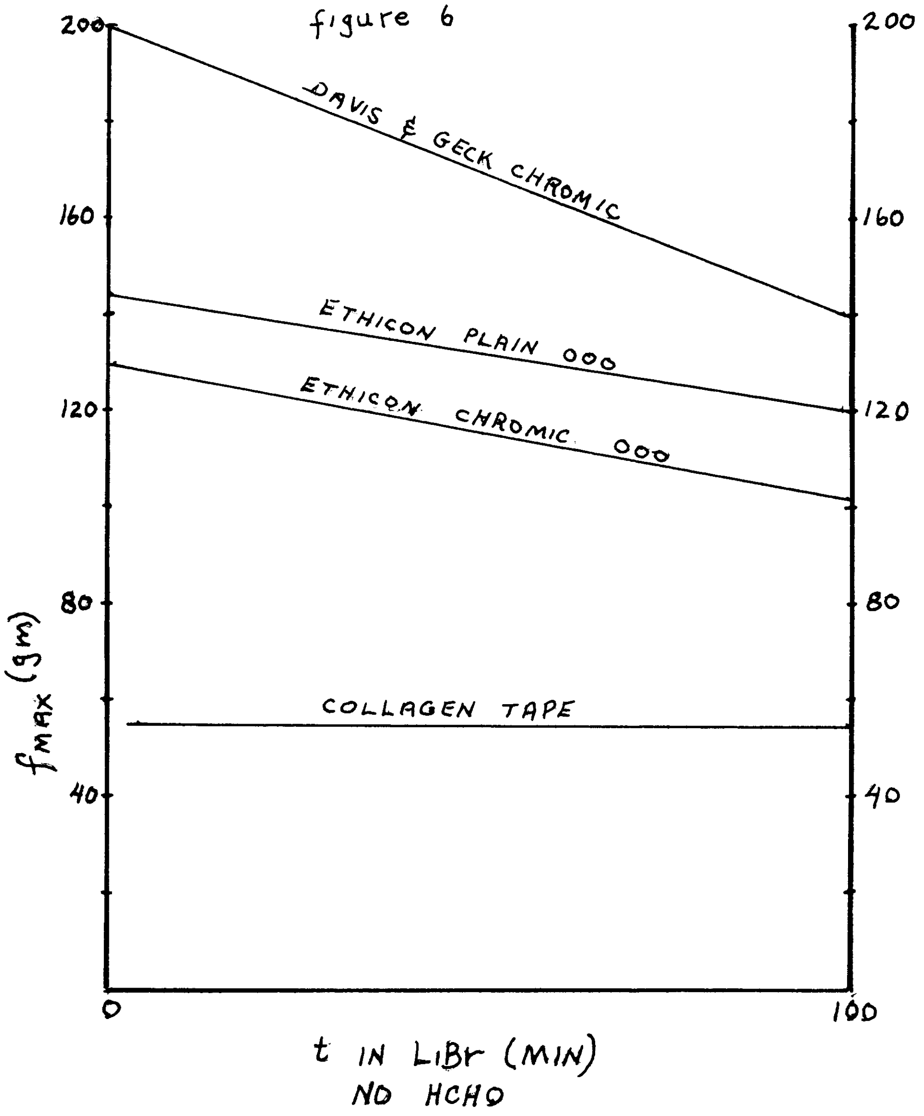
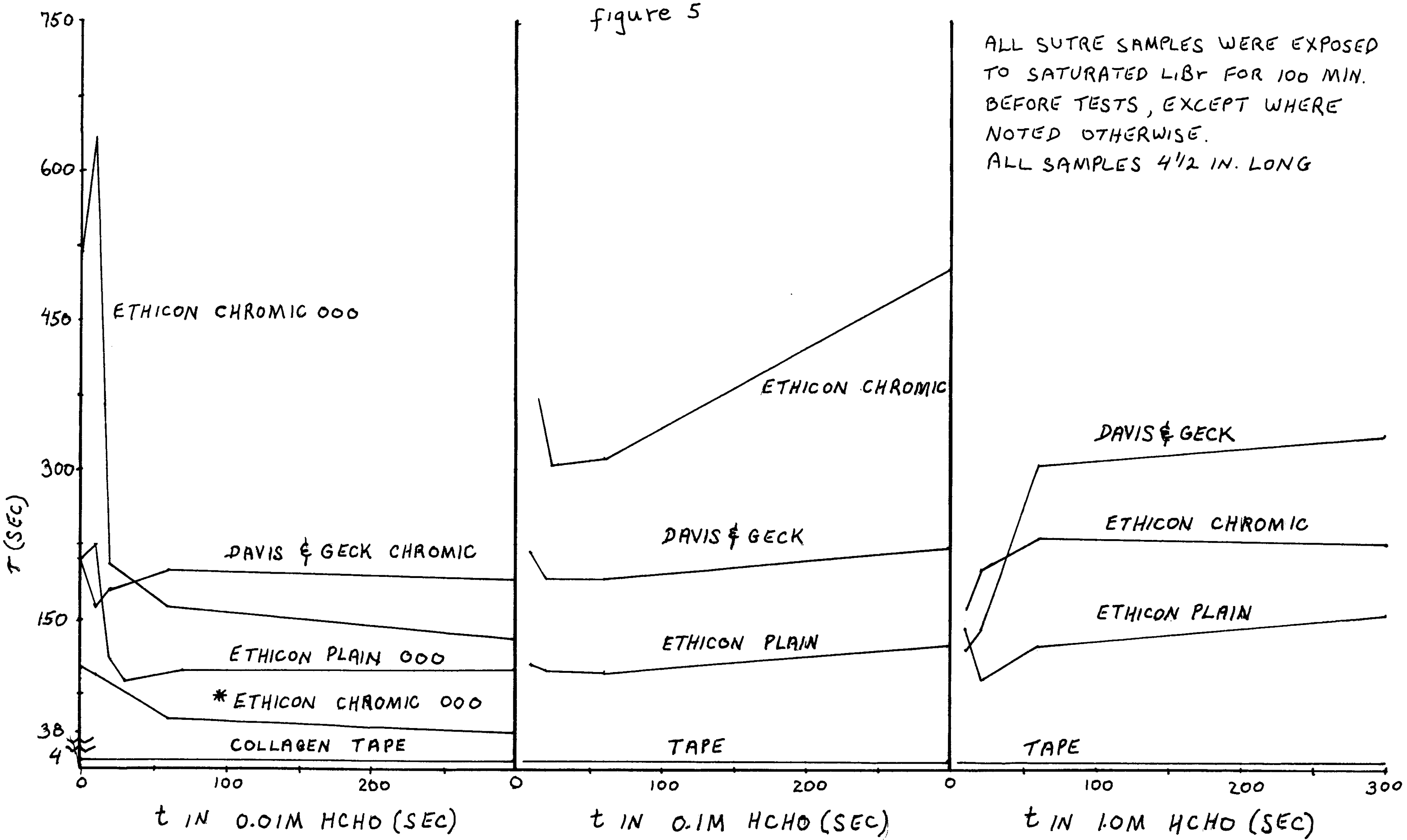


