IMPROVEMENT OF INTERLAMINAR SHEAR STRENGTH IN ORGANIC MATRIX COMPOSITES UTILIZING PLASMA DEPOSITED COUPLING AGENTS

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By:
A. P. DUHAMEL
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Covering the Period From:
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13. ABSTRACT

This final report on Contract N00017-70-C-4439 covers the time period April 1971 through April 1972. During this time the experimental work has been concerned primarily with cleaning and coupling agent experiments at 2450 MHz and 450 KHz utilizing Thornel 50 graphite fiber. Several thousand feet of Thornel 50 and Modmor II fiber were submitted to the Fiberite Corp., Winona, Minnesotat 55987, after being treated under optimum cleaning and coupling agent conditions at Commonwealth Scientific Corporation. The Fiberite Corporation will utilize the submitted fibers to prepare various specimens for further testing by the Navy. This report is, of course, concerned primarily with the experimental work performed at Commonwealth Scientific Corporation. An excellent cleaning technique has been developed for Thornel 50 fiber at 2450 MHz which has the advantage over other processes of increasing rather than decreasing the apparent tensile strength. The conditions found to be optimum for cleaning of the Thornel 50 are essentially as follows: N_2/O_2 ratio 10/90; power 100 watts, rate of traverse of fiber through the plasma 10 ft/min or greater; cleaning gas partial pressure of 250 u to 500 u. These general conditions were found to be ideal for cleaning Thornel 50 at 2450 MHz. At 450 KHz these conditions were found to be unsatisfactory and the 450 KHz plasma did not appear to be effective as a cleaning plasma. This lack of cleaning ability at 450 KHz is undoubtedly associated with the considerable energy difference between the 2450 MHz and the 450 KHz plasmas. Extensive coupling agent experiments were performed with ethanolamine and acetylene. To a lesser degree, based on the knowledge obtained from the ethanolamine and acetylene, experimental work on a new coupling agent, 2-phenethylamine, was also performed. Other compounds investigated to determine their ability to produce polymeric deposits were benzylamine, 1-Pentene, cyclohexane, and cyclohexylamine. All of these latter compounds readily gave deposits in the coupling agent reactor either at 2450 MHz or 450 KHz. The 2-Phenethylamine coupling agent was selected for limited experimental work based on the fact that the coupling agent work with ethanolamine and acetylene at 2450 MHz and 450 KHz indicated that unsaturation in the coupling agent molecule was of great assistance in the formation of polymeric deposits. In the limited time available, therefore, 2-phenethylamine was investigated utilizing optimum cleaning conditions previously established at 2450 MHz and a 450 KHz coupling agent plasma. The process rate was 10 ft/min. NOL rings were wound and evaluated. While the preliminary results were disappointing, it is felt that more experimental work should be performed in the area of introducing the coupling agent into the plasma. Considerable experimental difficulties were encountered in this latter area and ILSS data in this report should be interpreted accordingly. The data obtained for the deposition of polymeric materials from ethanolamine, cyclohexane, cyclohexylamine, 2-phenethylamine, benzylamine and 1-pentene at 450 KHz or 2450 MHz indicated that the amount of deposition of material was clearly a function of the degree of unsaturation of the molecule, i.e., ethanolamine was far less reactive than benzylamine. The data therefore supports the supposition previously suggested that compounds containing amino and hydroxy groups and unsaturation would produce the most useful coupling agents. Since the investigation of the new coupling agents of this type mentioned above was relatively limited due to the time factor involved, it is strongly recommended that more experimental work be performed in this area. In summary, an extremely efficient cleaning process for graphite fibers has been developed utilizing a 2450 MHz plasma. It also appears that unsaturated coupling agents can be utilized satisfactorily to deposit polymeric materials on the fibers using a 450 KHz plasma. Preliminary data obtained utilizing these two processes in series indicates that more experimental work is necessary to insure uniform deposition of polymeric materials on the fiber.

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FOREWORD

Naval Ordnance Systems Command; Contract N00017-70-C-4439 is a program designed to improve the interlaminar, flexure, compression and tensile strength of organic matrix fiber reinforced composites. This program is under the technical direction of Mr. Marlin A. Kinna, Electrical Systems and Materials Branch, Code ORD-0333A, Naval Ordnance Systems Command, Washington, D.C.

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ABSTRACT

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Extensive coupling agent experiments were performed with ethanolamine and acetylene. To a lesser degree, based on the knowledge obtained from the ethanolamine and acetylene, experimental work on a

new coupling agent, 2-Phenethylamine, was also performed. Other compounds investigated to determine their ability to produce polymeric deposits were benzylamine, 1-Pentene, cyclohexane, and cyclohexylamine. All of these latter compounds readily gave deposits in the coupling agent reactor either at 2450 MHz or 450 KHz. The 2-phenethylamine coupling agent was selected for limited experimental work based on the fact that the coupling agent work with ethanolamine and acetylene at 2450 MHz and 450 KHz indicated that unsaturation in the coupling agent molecule was of great assistance in the formation of polymeric deposits. In the limited time available, therefore, 2-phenethylamine was investigated utilizing optimum cleaning conditions previously established at 2450 MHz and a 450 KHz coupling agent plasma. The process rate was 10ft/min. NOL rings were wound and evaluated. While the preliminary results were disappointing, it is felt that more experimental work should be performed in the area of introducing the coupling agent into the plasma. Considerable experimental difficulties were encountered in this latter area and ILSS data in this report should be interpreted accordingly.

The data obtained for the deposition of polymeric materials from ethanolamine, cyclohexane, cyclohexylamine, 2-phenethylamine, benzylamine and 1-pentene at 450 KHz or 2450 MHz indicated that the amount of deposition of material was clearly a function of the degree of unsaturation of the molecule, i.e., ethanolamine was far less reactive than benzylamine. The data therefore supports the supposition previously suggested that compounds containing amino and hydroxyl groups and unsaturation would produce the most useful coupling agents. Since the investigation of the new coupling agents of this type mentioned above was relatively limited due to the time factor involved, it is strongly recommended that more experimental work be performed in this area.

In summary, an extremely efficient cleaning process for graphite fibers has been developed utilizing a 2450 MHz plasma. It also appears that unsaturated coupling agents can be utilized satisfactorily to deposit polymeric materials on the fibers using a 450 KHz plasma. Preliminary data obtained utilizing these two processes in series indicates that more experimental work is necessary to insure uniform deposition of polymeric materials on the fiber.

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1.0 INTRODUCTION

This report is the final report under Navy Contract No. N00017-70-C-4439 and presents the results of the work performed during the period April 1971 through April 1972.

During this program, the experimental work has been concerned primarily with the improvement of interlaminar shear strengths in organic matrix composites utilizing plasma deposited coupling agents. While previous phases of the program were concerned with glass reinforced composites, this phase of the program has been concerned with graphite fiber composites. The graphite fiber most thoroughly investigated during this period was Union Carbide's Thornel 50, although experimental work was also performed on Modmor I and II fibers.

The experimental program during this time was pursued as follows: (1) the investigation and development of the optimum cleaning techniques for the fibers at 2450 MHz and 450 KHz, (2) the investigation of acetylene and ethanolamine as coupling agents for the epoxy matrix at 2450 MHz and 450 KHz, (3) a brief investigation of unsaturated coupling agents, primarily 2-phenethylamine, utilizing the optimum 2450 MHz cleaning plasma conditions and the 450 KHz coupling plasma and (4) the submission of various lengths of fiber treated under the optimum conditions of (1) and (2) to the Fiberite Corporation, Winona, Minnesota 55987, for fabrication into various specimens for further Navy evaluation. The primary effort at Commonwealth Scientific was, of course, directed towards the investigation and development of suitable cleaning and coupling agent techniques utilizing 2450 MHz and 450 KHz plasmas. The variables studied were: (1) N_2/O_2 ratio; (2) power input; (3) traverse rate through the plasma and (4) N_2/O_2 pressure.

On the basis of extensive investigation with a 2450 MHz plasma, it was found that optimum cleaning conditions were as follows: (1) N_2/O_2

ratio: 10/90; power: 60 or 100 watts; (3) traverse rate: 10ft/min or greater, and (4) a N_2/O_2 pressure of approximately 250 to 500μ. It was found that the cleaning process at 2450 MHz was essentially independent of power under the conditions studied, however, the other three variables have a considerable effect on the process. At a N_2/O_2 ratio of 10/90 and pressures of 250μ to 500μ efficient cleaning was obtained. It appears that the mean free path of the reactive species in the plasma at a pressure of 1000μ is significantly reduced and therefore less efficient cleaning is obtained. One of the significant findings at 2450 MHz was that the traverse rates of the fiber through the plasma was a critical factor. At traverse rates of less than 5ft/min significant reductions in tensile strength were always observed. At traverse rates of 5ft/min to 10ft/min no appreciable degradation of the fiber was detected by strand tensile strength measurements. Indeed, the data indicates that even faster traverse rates through the plasma are desirable, however, time did not permit the investigation of faster traverse rates. In any future work in this area, traverse rates should be extensively investigated since fast traverse rates through the plasma would obviously be a prerequisite of any economically feasible cleaning process for graphite fibers.

The 450 KHz plasma was investigated as a cleaning technique under the same conditions as those investigated for the 2450 MHz plasma. Based on the experimental data obtained, it is clear that the 450 KHz plasma is not an efficient cleaning system. In fact, from the data on strand tensile strength it appears that the plasma is having no apparent effect on the fiber. This phenomenon is undoubtedly due to the fact that much lower energies are involved at 450 MHz. In addition, experimental evidence exists to indicate that electrodeless discharge plasma change significantly in nature at low frequencies, thereby

reducing the number of electrons available for reaction and consequently the number of excited species available for cleaning purposes. In addition, at frequencies below 2 MHz the excited molecules are no longer able to follow the electric field and their movement becomes diffusion controlled, i.e., the excited molecules have to diffuse to the fiber which is then the rate controlling process. It would appear then that the 450 KHz plasma would not be an efficient cleaning plasma under the conditions investigated during this phase of the program.

The second area of research which was extensively investigated during this program was the deposition of coupling agents on the graphite fiber to produce better bonding between the fiber and the epoxy matrix. The coupling agents investigated most extensively were ethanolamine and acetylene. A brief investigation of 2-phenethylamine was also performed utilizing the optimum 2450 MHz plasma cleaning technique and the 450 KHz plasma coupling agent reactor. This experimental work was based in large part on the results obtained from the ethanolamine and acetylene experiments. In addition to 2-phenethylamine, cyclohexane, cyclohexylamine, benzylamine and 1-pentene were also investigated to determine if polymeric deposits could be obtained from these compounds. In each case, polymeric deposits were obtained, both at 2450 MHz and 450 KHz. The latter compounds were not, however, used as active coupling agents in the experimental work. The experimental work with the compounds mentioned clearly shows, however, that what had been suggested previously was correct, i.e., unsaturation in the molecule is of considerable importance in the deposition of suitable polymeric materials. While the observations of the reactions with cyclohexane and benzylamine were only of a visual nature, it was obvious from the deposits formed and the rate of their deposition that benzylamine was much more reactive than cyclohexane both at 2450 MHz and 450 KHz.

All of the reactions conducted with the various coupling agents were performed as indicated under the experimental procedure section of this report. The apparatus used for this experimental work is shown schematically in Figure 1. For purposes of clarity, it should be understood that the ethanolamine and acetylene coupling agent work was performed utilizing two 2450 MHz reactors and two 450 KHz reactors. No experiments were performed with either acetylene or ethanolamine utilizing the optimum 2450 MHz cleaning plasma and the 450 KHz coupling agent plasma in series. The experiments utilizing the optimum 2450 MHz cleaning plasma and the 450 KHz coupling agent plasma in series were performed only with 2-phenethylamine.

At 2450 MHz the fiber was cleaned under the optimum conditions mentioned above and then passed through an ethanolamine or acetylene 2450 MHz plasma reactor. The data obtained from the ethanolamine work was somewhat difficult to interpret. In many cases it was very similar to data obtained for fiber which was cleaned but not reacted with ethanolamine. In fact, based on information obtained with acetylene (see below) it would appear that the ethanolamine does not react sufficiently in the plasma to produce species which can significantly react or deposit on the fiber.

With acetylene as the coupling agent, extensive reaction was observed in the 2450 MHz plasma. In fact the reaction was so extensive that heavy carbonaceous deposits were observed on the walls of both plasma reactors. Undoubtedly, such deposits were also formed on the fiber as it passed through the plasma. The strand tensile strength data and the NOL ring data reflect this fact in that as the pressure of acetyelen was increased from 250μ to 1000μ, the fiber showed a decrease in interlaminar shear strength and strand tensile strength. This observation would indicate that the thicker deposits produced from

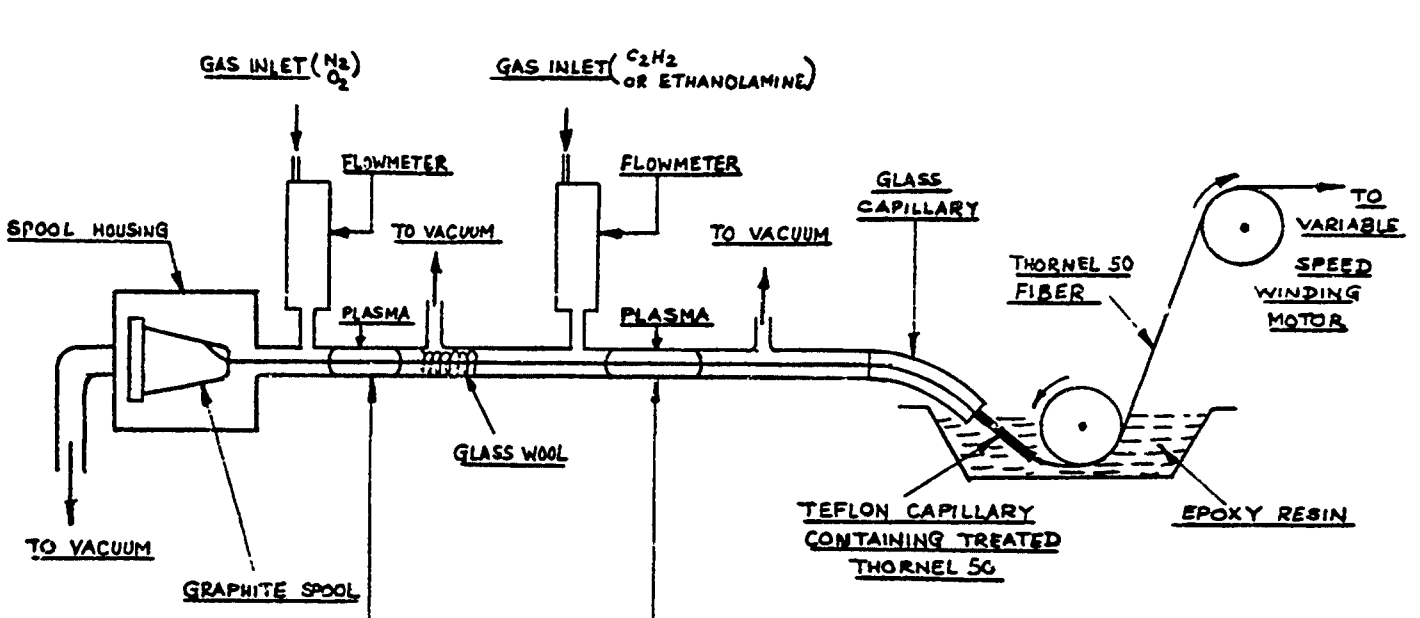

Figure 1 – Schematic Representation of Apparatus Used for 2450 MHz and 450 KHz Work

acetylene at higher partial pressures are not conducive to improving the interlaminar shear strength of graphite epoxy composites. This would be expected since the deposits formed undoubtedly do not contain functional groups which are reactive toward the epoxy matrix. From these experiments it was deduced that unsaturation in the coupling agent molecule leads to a high degree of reactivity. On the basis of these conclusions, it was therefore felt that unsaturated compounds containing amino and hydroxyl groups should be investigated. As indicated above, within the time limits available, a few compounds of this type were investigated with primary emphasis on 2-phenethylamine.

At 450 KHz, the plasma was cleaned under the optimum cleaning conditions found for the 2450 MHz plasma. While it was mentioned previously that the 450 KHz plasma was not an efficient cleaning technique, it was felt that for the sake of consistency the fiber should be passed through a 450 KHz "cleaning" plasma and then through a 450 KHz coupling agent plasma. Even with the low energies associated with the 450 KHz plasma, the acetylene was reactive and formed a polymeric deposit on the walls of the chamber which steadily carbonized on continued exposure. This observation leads to the conclusion that similar deposits were also found on the fiber. Interlaminar shear strengths of approximately 6200 psi were obtained with fibers treated in the 450 KHz plasma. The ethanolamine was not reactive in the 450 KHz plasma and this lack of reactivity is attributed to the stability of the molecule as well as the lack of unsaturation. Based on the data obtained during this phase of the program, the feasibility of utilizing the 450 KHz plasma for effectively cleaning graphite fibers is in considerable doubt. However, the use of highly reactive molecular species would make this low energy plasma practical for the application of coupling agents to previously cleaned fibers, and also for controlled polymerization reactions.

In summary of the experimental work performed at 2450 MHz during

this phase of the program it would appear that the 2450 MHz plasma is a very efficient cleaning process for Thornel 50 graphite fiber under the conditions specified previously. The 2450 MHz plasma also appears to be an efficient coupling agent plasma, however, careful selection of coupling agents must be made due to the high energies involved at this frequency.

In summary of the experimental work performed at 450 KHz during this phase of the program, it would appear that the 450 KHz plasma is not a particularly useful cleaning process for Thornel 50 graphite fiber under the conditions investigated. The 450 KHz plasma is however, very useful for the controlled polymerization of unsaturated compounds containing amino or hydroxyl groups.

In summary of the limited experimental work performed utilizing the optimum 2450 MHz cleaning plasma and the 450 KHz coupling agent plasma in series (with the coupling agent 2-phenethylamine) it is felt that further experimental work should be performed to optimize the overall process. In particular, experimental work should be directed toward determining the maximum rate of traverse of the fiber obtainable through the plasmas which would yield maximum cleaning and coupling agent efficiency. In the area of coupling agents, it has been established that unsaturated compounds containing hydroxyl and/or amino groups should be used. Experimentally, efforts should be directed toward obtaining uniform deposition of the polymeric materials on the fibers utilizing compounds such as those mentioned above.