figure 5



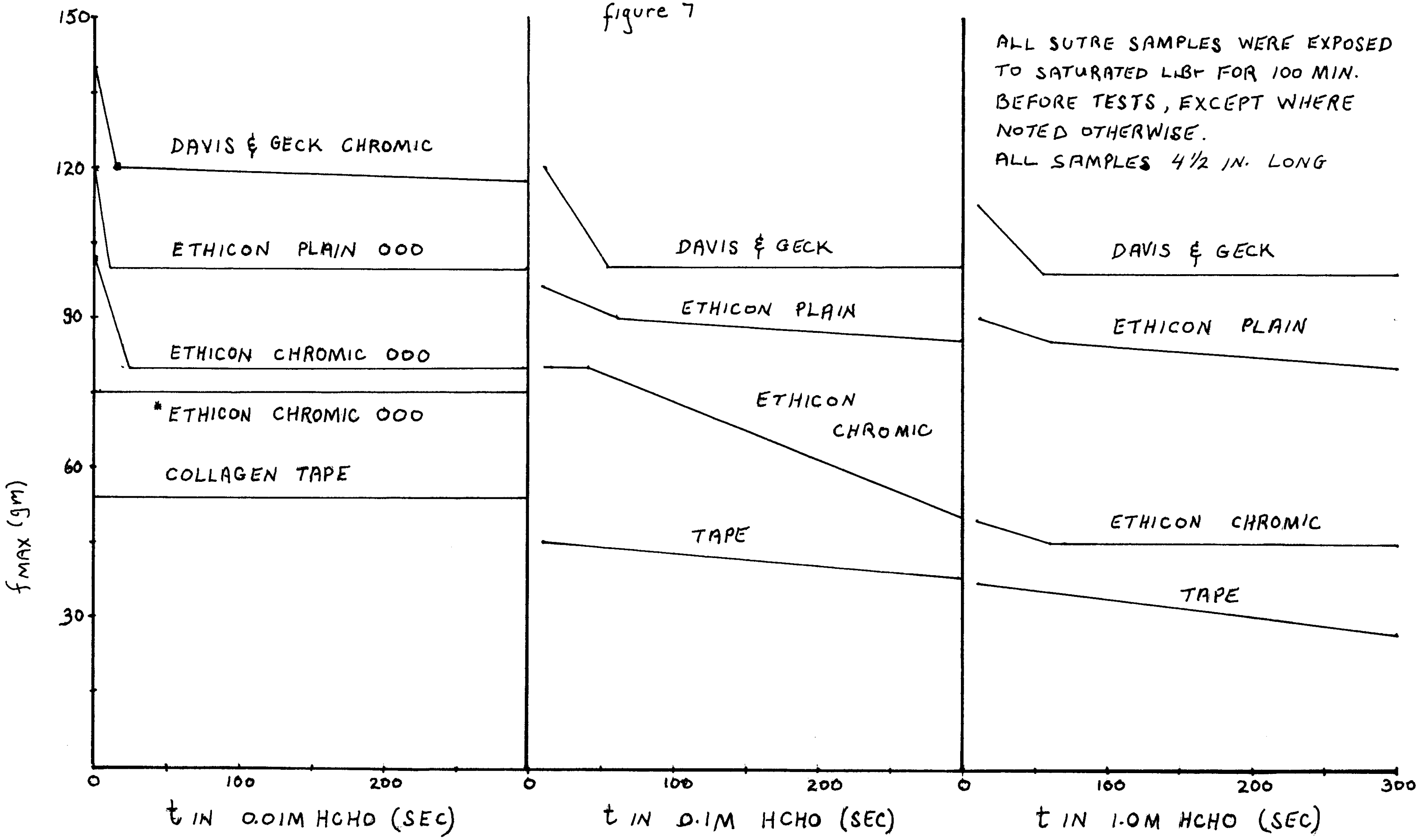
ALL SUTRE SAMPLES WERE EXPOSED
TO SATURATED LiBr FOR 100 MIN.
BEFORE TESTS, EXCEPT WHERE
NOTED OTHERWISE.
ALL SAMPLES 4 1/2 IN. LONG