2.0 EXPERIMENTAL PROCEDURE

The experimental procedure and apparatus used for the work performed under this phase of the program have been discussed in detail in References (1) and (2). These procedures will be presented again in this report for purposes of clarity.

2.1 Plasma Cleaning Experiments. The cleaning experiments at 2450 MHz and 450 KHz were performed with the apparatus shown schematically in Figure 1. This apparatus contains two plasma reactors, one for the cleaning process and one for the coupling agent process. During the investigation of the cleaning process the second plasma reactor was not utilized. The variables investigated for the cleaning process at both 2450 MHz and 450 KHz were as follows: (1) N_2/O_2 ratio; (2) N_2/O_2 cleaning gas pressure; (3) traverse rates through the plasma and (4) power. Specifically, N_2/O_2 cleaning gas pressures of 250μ, 500μ and 1000μ, traverse rates of 1ft/min, 5ft/min and 10ft/min, and power levels of 60 and 100 watts were investigated at 2450 MHz.

For the 450 KHz work the same variables were investigated except that the power levels were arbitrarily chosen as the minimum required to sustain a plasma and a power level which was twice that of the power required to maintain a plasma. These power levels were monitored as a function of plate and grid currents since no convenient method was available to monitor the power in terms of wattage for the energy source used. (The energy source for the 450 KHz plasma was a Scientific Electric Radio Frequency Generator Model S-18, 220 volts, 90 amps, 18 kw.)

After treatment in the plasma the fiber was impregnated with an epoxy (ERLA2256-ZZL-0820) and wound on NOL rings. Twenty foot lengths of the fiber were then removed from the ring and allowed to cure

at room temperature for three days. A minimum of ten strand tensile strength specimens were prepared from each fiber in the above manner and the apparent tensile strength was determined utilizing an Amtek tensile strength instrument. The data reported for strand tensile strength is therefore the average of the tests on ten individual specimens.

NOL rings were prepared in the same manner as described above and their interlaminar shear strengths were determined. The NOL rings were prepared utilizing the optimum cleaning conditions as determined by the strand tensile strength data. By utilizing the strand tensile strength data as a guide for the preparation of NOL rings considerable time and effort was made available for other experimental work. As mentioned previously the procedure outlined above for cleaning the Thornel 50 was followed for both the 450 KHz and the 2450 MHz work. The data obtained is presented in the appropriate section of this report.

2.2 Plasma Coupling Agent Experiments. The coupling agent experiments at 2450 MHz and 450 KHz were conducted with the apparatus shown schematically in Figure 1. In this case both reactors were utilized. The fiber was passed through the cleaning plasma under optimum conditions and then through the coupling agent plasma. Optimum cleaning conditions for the 2450 MHz plasma were found to be a N_2/O_2 ratio of 10/90, a cleaning gas pressure of 250μ, traverse rates of 10ft/min, and a power level of 100 watts. Unfortunately, the traverse rates of the fiber through the plasma had to be altered in order to perform the required coupling agent work. This has led to some difficulty in interpreting the results since it is known that slow traverse rates (1ft/min) through the plasma are detrimental to the fiber. However, with the apparatus currently available this effect could not be eliminated

without serious and time consuming modifications to the equipment. While the cleaning experiments at 450 KHz indicated that this plasma was not an effective cleaning process in order to obtain comparative data between the 2450 MHz and 450 KHz coupling agent work it was decided to utilize the same cleaning conditions as used in the 2450 MHz experiments. The coupling agents acetylene and ethanolamine were investigated at pressures of 250μ, 500μ and 1000μ and traverse rates of 1ft/min, 5ft/min and 10ft/min. The power levels used were the same as for the cleaning process. Utilizing the 450 KHz plasma, it must be noted that no data is reported at 1000μ partial pressure for acetylene. This is due to the fact that during two consecutive attempts to do this work, minor explosions were encountered in the system. Investigation failed to produce plausable causes for these explosions, and therefore the remainder of the work at this partial pressure of acetylene was discontinued.

As in the previous work after the fiber was passed through the cleaning and coupling agent plasma it was impregnated with epoxy resin (ERLA2256-ZZL-0820) and allowed to cure at room temperature for 3 days. Ten strand tensile strength specimens were prepared for each treated fiber. Again, strand tensile strength specimens were prepared and tested. The results given in the appropriate Tables are the average of ten strand tensile strength measurements on each fiber. Based on the optimum coupling agent conditions derived from the strand tensile strength data NOL rings were prepared and interlaminur shear strengths were determined. This data is given in the appropriate section of this report.

2.3 Rationale for and Detailed Test Procedures. Since there were to be well over two hundred experiments to be performed during this phase of the program it was felt that some easily monitored functions which could be related (directly or indirectly) to interlaminar shear strength should be utilized for testing purposes. It was felt,

obviously, that such a procedure would allow time to perform more significant experiments and this was found to be the case. The two testing procedures selected were: (1) the apparent tensile strength of the fiber and (2) the mode of fracture of the fiber after treatment.

The apparent tensile strength testing procedure described below was selected because it was felt that severe losses in apparent tensile strength would indicate that the fiber was being degraded, that no loss in apparent tensile strength would indicate that either the fiber was not being affected by the plasma, or that it was at least not being degraded, and increases in apparent tensile strength would be an indication that the surface of the fiber was being effectively prepared for bonding to the epoxy matrix.

The mode of fracture was selected as a test procedure because it was felt that by observing the fracture surface under the microscope and relating this information to the apparent tensile strength data, reasonable predictions could be made relative to the probability of achieving improved interlaminar shear strengths with a given set of process variables. For example, in Figure 2-A is a microphotograph at 80X of a specimen that had an above average apparent tensile strength with some fiber "pull-out." The amount of "pull-out" is considerably less than the as-received material and therefore the process would be a likely candidate for improved interlaminar shear strength, as proved to be the case. In Figure 2-B is another microphotograph, also at 80X, which shows a specimen that had an apparent tensile strength equal to the as-received material, but without fiber "pull-out." This specimen again was selected for ILSS testing and proved to be thirty percent stronger than the as-received material.

The tensile testing was performed utilizing twenty foot lengths of the treated fiber which had been vacuum impregnated with Union Carbide's ERLA2256/ZZL-0820 epoxy matrix and allowed to cure at room temperature under a one ounce tensile load for three days. The cured samples were then cut into three inch lengths, fitted and epoxied into cannula with an internal diameter of .018 to .021 inches and a length of 1 and 3/16 inches. These samples were then oven cured at 100°C for one hour, 150°C for one hour and 200°C for three hours. The specimens were then removed, allowed to cool, and then tested for apparent tensile strength in an Amtek Tensile Tester Model CTM.

On the basis of the apparent tensile strength data and the mode of fracture observations, various plasma processes were selected for the preparation of standard NOL rings for interlaminar shear strength testing. The organic matrix used was ERLA2256/ZZL-0820 and the rings were oven cured as above. The specimen rings were then allowed to cool, removed from the fixtures, and machined to the specifications set forth in the ASTM Designation: D2344-67. The interlaminar shear strength tests were performed by an independent laboratory.

3.0 DISCUSSION OF RESULTS

The results of the experimental work performed on this program during the current contract period are discussed under the categories of 2450 MHz and 450 KHz in order to insure clarity in the presentation of the data. The data presented in this final report is a summary of significant information obtained during the contract period. The reader is referred to References (1) and (2) for complete details of the experimental work.

3.1 2450 MHz Plasma Cleaning Experiments. In this section a discussion of the most significant data obtained on cleaning the Thornel 50 fiber at 2450 MHz is presented. The data is given in Tables 1 - 3. As in the previous reports the data has been plotted as (1) tensile data vs. power, (2) tensile data vs. process rate, (3) tensile data vs. precursor pressure (60 watts) and (4) tensile data vs. precursor pressure (100watts). In the discussion below reference is made to the appropriate Figures and Tables in the Data section of this report.

3.1.1 Tensile Data vs. Power. The data on apparent tensile strength vs. power for the cleaning process at 2450 MHz indicated wide scattering. Although the data is not plotted in this report due to the wide scatter, a general conclusion that can be realized from a study of this data is, at the power levels studied (60 and 100 watts), other factors appear to be controlling the cleaning process, i.e., the difference between 60 watts and 100 watts is not significant in the cleaning process. No further attempt was made to reproduce this data during the course of the program since it was felt that more important information could be obtained from other experimental work.

3.1.2 Tensile Data vs. Process Rate. Typical data obtained for the cleaning of Thornel 50 at 2450 MHz have been plotted in Figure 3 - 6. From the data shown in Figure 3 it can be easily seen that, at least in part, the tensile strength is a function of N_2/O_2 ratio and the process rate. As has been mentioned above the effects of power appear to be minimal as can be seen by the fact that the two curves lie in such close proximity and eventually produce the same tensile strength at a rate of 1ft/min.

Figures 4 and 5 are 70/30 N_2/O_2 and 30/70 N_2/O_2 respectively at a cleaning gas pressure of 500μ. Again it can be seen that the curves produced are essentially power independent but clearly traverse rate dependent as can be seen by the low strand tensile data obtained at 1ft/min.