* LiBr PRE-EXPOSURE OF 20 HRS.

The last parameter, f_{max}, varied as expected. It consistently exhibited a dramatic decrease after exposure to LiBr (see Figure 6) and an even further decrease with HCHO treatments, usually leveling off after a certain amount of cross-linking (see Figure 7). Collagen tape exhibited the lowest f_{max} for every test.

Some of the above phenomena can be easily explained; some are more complex. When f_{max} is being examined, we're dealing strictly with the modulus of the material. The phenomenon of increase in modulus with cross-linking is well known in most polymers. Cross-linking a polymer constrains the chains in their sliding past one another. In this manner a viscous liquid is changed to an elastic material. As cross-link density increases, straining a polymer becomes increasingly difficult. A similar, but somewhat reversed,phenomenon is occuring here. The collagen fiber in its elongated state is kept elongated because of the mutual repulsion of the H^+ radicals lodged in certain sites along the chain. When the fiber is exposed to a LiBr environment, these electrostatic forces are neutralized and the fiber returns to its thermodynamically more probably state, that of a random coil, and undergoes shrinking. To strain it again to its original length, while it is still in the same LiBr environment takes a certain stress, that needed to counterbalance the thermodynamic effect. But if cross-links are imposed in the elongated state, as was done in these tests, these cross-links will exert forces which will help counter the thermodynamic effect. Thus it becomes easier to restrain the fiber, or in other words f_{max} decreased. If we choose to adopt the Voight Model and assume that $\tau = \eta / E$, then the initial drop in t_{40} and τ must be explained in terms of a decrease in the viscosity component η, which is

figure 7



ALL SUTRE SAMPLES WERE EXPOSED TO SATURATED LiBr FOR 100 MIN. BEFORE TESTS, EXCEPT WHERE NOTED OTHERWISE.
ALL SAMPLES 4½ IN. LONG

*LiBr PRE-EXPOSURE OF 20 HRS.

faster than the decrease in E. The final increase in t_{40} and τ with high degree of cross-linking indicates that the effect of a decreasing modulus is predominating.

While all the sutre samples were tested with a LiBr treatment of 100 minutes and without, the tape was never successfully tested without a previous exposure to LiBr for at least a few seconds. When this was attempted, the fiber ruptured after about 3 seconds. This was probably due to the uneven distribution of LiBr across the cross-sectional area of the fiber. Due to the lack of "wetting", some fibrils were influenced by the LiBr much sooner than others and thus had to bear a disproportionate stress concentration. The actual rupturing of the fibrils took place slowly enough for the eye to follow.

CONCLUSION

The data recorded indicates that the present engine design will probably operate with some of the treated sutre fibers tested, such as the Davis and Geck chromic with a 100 minute LiBr exposure and with a 10 second 1.0 M HCHO treatment, or the Ethicon chromic with a LiBr exposure of 20 hours and a 300 second 0.01M HCHO treatment, but the engine may not turn at 20 r.p.m. On the other hand, some better sutre fibers may yet be found if this investigation is continued. Although the effects of LiBr exposures were not studied in detail, some of the results indicate that prolonged exposure of sutre to LiBr may have very favorable effects. As is illustrated in Figure 3, samples of Ethicon chromic sutre after being exposed to LiBr for 20 hours gave the best results of any sutre material tested. The t_{40} for such a fiber after a 300 seconds exposure to 0.01M HCHO was 27 seconds. Thus it seems logical that an extensive investigation of the effects of LiBr on these properties be undertaken. Perhaps an Ethicon plain sutre or Davis and Geck chromic sutre after a 20 hour exposure to LiBr will have a t_{40} of close to 4 seconds. These LiBr effects resemble to a great extent the effects of the HCHO exposures. Thus it may be that the LiBr is influencing the cross-linking of the collagen. To test this theory one could employ a swelling technique which would give a measure of cross-link density. This same technique could also be used in conjunction with tests such as the above. The relation between the parameters f_{max}, t_{40} and τ and the cross-link density could be determined and used as a future guide line for optimization cross-linking treatments.