Figure 6 presents tensile data vs. process rate for a N_2/O_2 ratio of 30/70 and a cleaning gas pressure of 1000μ. It would appear from this data that the nature of the reactions proceeding in the plasma at 1000μ is different from the reactions preceeding at 250μ or 500μ.

In summary of Figures 3 - 5 it should be concluded that at 250μ and 500μ there is little effect of power (60 and 100 watts) and that the cleaning process is definitely pressure dependent and rate dependent (traverse rate through plasma). At 1000μ (Figure 6) the reaction appears to be altered in characteristics, probably due to the higher number of molecules in the plasma and a consequent reduction in the mean free path of the active species.

3.1.3 Tensile Data vs. Cleaning Pressure (60 Watts). Figure 7 is a plot of tensile data vs. cleaning gas pressure at a N_2/O_2 ratio of 30/70 and traverse rates of 1ft/min, 5 ft/min and 10ft/min.

Figure 7 shows clearly the effect of gas pressure on the cleaning process and the figure also shows the effect of traverse rate of the fiber through the plasma. From Figure 7 it can be seen that at slow traverse rates (1ft/min) pressures as high as 500μ are detrimental to the tensile strength of the fiber, however, deleterious effects on the fiber do not appear except at pressures of 250μ at the faster traverse rate (5ft/min). It can be concluded from the data shown in Figure 7 that low cleaning gas pressures (250μ - 500μ) are the most efficient for the cleaning process.

The significant factor about the rate of 10ft/min is that the slope of the curve is essentially reversed from those shown at 1 & 5 ft/min. Since the only significant variable which was altered was the rate of traverse through the plasma, it must be assumed that at high rates of traverse (10ft/min) and low cleaning gas pressures effective cleaning is accomplished in a short period of time and that extended exposure tends to obviate the initial beneficial results.

In summary, it would appear from the data on tensile strength vs. cleaning gas pressure that the ultimate tensile strength of the cleaned fiber is definitely a function of rate of traverse of the fiber through the plasma and the pressure of the cleaning gas. It can be concluded that traverse rates greater than 10ft/min would be satisfactory and that cleaning gas pressures of the order of 250μ - 500μ are the most efficient.

The data on tensile strength vs. cleaning gas pressure at 100 watts are not plotted in this report. The data is, however, given in the data section of this report. In general the same comments apply to this data as to the data obtained at 60 watts. This would be expected since it has been shown previously that at the power levels studied no significant effect could be detected between 60 and 100 watts.

3.1.4 Tensile Data vs. Nitrogen-Oxygen Ratio. The data obtained with various N_2/O_2 cleaning gas ratios is shown in Figures 8-10. Figure 8 clearly indicates that at a cleaning gas pressure of 250μ and a

rate of traverse of 10ft/min, N_2/O_2 ratios of 10/90 are the most efficient cleaning gas composition. Figures 9 - 10 clearly indicate the effect of cleaning gas pressure and the cleaning process appears to be a linear function of N_2/O_2 ratio at 500μ. It would also appear that the cleaning process is relatively independent of traverse rate at 5ft/min and 10ft/min. No experimental data were obtained at traverse rates of 1ft/min. However, other data shown previously indicated that traverse rates of 1ft/min are detrimental to the fiber. As mentioned above, it is very interesting to note that as the cleaning gas pressure is increased from 250μ to 500μ the cleaning process efficiency becomes almost a linear function of the N_2/O_2 ratio. On the basis of this data it is clear that high oxygen concentrations are beneficial to the cleaning process and therefore in all further cleaning and coupling agent work on this program N_2/O_2 ratios of 10/90 were used.

The data in Table 11 gives the interlaminar shear strength results obtained for Thornel 50 fiber cleaned under optimum conditions. The conditions used for the preparation of the NOL rings are indicated in the Tables. It can be observed that thoroughly cleaning the Thornel 50 fiber increased its interlaminar shear strength approximately 20%. While this increase in interlaminar shear strength is not considered to be overwhelming improvement, it is significant that improvement in ILSS was observed in every specimen tested and this would tend to indicate that the Thornel 50 filament surface is rendered more active for bonding after the plasma cleaning process. The ILSS data obtained clearly indicates the need for the application of suitable coupling agents to bond the epoxy matrix to the graphite.

In summary of all the data obtained on the cleaning experiments at 2450 MHz it can be concluded that the cleaning process is definitely dependent upon cleaning gas pressure, N_2/O_2 ratio, and rate of traverse of the fiber through the plasma. It would appear on the basis of the data that cleaning gas pressures of the order of 250μ to 500μ N_2/O_2 ratios of 10/90 and traverse rates of 10ft/min or greater would be the optimum conditions for cleaning the fiber.

3.2 450 KHz Plasma Cleaning Experiments. The variables investigated in the cleaning process for 450 KHz were identical to those in the 2450 MHz plasma. The only significant difference was the energy source and the power levels utilized. The plasma source was a Scientific Electric Radio Frequency Generator (Model S-18, 220 volt, 90 amps, 18kw). The induction coil was approximately 2" I.D., 12" long with 12 turns. Due to the high electrical energies associated with these generators no simple method exists for measuring power input to the fiber as in the case of the 2450 MHz plasma generator. It was decided therefore to measure power as a function of plate current and two levels were arbitrarily selected. The first level of power input was just sufficient to maintain a plasma; the second level of power input was chosen as twice the first level. Using this technique reproducible experimental conditions could be established. As mentioned previously the variables studied, i.e., N_2/O_2 ratio, cleaning gas pressure and traverse rates through the plasma, were the same as for the 2450 MHz plasma. Data obtained at 450 KHz are given in Tables 4-6.

3.2.1 Tensile Data vs. Power. Some of the experimental data obtained on tensile strength vs. power are shown in Figures 11 - 13. It can readily be seen from this data that at the power levels studied no significant effect on tensile strength was observed. In this respect the data is similar to that obtained in the 2450 MHz work, i.e., under the power conditions utilized no significant effect on tensile strength was found.

3.2.2 Tensile Data vs. Process Rate. Typical curves for tensile strength vs. process rate are shown in Figures 14-16. As can be seen from these curves the tensile strength is clearly independent of traverse rate and power. In general the data obtained on tensile strength vs. process rates at 450 KHz indicates that at the process rates studied no significant

effect was observed. In this respect the data is in sharp contrast to that obtained at 2450 MHz where tensile strength was found to be strongly dependent upon process rate.

3.2.3 Tensile Data vs. Cleaning Gas Pressure (0.16 and 0.30 amps). Typical tensile strength vs. cleaning gas pressure are shown in Figure 17. In general all of the experimental data obtained in this area of the investigation indicated that at the pressures investigated no effect on tensile strength was observed. Again, in this respect the data is in sharp contrast to that obtained at 2450 MHz where tensile strength was found to be strongly dependent upon the cleaning gas pressure.

3.2.4 Tensile Strength vs. Cleaning Gas Ratio. Typical curves obtained for tensile strength vs. cleaning gas ratio are shown in Figure 18. Again, a careful review of all the data indicates that no significant change occurs in tensile strength as a function of the N_2/O_2 ratio. Again, these results are in sharp contrast to those obtained at 2450 MHz where the tensile strength was found to be a strong function of the N_2/O_2 ratio.

In summary, all of the data obtained at 450 KHz indicates that the tensile strength of the fiber is not effected by plasma cleaning at this frequency. The reason for the ineffectiveness of the 450 KHz cleaning plasma is not specifically known, however, it is known that the characteristics of plasmas change significantly at approximately 2 MHz. These changes in the characteristics of the plasma are believed to be caused primarily by two effects: (1) the nature of the collisions of electrons with neutral molecules is altered and (2) positive ions produced by electron collision are no longer able to follow the electrical field. The first effect is caused by the fact that at frequencies below 2 MHz many of the electron-molecule collisions become in-elastic as compared to a high degree of elastic collisions at frequencies above 2 MHz. These inelastic

effect was observed. In this respect the data is in sharp contrast to that obtained at 2450 MHz where tensile strength was found to be strongly dependent upon process rate.

3.2.3 Tensile Data vs. Cleaning Gas Pressure (0.16 and 0.30 amps). Typical tensile strength vs. cleaning gas pressure are shown in Figure 17. In general all of the experimental data obtained in this area of the investigation indicated that at the pressures investigated no effect on tensile strength was observed. Again, in this respect the data is in sharp contrast to that obtained at 2450 MHz where tensile strength was found to be strongly dependent upon the cleaning gas pressure.

3.2.4 Tensile Strength vs. Cleaning Gas Ratio. Typical curves obtained for tensile strength vs. cleaning gas ratio are shown in Figure 18. Again, a careful review of all the data indicates that no significant change occurs in tensile strength as a function of the N_2/O_2 ratio. Again, these results are in sharp contrast to those obtained at 2450 MHz where the tensile strength was found to be a strong function of the N_2/O_2 ratio.

In summary, all of the data obtained at 450 KHz indicates that the tensile strength of the fiber is not effected by plasma cleaning at this frequency. The reason for the ineffectiveness of the 450 KHz cleaning plasma is not specifically known, however, it is known that the characteristics of plasmas change significantly at approximately 2 MHz. These changes in the characteristics of the plasma are believed to be caused primarily by two effects: (1) the nature of the collisions of electrons with neutral molecules is altered and (2) positive ions produced by electron collision are no longer able to follow the electrical field. The first effect is caused by the fact that at frequencies below 2 MHz many of the electron-molecule collisions become in-elastic as compared to a high degree of elastic collisions at frequencies above 2 MHz. These inelastic

collisions of electrons with neutral molecules effectively removes electrons from the electrical field and as a consequence the effective concentration of reactive oxidizing species is drastically reduced. The second effect essentially reduces the concentration of reactive species which can reach the fiber for cleaning purposes since the movement of the excited species to the fiber by diffusion is a relatively slow process when compared to the movement of the excited species in an electric field.

Other factors are also undoubtedly of importance in explaining the ineffectiveness of the 450 KHz plasma for cleaning Thornel 50 fiber, however, it is felt that the effects mentioned briefly above are the primary ones associated with changes in the plasma at frequencies at and below 2 MHz.

3.3 2450 MHz Plasma Coupling Agent Experiments. The coupling agent experiments utilizing ethanolamine and acetylene were performed as described under Section 2.2. The optimum cleaning conditions indicated were used. The coupling agents were investigated at pressures of 250μ, 500μ and 1000μ, and traverse rates of 1ft/min, 5ft/min and 10ft/min. The power levels used were the same as for the cleaning process. As in previous reports the data have been plotted as (1) tensile data vs. power, (2) tensile data vs. process rate, (3) tensile data vs. coupling agent pressure (100 watts).

3.3.1 Tensile Data vs. Power. The data obtained for tensile strength vs. power are shown in Figures 19 - 21 and 22 - 24 for ethanolamine and acetylene, respectively. Comparison of data in Figures 19 and 20 for ethanolamine shows that at a traverse rate of 1ft/min the fiber is significantly affected by power input. It is significant that at traverse rates of 5ft/min and 10ft/min the effects of power input become

almost identical, i.e., the data indicate that the effect of the power levels studied become independent of traverse rate. The data in Figure 21 for ethanolamine again reveals the anomalies previously reported for high concentrations of precursor materials at 1000μ.[1]

The data shown in Figures 22-24 with acetylene as the coupling agent are considerably different from those shown in Figures 19-21 for ethanolamine. The effects of power input appear to be completely independent of traverse rate for pressures of 250μ and 500μ and for all practical purposes at 1000μ. It would appear that the acetylene coupling agent has no significant effect on the tensile strength of the fiber. This phenomena will be seen to have occured throughout much of the experimental work with acetylene. It should be noted that in the case of acetylene some difficulty was encountered in preventing the acetylene from "back diffusing" into the plasma cleaning reactor. Heavy black deposits of carbonaceous materials were formed in both plasma reactors when acetylene was used as the coupling agent. This back diffusion phenomena was not observed in the ethanolamine experiments except at high pressures (1000μ) and in no case did the ethanolamine coupling agent leave a visible deposit in the reactors.

3.3.2 Tensile Data vs. Process Rate. The data for tensile strength vs. process rate for ethanolamine and acetylene are shown in Figures 25-27 and Figures 28-30. As anticipated from the tensile strength vs. power data, a significant effect on the tensile strength of the fibers is observed at traverse rates of 1ft/min for ethanolamine. At traverse rates of 5ft/min and 10ft/min and a pressure of 250μ and 500μ the tensile strength of the fibers is nearly identical for ethanolamine. At pressures of 1000μ for ethanolamine the data indicates that the tensile strength of the fiber appears to be a linear function of the traverse rate. Again, it should be noted from the data in Figures 25-27 that the effect of the

two power levels studied on the tensile strength of the fibers is almost identical. In general, from the ethanolamine data it should be observed that traverse rates slower than 5ft/min should be avoided. The data for ethanolamine at 1000μ and a traverse rate of 10ft/min indicate that there is no apparent effect on the tensile strength of the fiber. No attempts have been made to date to study faster traverse rates. It should be noted, however, that at traverse rates of 1ft/min the fiber is in the plasma five times longer than at 5ft/min and ten times longer than at 10ft/min, whereas in the case of the 5ft/min and 10ft/min traverse rates the fiber is in the plasma for only twice the time and therefore the effect of the plasma, as a function of time could be almost identical for traverse rates of 5ft/min and 10ft/min. More experimental work on the effect of traverse rates would undoubtedly be useful in clarifying this area of interest.

From the data presented in Figure 28 - 30 for acetylene it can be seen that the traverse rate has no apparent effect on the tensile strength of the fiber. Again, the effects of power input appear to give identical results for tensile strength and again the results are similar to those observed for tensile strength vs. power for acetylene. It is interesting to note that tensile strength is independent of traverse rate, especially at 1ft/min. This phenomena has never been observed before in the 2450 MHz work. The only explanation that can be presented at this time for this phenomena is perhaps the fact that the acetylene is back diffusing into the cleaning plasma reactor and absorbing significant quantities of the energy available. This suggestion is substantiated to some degree by the fact that both plasmas reactors became coated with heavy deposits of carbonaceous materials during the course of the experiments. This observation would certainly indicate that the acetylene is producing excited species in the plasma, however, the excited species and reaction mechanisms involved are beyond the scope of the present work. Such structures would be of interest, however, in furthering the understanding of the reactions which are actually occurring in electrodeless discharge plasmas.

Again it should be mentioned that no carbonaceous deposits are observed when ethanolamine is used as the coupling agent - in fact no visible deposits of any type are observed with ethanolamine as the coupling agent.

3.3.3 Tensile Data vs. Coupling Agent Partial Pressure (60 watts and 100 watts). The tensile strength vs. coupling agent pressure for ethanolamine and acetylene are presented at 60 watts in Figures 31 and 32 respectively. The tensile strength data at 100 watts is not reproduced in this report since it is not significantly different from the data at 60 watts. The data for ethanolamine again appears to be clearly traverse rate dependent. The data shown in all the Figures for ethanolamine clearly indicated that the effects of the treatment on tensile strength of the fiber are greatest at pressures of 250μ. As expected, this effect is most pronounced at a traverse rate of 1ft/min. At traverse rates of 5ft/min the effects on tensile strength tend to become almost linear and in fact at traverse rates of 10ft/min for tensile strength the observed effects are linear. The linearity observed at 10ft/min for tensile strength vs. coupling agent pressure is interesting because it tends to indicate that the effective concentration of reactive species is a direct function of the coupling agent pressure. The data in Figure 31 shows quite clearly that at pressures of 250μ the tensile strength of the fiber is more clearly effected than at pressures of 1000μ. This data tends to again indicate the effect of the traverse rate since it is obvious that ethanolamine is reacting more strongly at 250μ than at 1000μ for a constant traverse rate (10ft/min). It might be concluded that the reaction of ethanolamine at 1000μ is less efficient at 10ft/min, however, it should also be noted that the reaction of ethanolamine at 1000μ has not reduced the tensile strength of the fiber. Higher traverse rates (i.e., shorter residence time in the plasma) might actually improve the tensile strength of the fiber. This phenomena was observed repeatedly in the data previously reported for the cleaning process experiments. While all the data taken to date clearly indicate (both)

in the plasma cleaning and the ethanolamine coupling work) that precursor pressures of 250μ yield the most effective reaction, the data indicates that this reaction is also a strong function of traverse rate (i.e., residence time in the plasma). The data in Figure 31 for ethanolamine shows rather dramatically the effect of low traverse rates on the tensile strength of the fiber, while the data for a traverse rate of 5ft/min clearly shows results which are intermediate between those obtained at 1ft/min and 10ft/min and as mentioned previously are more nearly approaching linearity. If the interpretation of the data is correct then suitable adjustment of traverse rate and coupling agent pressures should yield fibers with improved tensile strengths. These observations are quite significant for the 2450 MHz work since they indicate that much higher traverse rates than previously thought desirable may be possible while still maintaining efficient cleaning and coupling reactions. This situation would be important for a production process since cleaning and coupling agent processes of from 1 to 10ft/min are not particularly feasible on a mass production scale.

As mentioned previously the data for tensile strength vs. coupling agent pressure for acetylene at 60 watts is presented in Figure 32. (The data for 100 watts is not reproduced in this report since it is essentially identical to the 60 watts data). The data indicates that the reaction of acetylene is not particularly sensitive to process rate, however, the reaction does appear to be sensitive to acetylene pressure. All of the data indicates, regardless of process rate, that the tensile strength of the fiber is decreasing as the acetylene pressures is increasing. The data suggests that as acetylene pressure is increased thicker polymeric deposits are being formed on the fiber. If this hypothesis is true, the deposition of such polymeric materials from acetylene in relatively thick coatings is not conducive to improving the effective transfer strength of the fiber. This conclusion has been substantiated previously by others, namely P. Erickson of NOL and W. Zissman of NRL. It should be mentioned that the comments here relate only to polymeric materials deposited from acetylene and the conclusions should not be extrapolated to other coupling agents. In fact

from the data it may be concluded that coupling agents containing amino and hydroxyl groups and a center of unsaturation might yield very satisfactory deposits for bonding to the epoxy matrix. As mentioned previously, the deposits observed on the walls of the plasma reactors tend to be carbonaceous in appearance and undoubtedly are mixtures of carbon and high molecular weight polymeric materials. It is interesting to note from the data that the concentration of deposited undesirable materials is for all practical purposes a direct function of the acetylene pressure with little or no effect shown as a function of traverse rate. Therefore, if acetylene can be utilized as an effective coupling agent, pressures in the order of 250μ will have to be employed, since at these pressures the tensile strength was neither increased nor decreased.