The other possibility, of course, is the alteration of the engine design to compensate for the longer t_{40} of the sutre. The analysis in the appendix shows that if we cannot bring t_{40} below 27 seconds, we can only get a theoretical output of 20 r.p.m. if we let a fiber of length 9 feet pass through the LiBr bath at any given time. This analysis has not taken into account the added hydrodynamic drag that would be incurred by the additional fiber traveling through the baths. Thus if the present engine design-concept would be used, the engine size would become very cumbersome. If a new pulley system is designed to alleviate the size problem, additional pulleys would be inevitable, and friction losses would increase as a result. A fiber tension higher than 40 grams would be needed to operate the engine and thus t_{40} will no longer suffice. A longer time constant would again require a longer immersion time. Aside from these problems, bearing friction will be linearly increasing as the force is increased.

On the other hand, if 6 r.p.m. would be satisfactory, an engine turning at such a rate could operate with a fiber whose $t_{40} = 27$ seconds and which has only 2.7 feet of fiber immersed in LiBr at a time. This length of immersion is compatible with the present engine design. The r.p.m. is a reasonable one for observation and incurrs relatively low losses due to hydrodynamic drag. On the water side there would naturally be no need for quite such an extended bath period since t'_{40} is relatively lower than t_{40}. For a t'_{40} of 12 seconds only a length of 1.2 feet would have to be immersed at a time. Thus a successful collagen engine could be operated using collagen sutre.

APPENDIX

TABLE 1

I. Ethicon plain
sutre size 000
diameter = 0.012 in., length = 4.5 in.
cross-sectional area = 9.45×10^{-5} in.^{2}

Sample[1]	f_{max}(gm)[2]	t_{40}(sec)[3]	t'_{40}(sec)[4]	τ(sec)[5]
no LiBr, no HCHO	145	180	10	1050
no HCHO	120	44	8	210
10 sec. in 0.01M[6]	100	94	10	225
20 sec. in 0.01M	100	55	10	110
30 sec. in 0.01M	100	40	10	90
70 sec. in 0.01M	100	50	8	98
300 sec. in 0.01M	100	50	10	100
820 sec. in 0.01M	100	50	10	97
10 sec. in 0.1M	96	60	10	105
20 sec. in 0.1M	96	52	12	100
60 sec. in 0.1M	90	60	13	98
300 sec. in 0.1M	85	80	10	124
10 sec. in 1.0M	90	72	12	142
20 sec. in 1.0M	90	60	16	95
60 sec. in 1.0M	85	80	12	121
300 sec. in 1.0M	80	100	10	153
no LiBr,70 sec. in 0.01M	148	290	10	1120

[1] All samples were exposed to 100 min. of saturated LiBr except where noted otherwise.

[2] Equilibrium force developed in constrained fiber as it is exposed to saturated LiBr.

[3] Time required for the force to reach 40 gm.

[4] Time required for the constrained fiber, relaxing in H_2O to decrease its tension by 40 gm.

[5] Time required for the forces developed to come within 1/e of their equilibrium values.

[6] All such concentrations refer to solutions of HCHO

II. Ethicon chromic

sutre size 000

diameter = 0.012 in., length = 4.5 in.

cross-sectional area = 9.45×10^{-5} in.^{2}

Sample	f_{max}	t_{40}	t'_{40}	τ
no LiBr, no HCHO	130	425	16	1340
no HCHO	102	185	15	520
10 sec. in 0.01M	100	230	25	632
20 sec. in 0.01M	80	130	27	205
60 sec. in 0.01M	80	100	27	162
300 sec. in 0.01M	80	85	27	130
15 sec. in 0.1M	80	200	17	372
25 sec. in 0.1M	80	155	18	304
60 sec. in 0.1M	80	155	20	312
300 sec. in 0.1M	50	275	22	502
10 sec. in 1.0M	50	164	20	162
20 sec. in 1.0M	50	176	18	202
60 sec. in 1.0M	45	196	21	232
300 sec. in 1.0M	45	194	19	225
LiBr 20 hrs; no HCHO	75	57	16	101
LiBr 20 hrs; 15 sec. in 0.01M	75	50	15	93
LiBr 20 hrs; 60 sec. in 0.01M	75	36	12	47
LiBr 20 hrs; 300 sec. in 0.01M	75	27	12	38