3.4 450 KHz Plasma Coupling Agent Experiments. The coupling agent experiments were performed as described in Section 2.2. The optimum cleaning conditions for the 450 KHz plasma were selected as being identical to the optimum cleaning conditions at 2450 MHz. These cleaning conditions were arbitrarily chosen for the 450 KHz experiments since previous work has shown that the 450 KHz frequency does not yield a particularly efficient cleaning plasma. The coupling agents were investigated at partial pressures of 250μ, 500μ and 1000μ except for the acetylene which had a tendency to cause small explosions at partial pressures of 1000μ. Traverse rates studied were 1ft/min, 5ft/min and 10ft/min, and the power levels used were the same as for the cleaning process. As in the past, the data has been plotted as (1) Tensile data vs. power, (2) Tensile data vs. process rate, and (3) Tensile data vs. coupling agent partial pressure. The complete data is presented in Tables 9 and 10.

3.4.1 Tensile Data vs. Power. The data obtained for Tensile Strength vs. Power are shown in Figures 33 - 35 and 40 - 41 for ethanolamine and acetylene, respectively. A comparison of the data

in Figures 33 and 34 shows that at a traverse rate of 1ft/min, the fiber is affected by power, showing a slight increase. It is significant that at traverse rates of 5ft/min and 10ft/min the effects of power input becomes almost identical, which suggests that the effect of the power levels studied becomes independent of traverse rate. It is also significant that at the higher power level, the apparent tensile strength decreases, indicating that the fiber is being degraded.

The data shown in Figures 40 and 41 with acetylene as the coupling agent are similar to those shown for ethanolamine. In this set of data it is shown that increasing the power has the same detrimental effect on tensile strengths as with ethanolamine, but the effect is more pronounced. It should be noted that, as in the experiments with 2450 MHz and acetylene, back diffusion of the acetylene into the cleaning chamber was occurring. Polymeric deposits were formed on the walls of both chambers. The original thin films were translucent and upon continued exposure became thicker and darker and appeared to be carbonizing. In the 450 KHz apparatus, this process occurred more slowly than in the 2450 MHz apparatus, again testifying to the lower energies in the 450 KHz plasma. The back diffusion rate into the cleaning plasma was of course increased with increased partial pressures of acetylene, and the deposition rate therefore was also increased.

3.4.2 Tensile Data vs. Process Rate. The data for Tensile Strength vs. Process Rate for ethanolamine and acetylene are shown in Figures 36 - 38 and 42 - 43. As expected from tensile strength vs. power data, a significant effect on the tensile strength of the fiber is observed at rates of 1ft/min for ethanolamine. From Figures 36 - 38 it can be seen that effect of the two power levels studied

is very similar, since all curves retain the same basic pattern. In general, from the ethanolamine data, it should be observed that traverse rates slower than 5ft/min should be avoided and the upward trend of the curves at 10ft/min suggest that much faster rates could be utilized with more success. No attempt has been made to study faster traverse rates. More experimental work on the effect of traverse rates would undoubtedly be useful in clarifying this area of interest.

From the data presented in Figures 42 and 43 for acetylene, it can be seen that the traverse rate has little effect on the tensile strengths of the fibers at the lower power level. At the higher level however, the tensile strength drops off at low pressures and high traverse speeds, indicating insufficient exposure to the reactive species. Again, the back diffusion of the acetylene into the cleaning chamber may have an interfering effect. The excited species and reaction mechanism involved are beyond the scope of the present work. Such structures would be of interest, however, in furthering the understanding of the reactions which are actually occurring in electrodeless discharge plasmas.

3.4.3 Tensile Data vs. Coupling Agent Partial Pressure. The tensile strength vs. coupling agent pressure for ethanolamine and acetylene are presented at power level I (.21 amps Plate Current) in Figures 39 and 44 respectively. The tensile strength data at power level II (.33 amps Plate Current) is not reproduced in this report since it is not significantly different from the data at power level I. The data for ethanolamine appears to be clearly traverse rate dependent. The data shown in all the figures for ethanolamine clearly indicates that the effects of the treatment on the tensile strength of the fiber are greatest at pressures of 250μ. As expected, this affect is most pronounced at a traverse rate of 1ft/min. This data, coupled with the previously cited data on the ethanolamine work clearly shows that no increases over the

base line data were achieved with ethanolamine. However, at higher traverse rates, it did not degrade the tensile properties of the fiber. This leads to the theory that ethanolamine is basically ineffective as a coupling agent due to its lack of unsaturation and its inherent stability at the energies associated with the 450 KHz plasma.

The data for acetylene in Figure 44 indicates that there is a definite rate-pressure interrelation. All of the data indicates, regardless of process rate that the tensile strength of the fiber is decreasing as the acetylene pressure is increasing. The data suggests that as acetylene pressure is increased, thicker polymeric deposits are being formed on the fiber. If this hypothesis is valid, the deposition of such polymeric material from acetylene in relatively thick coatings is not conducive to improving the effective transfer strength of the fiber, as previously substantiated by P. Erickson of NOL and W. Zissman of NRL.

A few comments about the interpretation of the data relating to the acetylene and ethanolamine coupling agent experiments should be made at this point. All of the tensile strength data has been interpreted as if it were derived strictly from the reaction of the fiber with the coupling agent in the plasma reactor. This of course, is not strictly accurate since the fibers were cleaned in a plasma reactor prior to being introduced into the coupling agent reactor. Plasma cleaning of the fiber obviously has an effect on the apparent tensile strength, i.e., plasma cleaning of the fiber can reduce or increase the apparent tensile strength. While the conditions chosen to clean the fibers were optimum from a N_2/O_2 ratio (10/90) and pressure (250μ) point of view to yield maximum tensile strength, they were not optimum from a traverse rate point of view since this rate was variable during the experiments.

Since traverse rates effect the tensile strength observed for the fibers, it is obvious that at low traverse rates the cleaning plasma effected the tensile strength of the fibers adversely. The tensile data obtained, therefore,

is a combination of the effects of both the cleaning plasma and the coupling agent plasma. It is especially interesting to note that the tensile data obtained with ethanolamine as the coupling agent has many similarities to the tensile data obtained for the cleaned fiber whereas with acetylene as the coupling agent, the data appears to indicate no effect from the cleaning plasma, even at traverse rates of 1ft/min where the cleaning plasma has been shown to be most detrimental to the fiber. A complete explanation of this phenomena is not known, but it is suggested that acetylene diffusing into the cleaning plasma absorbs a considerable portion of the available energy. In any case, the experimental evidence indicates that acetylene is far more reactive in the plasma than ethanolamine, It is assumed that this high degree of reactivity in the plasma is associated with the high degree of unsaturation in acetylene. From this information, it can be logically deduced that coupling agents containing amino and hydroxyl groups and a relatively high degree of unsaturation could well produce polymeric materials with a degree of compatability for both the graphite fiber and the epoxy matrix. An example of such a coupling agent would be $H_2N-CH_2-CH=CH-CH_2OH$. A few experiments with compounds of this type as the coupling agent are described below.

3.5 Coupling Agent Experiments Utilizing Optimum 2450 MHz Cleaning Plasma and 450 KHz Coupling Agent Plasma and a 10ft/min Process Rate. The experimental work was performed with the apparatus shown in Figure 1. The fiber was cleaned with the 2450 MHz plasma under optimum conditions and the coupling agent 2-phenethylamine was used in the 450 KHz plasma. Two NOL rings were wound at 10ft/min using ERLA2256/ZZL-0820 epoxy marrix. The procedure has been discussed in Section 2.0, but is repeated here for purposes of clarity.

The interlaminar shear strengths obtained from two rings prepared at pressures of 250μ and 500μ of 2-phenethylamine are given in Table 14A-14B. While the data indicate no significant improvement in ILSS for fiber treated by this process, it is felt the results obtained were largely due to the experimental technique utilized, i.e., considerable difficulty was encountered in introducing the 2-phenethylamine into the plasma reactor. It is felt that this difficulty yielded uneven distribution of polymeric deposit on the fiber, therefore, yielding low interlaminar shear strengths. It is clear that more experimental work should be performed to develop suitable techniques for depositing thin uniform coatings of reactive polymeric materials on the fibers. Experimental difficulties were also found in maintaining the 450 KHz plasma with 2-phenethylamine when the 2450 MHz cleaning was being performed and the fiber was passing through the reactor. Prior experiments with pure 2-phenethylamine without the cleaning plasma and without the graphite fiber indicated that this coupling agent readily reacted in the 450 KHz plasma to yield a polymeric deposit. The complete explanation for this phenomenon is not understood, however, it is felt that the 2-phenethylamine may be condensing on the fiber, as it passes through the coupling agent reactor and thereby quenching the plasma. It was observed during the course of the experiments that the 2-phenethylamine appeared to be condensing on the glass walls of the reactor prior to entering the induction coil. Since the plasmas must be generated in the vapor phase condensation of the coupling agent on the fiber would cause great difficulty in initiating and maintaining the plasma. It is clear from the above discussion that more experimental work would be required to develop the required techniques to introduce the coupling agent into the 450 KHz plasma and prevent condensation. It would be extremely beneficial to further investigate process rates to establish optimum conditions

for treating the fibers. In effect, then the results obtained for ILSS utilizing 2-phenethylamine as a coupling agent at 450 KHz and optimum cleaning conditions at 2450 MHz are not considered to be negative. Instead, the results clearly indicate the need for further experimental work which should be aggressively pursued since it is felt that the overall process has considerable merit for eventual development into a commercial process for treating graphite fibers.

3.6 Plasma Reactions at 2450 MHz and 450 KHz Utilizing 2-Phenyethylamine, Benzylamine, Ethanolamine, Cycloxhexane, Cyclohexylamine and 1-Pentene. In a brief effort to determine if the compounds mentioned above would yield polymeric deposits, each material was introduced into the coupling agent reactor and subjected to a 2450 MHz or 450 KHz plasma. The results observed for each compound are discussed below.

Ethanolamine

This compound was reasonably reactive in the 2450 MHz plasma when introduced directly into the reactor at a pressure of approximately 500μ. A light tan deposit was formed on the walls of the reactor. The pressure in the reactor increased significantly when the ethanolamine was subjected to the 2450 MHz plasma indicating considerable decomposition of the material. At 450 KHz, the ethanolamine was considerably less reactive but still did yield a thin yellow deposit on the walls of the reactor.

Phenethylamine

This compound rapidly produced a deposit on the walls of the reactor when subjected to a 2450 MHz plasma. The plasma was originally blue in color and eventually changed to an orange-yellow color and the intensity of the color appeared to increase as the amount of deposit increased. It was noted that when the plasma generator

was placed in a region where little deposit had formed, that the plasma immediately became blue again. The first deposit observed was white in color which slowly turned brown as the quantity of deposit increased. The exit portion of the reactor slowly turned light brown indicating that the reaction was still proceeding downstream from the actual plasma source. This phenomenon would tend to indicate that the reactive species has a relatively long lifetime and therefore is relatively stable. The pressure in the reactor remained essentially constant indicating no great degree of dissociation of the 2-phenethylamine. At 450 KHz, a deposit was also readily obtained, but the deposit appeared to be clearer than that obtained at 2450 MHz. Again the compound appeared to be less reactive at 450 KHz than at 2450 MHz.

Benzylamine

At 2450 MHz, this material gave an immediate heavy deposit of polymeric material. The amount of deposit appeared to be dependent only on time of exposure. The results obtained were essentially similar to those obtained for 2-phenethylamine except that the reactivity appeared to be higher. Again at 450 KHz, no difficulty was encountered in depositing a relatively thick coating of material on the reactor walls. The pressure in the reactor remained essentially constant at 500μ indicating little dissociation of the benzylamine.

Cyclohexane

At 2450 MHz, the original pressure in the reactor (30μ) increased slowly to approximately 1000μ. The plasma was light blue in color and remained so throughout the experiment, although the intensity of the plasma tended to increase as material was deposited on the glass reactor walls. The first deposited material was white in color, tinged with yellow and after an initial deposition of coating, new material appeared

to deposit at a much faster rate. The deposit tended to be clear in color and rather crystalline in nature. The cyclohexane appeared to be much less reactive than 2-phenethylamine or benzylamine in the plasma. Again at 450 KHz, the cyclohexane yielded a slightly tan colored deposit and the reaction was much less intense than at 2450 MHz.

Cyclohexylamine

The comments concerning cyclohexane are in general applicable to this compound. Cyclohexylamine appeared to be slightly more reactive than cyclohexane.

1-Pentene

This compound was tested only briefly at 2450 MHz. An initial light tan deposit was obtained and the material did not appear to be more reactive than cyclohexane.

The results of the above work indicate very clearly that polymeric deposits can be easily obtained with either a 450 KHz or 2450 MHz plasma under the proper conditions. As anticipated from previous experimental work, unsaturation greatly enhances the capability of a given compound to form polymeric deposits, i.e., the reactivity of benzylamine in either plasma is much greater than cyclohexane.

3.7 2450 MHz and 450 KHz NOL Ring Evaluation. As mentioned in Section 2.3, on the basis of apparent tensile strength, as well as the mode of failure, the Thornel 50 fiber was treated, impregnated and wound onto a mandrel. The ring was then cured and machined to the specifications set out in the ASTM Designation D 2344-67 entitled "Standard Method of Test for Apparent Horizontal Shear Strength of Reinforced Plastics by Short Beam Method." At least three segments

and in many cases more than five segments were tested for apparent interlaminar shear strengths. The testing was performed by an independent laboratory. Some of the rings prepared, however, did not have sufficient strength to withstand machining. In particular, this included most of the rings wound under the 450 KHz plasma cleaning process. The average test results from those rings which were satisfactory are given in Tables 11 through 13.

3.7.1 NOL Rings Wound Under Optimum Cleaning Conditions at 2450 MHz. NOL rings prepared under optimum cleaning conditions showed definite increases in interlaminar shear strength in all cases indicating definite improvement in structure properties and that the surface of the fiber has been improved for bonding with the epoxy resin matrix. Results of approximately 5400 psi interlaminar shear strength were achieved as compared to 4500 psi for the as-received material. These data are reported in Table II.

3.7.2 NOL Rings Wound Under Optimum Cleaning Conditions at 450 KHz. Since all of the strand tensile tests indicated that the 450 KHz plasma was not an effective cleaning process, little was expected from the NOL rings. Three NOL rings were wound utilizing differen parameters, but the effect of the 450 KHz plasma on the fiber was so detrimental that the rings splintered when attempts were made to machine them to the size described in ASTM D 2344-67. Splintering and cracking occurred to such an extent that attempts to test the section for interlaminar shear strength proved fruitless.

3.7.3 NOL Rings Wound Under Optimum Cleaning and Coupling Agent Conditions at 2450 MHz. The data for NOL rings wound under optimum cleaning conditions and utilizing ethanolamine or acetylene as a coupling agent is given in Tables 12 and 13. The data given

in Table 12 indicates that the interlaminar shear strength of the composite fiber has not been significantly improved by treatment with ethanolamine at pressures of 500 μ and 1000 μ. The ILSS in fact, was reduced from the "standard" NOL ring sample at 500 μ, while at 1000 μ of ethanolamine the values were essentially the same. As mentioned previously in this report, many similarities between the ethanolamine coupling agent work and the cleaning work previously reported were noted in the experimental work. At the present time, it is not certain that the ethanolamine is reacting in the plasma to form an excited species. The ILSS value obtained for ethanolamine at 1000 μ is very close to the value previously obtained for the fiber which had been cleaned, but not treated with coupling agent. The low values obtained at 500 μ, which correspond to ILSS values for normal as-received materials, cannot be satisfactorily explained at this time.

The NOL ring data as shown in Table 13 indicates that the interlaminar shear strength of the composite has not been significantly improved by treatment with acetylene at pressures of 500 μ and 1000 μ. The data in this case, however, is consistent with the data obtained from strand tensile strength data. As mentioned previously, the quantity of carbonaceous material deposited on the fiber appears to be a function of the acetylene pressure. This phenomena was reflected in the strand tensile strength data. But, in the NOL ILSS data, an increase in strength is observed as a function of the acetylene pressure.

It should be noted that one of the NOL "Standard" ring prepared for comparative purposes was prepared from Thornel 50 fiber coated with a special epoxy compatible resin furnished to Commonwealth Scientific Corporation in error by the Union Carbide Corporation. It would be expected therefore,

that the "standard" ILSS sample would have a higher interlaminar shear strength than normally observed (approximately 4500 psi) for Thornel 50 coated with polyvinyl alcohol. It is felt, therefore, that the data on ILSS for ethanolamine and acetylene should be viewed more realistically using a value of 4500 psi as the interlaminar shear strength of the "standard" sample and therefore, this value is used for comparison purposes in the totals. Even utilizing a value of 4500 psi, no significant improvement can be seen in the interlaminar shear strength. It does not appear, therefore, that the ILSS is significantly improved using acetylene or ethanolamine as coupling agents.

3.7.4 NOL Rings Wound Under Optimum Cleaning and Coupling Agent Condition at 450 KHz

The data for NOL rings wound under optimum cleaning conditions and utilizing ethanolamine or acetylene as a coupling agent is given in Tables 12 and 13. The data given in Table 12 indicates that at 1000 μ partial pressure of ethanolamine effects of the 450 KHz plasma was detrimental to the adhesion characteristics at the fiber surface. Rings were wound at 250 μ and 500 μ partial pressures of ethanolamine, but once again, the 450 KHz plasma proved so detrimental to the fiber surface that the rings cracked and splintered during machining to size. This premature delamination made it impossible to test the sec tion. The results again were similar to the data on the fiber when it was cleaned only. This again reinforces the belief that ethanolamine is too stable a molecule to be used in reactions of this nature.