III. Davis and Geck

chromic C medium

diameter = 0.02 in., length = 4.5 in.

cross-sectional area = 3.14×10^{-4} in.^{2}

Sample	f_{max}	t_{40}	t'_{40}	$\mathcal{T}$
no LiBr, no HCHO	200	230	12	1005
no HCHO	140	60	10	210
10 sec. in 0.01M	120	60	10	163
20 sec. in 0.01M	120	68	12	174
60 sec. in 0.01M	120	72	16	200
300 sec. in 0.01M	117	68	16	189
10 sec. in 0.1M	120	80	10	217
20 sec. in 0.1M	110	64	10	192
60 sec. in 0.1M	100	73	12	192
300 sec. in 0.1M	100	90	13	221
10 sec. in 1.0M	112	30	10	120
20 sec. in 1.0M	110	65	12	140
60 sec. in 1.0M	100	105	10	306
300 sec. in 1.0M	100	116	11	332

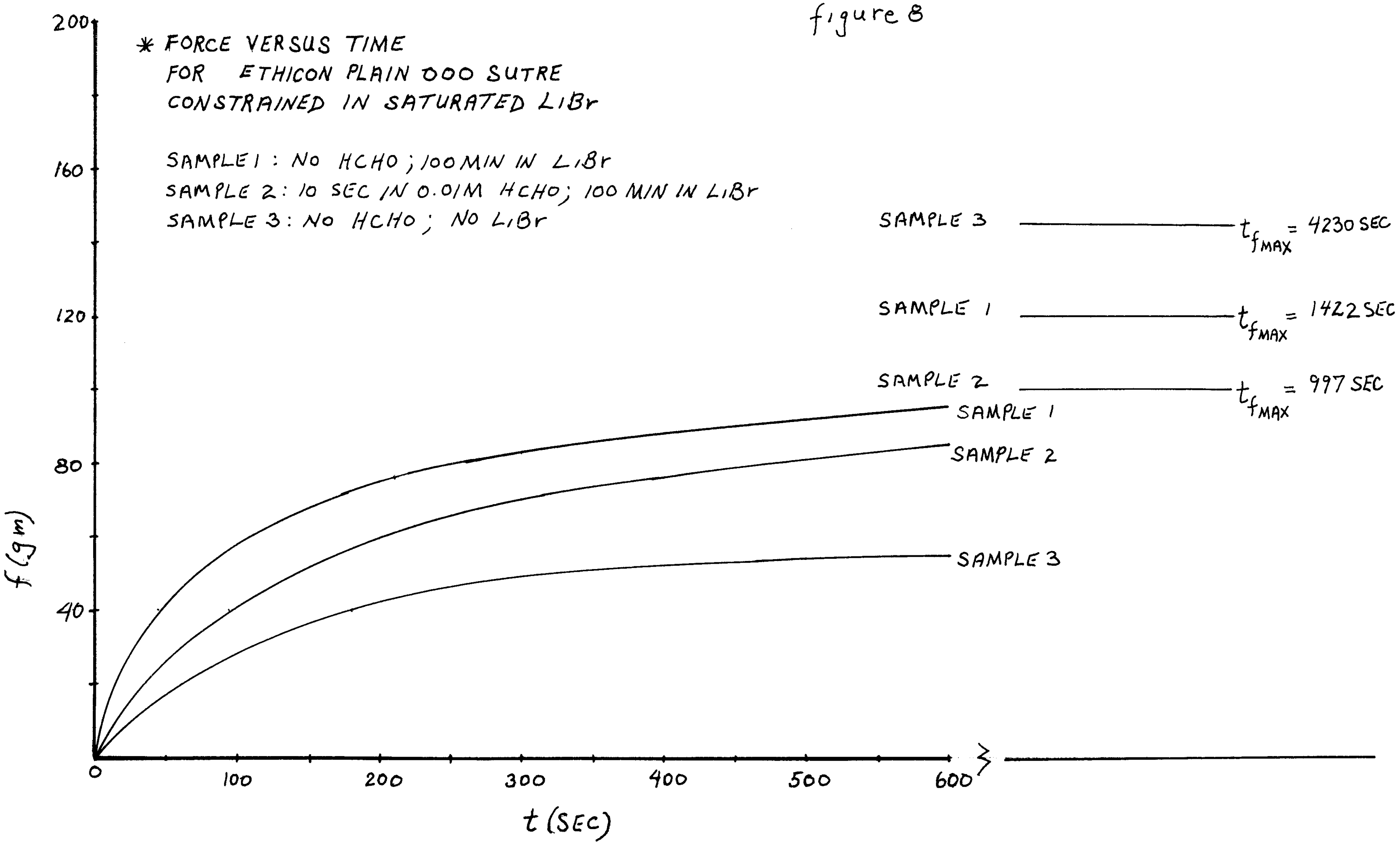
IV. Collagen Tape

length = 4.5 in.

cross-sectional area = 10^{-4} in.^{2}

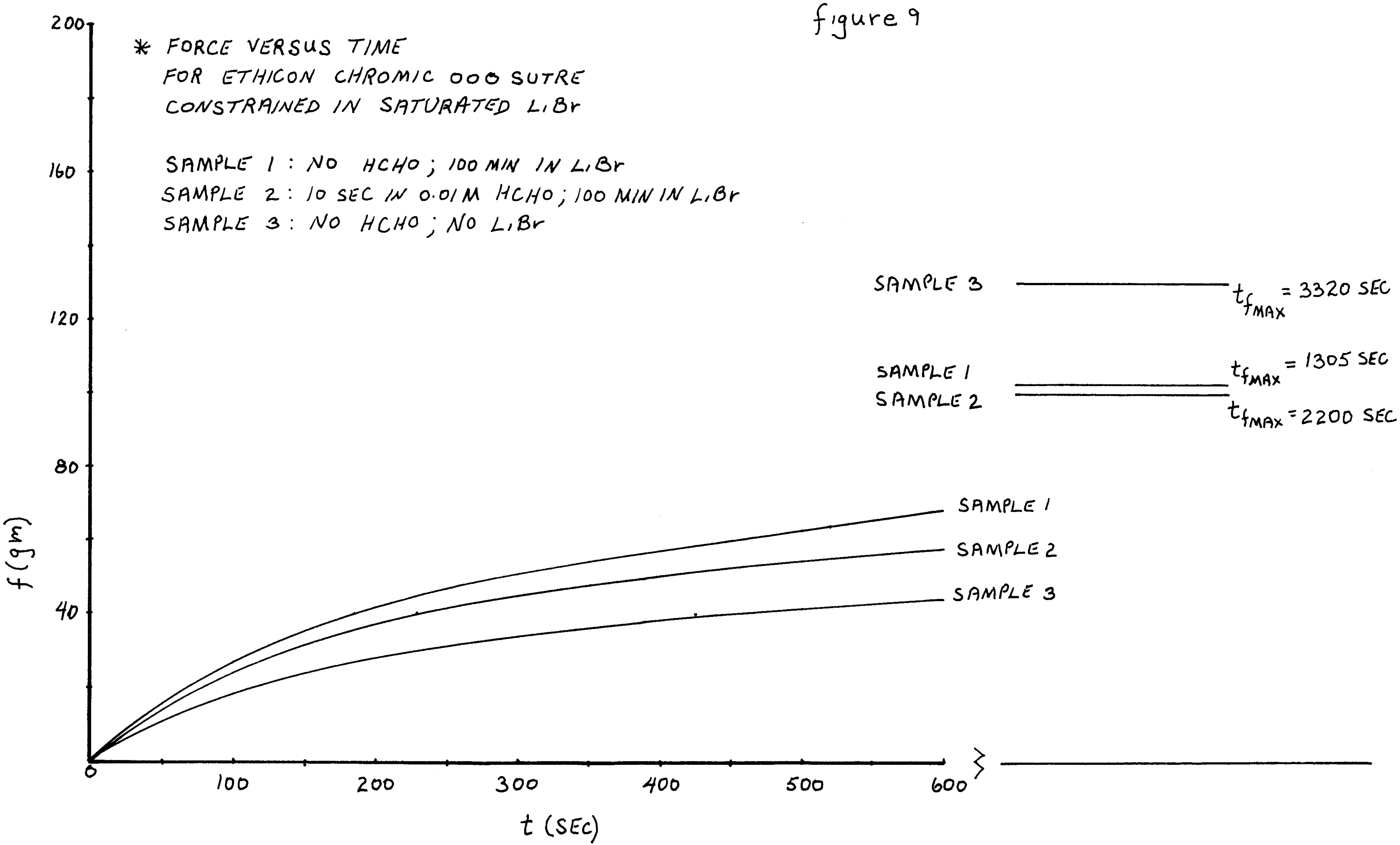
Sample	f_{max}	t_{40}	t'_{40}	τ
no HCHO	55	4	5	4
10 sec. in 0.01M	55	4	5	4
20 sec. in 0.01M	54	4	4	4
60 sec. in 0.01M	52	7	4	4
120 sec. in 0.01M	54	4	5	5
300 sec. in 0.01M	55	4	5	4
10 sec. in 0.1M	46	13	13	5
20 sec. in 0.1M	42	22	29	5
60 sec. in 0.1M	48	7	10	4
300 sec. in 0.1M	38	-	-	4
10 sec. in 1.0M	38	-	-	5
20 sec. in 1.0M	34	-	-	4
60 sec. in 1.0M	30	-	-	4
300 sec. in 1.0M	28	-	-	4
600 sec. in 1.0M	28	-	-	4
10 sec. in 10M	29	-	-	4

figure 8



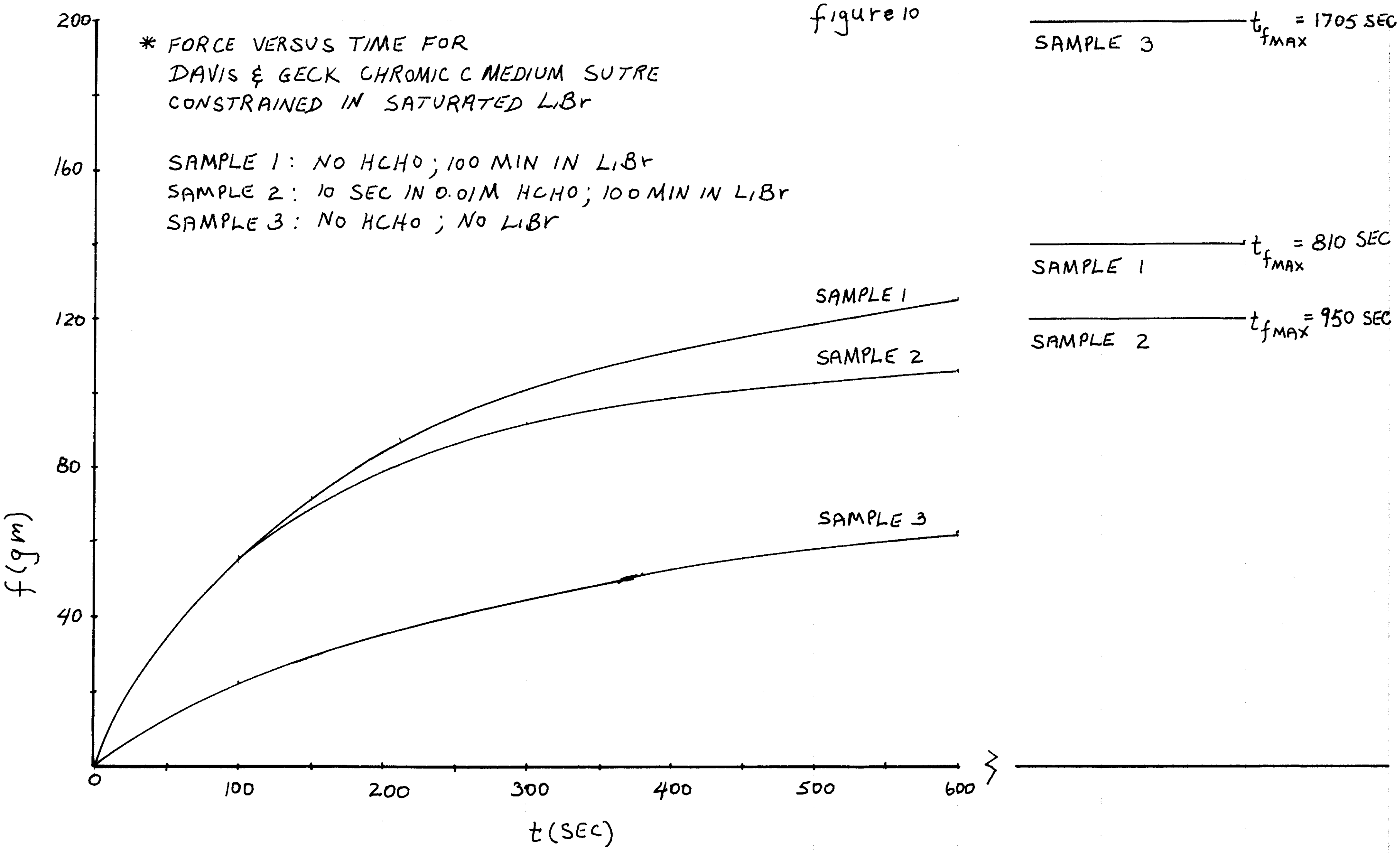
* COMPOSITE OF THREE RUNS
DEVIATION : ± 9 %

figure 9



* COMPOSITE OF THREE RUNS
DEVIATION: ± 10%

figure 10



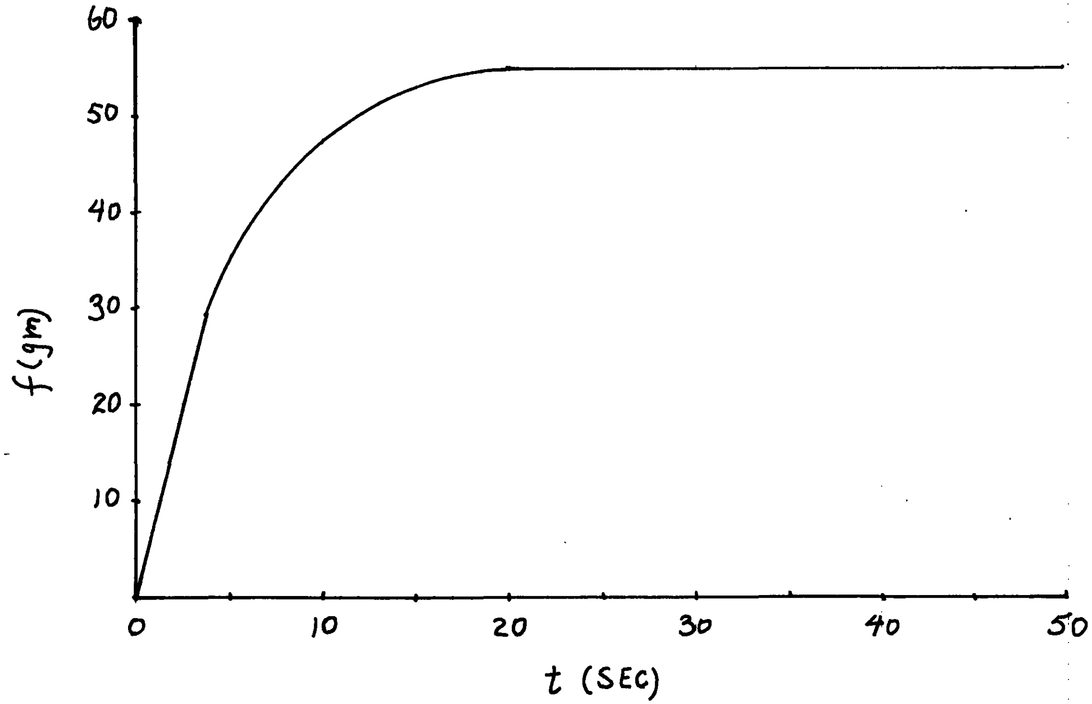
* FORCE VERSUS TIME FOR
DAVIS & GECK CHROMIC C MEDIUM SUTRE
CONSTRAINED IN SATURATED LiBr

SAMPLE 1 : NO HCHO ; 100 MIN IN LiBr
SAMPLE 2 : 10 SEC IN 0.01M HCHO ; 100 MIN IN LiBr
SAMPLE 3 : NO HCHO ; NO LiBr

* COMPOSITE OF THREE RUNS
DEVIATION : ±12 %

figure 11

* FORCE VERSUS TIME
FOR COLLAGEN TAPE
CONSTRAINED IN SATURATED LiBr
NO HCHO EXPOSURE ; "100 MIN IN LiBr" TREATMENT



* COMPOSITE OF THREE RUNS
DEVIATION: ± 3%

COLLAGEN ENGINE DESIGN ANALYSIS

Let $L \equiv$ the length of fiber immersed in the LiBr bath at any given time (feet)

$V \equiv$ the velocity of the fiber (feet/second)

$t_{40} \equiv$ time for constrained fiber in LiBr to develop 40 grams of force (seconds)

$C \equiv$ outer circumference of center pulley in the collagen engine $= 1$ foot.

The r.p.m. is measured in terms of this pulley's rotation.

Extended manipulations of the collagen engine operated with collagen tape led to an optimum r.p.m. of 20 at $L = 1.33$ feet.

<u>Assumptions</u>:

1. No hydrodynamic drag. It must be remembered, though, that this factor increases with an increasing L and V.
2. No slip between fiber and pulleys. Empirically this seems to be virtually true.

Since $C = 1.0$ feet

$$V = \frac{\text{r.p.m}}{60} \quad \text{ft./sec.}$$

for the optimal operation above,

$$V = 0.33 \text{ ft./sec.}$$

Thus each infinitesimal tape segment spends L/V seconds in the LiBr bath.

$$L/V = 1.33/.33 \text{ sec.}$$

$$= 4 \text{ seconds}$$

Our data indicates that in 4 seconds the tape develops a force of 40 grams. Thus the sutre too should develop 40 grams and t_{40} is the critical time constant with which we should be concerned.

Thus within appropriate limits set by our assumptions, the equation governing the engine r.p.m is:

$$V \cdot t_{40} = L$$

or

$$\frac{\text{r.p.m.}}{60} \cdot t_{40} = L$$

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LEGENDS

figure 3 ... t_{40} versus time in HCHO

figure 4 ... t_{40} versus time in LiBr, no HCHO

figure 5 ... τ versus time in HCHO

figure 6 ... f_{max} versus time in LiBr, no HCHO

figure 7 . . . f_{max} versus time in HCHO

figure 8 ... force versus time for Ethicon plain 000 sutre constrained in saturated LiBr

figure 9 ... force versus time for Ethicon chromic 000 sutre constrained in saturated LiBr

figure 10 ... force versus time for Davis & Geck chromic C medium sutre constrained in saturated LiBr

figure 11 ... force versus time for collagen tape constrained in saturated LiBr