The NOL ring data as shown in Table 13 for acetylene in the 450

KHz plasma indicates that the interlaminar shear strength of the composite has been significantly improved. This result is somewhat surprising, as all previous work with the 450 KHz plasma had shown it to be ineffective in increasing either the tensile strength or the interlaminar shear strength. The results with acetylene at a partial pressure of 500 μ showed an average increase of 40% in interlaminar strength over the value of the untreated Thornel 50 fiber. This result reinforces the belief, as stated in the conclusion, that investigation of the possibility of using the 2450 MHz plasma as the cleaning step, and 450 KHz plasma as the coupling agent should be pursued.

3.7.5 NOL Rings Wound Under Optimum 2450 MHz Cleaning Plasma and 450 KHz Coupling Agent Plasma Using 2-Phenethylamine

The data for NOL rings wound under optimum 2450 MHz cleaning conditions using 2-phenethylamine as the coupling agent in the 450 KHz plasma are given in Table 14. The data in Table 14 indicates that no significant improvement in interlaminar shear strength was obtained at partial pressures of 250 μ and 500 μ of 2-phenethylamine using the 2450 MHz cleaning process and 450 KHz coupling agent process. Experimental difficulties associated with this process have been discussed in considerable detail in Section 3.5 and will not be repeated at this point. Suffice it to say that if the experimental work suggested in Section 3.5 were to be performed, it is felt that a highly successful commercial process could be developed for the treatment of graphite fibers.

4.0 CONCLUSIONS

As in the previous sections of this report the conclusions reached from the experimental data are presented under the categories of 2450 MHz and 450 KHz.

4.1 2450 MHz

The principal conclusions reached during this phase of the program are as follows:

(1) The cleaning process is definitely a function of the precursor pressure, i.e., lower precursor pressures tend to produce more efficient cleaning (250 μ and 500 μ).

(2) The cleaning process appears to be independent of the power used in this experimental work (60 and 100 watts).

(3) The cleaning process is definitely a function of the N_2/O_2 ratio (70/30, 30/70 and 10/90).

(4) The cleaning process is definitely a function of the traverse rate through the plasma, i.e., slow traverse rates are detrimental to the fiber.

(5) At precursor pressures of approximately 1000 μ, the mechanism of the plasma reaction appears to change. This is probably due to the shortening of the mean free path of the active species at the relatively high pressures.

(6) With the coupling agent ethanolamine the tensile strength of the fiber is a critical function of the traverse rate of the fiber through the plasma.

(7) With the coupling agent ethanolamine, the tensile strength of the fiber is a function of ethanolamine pressure and the

cleaning plasma conditions.

(8) With the coupling agent ethanolamine, the tensile strength of the fiber is independent of the power used within the power levels studied.

(9) With the coupling agent acetylene, the tensile strength of the fiber appears to be independent of the traverse rate of the fiber through the plasma.

(10) With the coupling agent acetylene, the tensile strength of the fiber appears to be dependent upon precursor pressure.

(11) With the coupling agent acetylene, the tensile strength of the fiber appears to be independent of the plasma cleaning conditions.

(12) With the coupling agent acetylene, the tensile strength of the fiber is independent of the power used within the power levels studied.

(13) In general, the work with acetylene as the coupling agent indicated that this material had little or no effect on the tensile strength of the fiber under all the various conditions investigated. With ethanolamine as the coupling agent strong effects were observed particularly with respect to traverse rates, all other conditions being equal. In addition, with ethanolamine the tensile strengths observed were definitely a function of both the cleaning plasma conditions and the coupling agent plasma conditions.

(14) On the basis of all the experimental work performed to date at 2450 MHz it is clear that the traverse rate of the fiber through the plasma is a critical factor.

(15) NOL rings prepared under optimum cleaning conditions show definite increases in interlaminar shear strength in all cases indicating improvement in structural properties and that the surface of the fiber has been improved for bonding with the epoxy resin matrix.

(16) NOL rings prepared under optimum cleaning conditions and treated with ethanolamine or acetylene showed the following:

(a) NOL rings wound with ethanolamine as the coupling agent indicated a decrease in interlaminar shear strength at 500 μ, and practically identical values for ILSS at 1000 μ when compared to the "standard" prepared from "as-received" material.

(b) NOL rings wound with acetylene as the coupling agent indicated an increase in ILSS for both the 500 μ and 250 μ pressures when compared to the standard sample prepared from as-received material.

4.2 450 KHz

The principal conclusions reached in this area are as follows:

(1) Under all conditions investigated, i.e., power input, precursor pressure, N_2/O_2 ratio, and traverse rate no significant improvement in the tensile strength or in the breaking mode of the fiber were observed. It is therefore concluded that under the conditions investigated for cleaning Thornel 50 the 450 KHz plasma is not effective.

(2) With the coupling agent ethanolamine, there were no improvements in the tensile strength or the ILSS of the fibers.

(3) With the coupling agent acetylene, it was found that irregardless of the parameters selected, there was little or no effect on the tensile properties of the fiber.

(4) With the coupling agent acetylene, it was found that it could significantly improve the ILSS without detracting from the fiber tensile strength.

(5) For ILSS improvement with acetylene, it was found that traverse rates are critical - faster rates being preferred.

(6) With acetylene, the precursor partial pressure was also found to be critical, with 500 μ being optimum for the traverse rates studied.

(7) With acetylene, it was also found that the tensile breaking mode of the fiber was improved (See Figure 2B) with very little fiber "pull-out."

4.3 Combined 2450 MHz and 450 KHz Process Using 2-Phenethylamine as the Coupling Agent

On the basis of the data obtained from the NOL rings which were prepared using the optimum cleaning process at 2450 MHz and 450 KHz coupling agent process it is felt that the combined process has potential merit even though significant improvements in ILSS were not obtained. A detailed discussion of this point is presented in Section 3.5.

4.4 Summary of Conclusions

An efficient cleaning process has been developed for Thornel 50 graphite fiber utilizing a 2450 MHz plasma. The variables investigated were: (1) N_2/O_2 ratio; (2) N_2/O_2 gas cleaning pressure; (3) power and (4) traverse time through the plasma. The optimum cleaning conditions were found to be: (1) N_2/O_2 ratio = 10/90; (2) N_2/O_2 gas pressure = 250 μ to

500 μ; (3) power not significant at 60 or 100 watts and (4) traverse rates greater than 10 ft/min.

The experiments at 2450 MHz with the coupling agents ethanolamine and acetylene indicated that ethanolamine was not particularly reactive at this frequency whereas acetylene was extremely reactive. From this data it was concluded that coupling agents with a high degree of unsaturation and containing amino and hydroxyl groups would lead to polymeric materials which would be more compatible with the epoxy matrix.

The experimental work conducted at 450 KHz with the coupling agents indicated that ethanolamine also was not reactive at this frequency, however, the acetylene definitely reacted even at the low energies associated with this frequency. This observation is significant since it would permit the high energy (2450 MHz) cleaning of the fiber and a low energy (450 KHz) controlled polymerization of reactive coupling agents. Such a process could be made into a practical production technique.

The experimental work conducted with 2-Phenethylamine as the coupling agent utilizing optimum cleaning conditions at 2450 MHz and a 450 KHz coupling agent plasma indicated that the combined process probably could be made successful with more development effort. The experimental work conducted with compounds of the type $H_2N\text{-}R_1\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}R_2\text{-}OH$ all indicated that they yielded polymeric materials both at 2450 MHz and 450 KHz indicating that compounds of this general type should definitely prove useful as candidate coupling agents.

The above comments are intended, of course, to present only a brief encapsulation of the conclusions reached on the basis of the experimental work performed on this program. Considerably more detailed conclusions are presented in Section 4.0.

5.0 TABLES & FIGURES

The following Section of this report presents the data obtained during this program in the form of Tables and Figures. Conditions under which the experiments were performed are given in the Tables and on the Figures. The horizontal bars shown on all the Figures represents the "as-received" apparent tensile strength of the fiber. This data is given as a footnote to each Table.

TABLE I

Apparent Tensile Strength of 2450 MHz Plasma treated Thornel 50 at a 70/30 Ratio of N_2/O_2; 60 and 100 watts, traverse rates of 1 ft/min and 10 ft/min; and precursor pressures of 250 μ, 500 μ and 1000 μ.

Precursor Pressures (μ)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs)
250	1	60	21.9
250	1	100	12.9
250	5	60	16.5
250	5	100	22.8
250	10	60	22.8
250	10	100	22.6
500	1	60	19.2
500	1	100	18.2
500	5	60	21.0
500	5	100	20.2
500	10	60	20.0
500	10	100	19.8
1000	1	60	20.7
1000	1	100	21.9
1000	5	60	14.2
1000	5	100	18.0
1000	10	60	17.8
1000	10	100	23.0

*Average breaking load of "as-received" material = 20.0 lbs.

TABLE 2

Apparent Tensile Strength of 2450 MHz Plasma Treated Thornel 50 at a 30/70 Ratio of N_2/O_2; 60 and 100 Watts; traverse rates of 1 ft/min, 5 ft/min and 10 ft/min; and precursor pressures of 250 μ, 500 μ and 1000 μ

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs)
250	1	60	17.0
250	1	100	15.5
250	5	60	18.5
250	5	100	21.5
250	10	60	22.0
250	10	100	21.8
500	1	60	18.3
500	1	100	18.3
500	5	60	21.5
500	5	100	22.5
500	10	60	---
500	10	100	25.1
1000	1	60	24.1
1000	1	100	10.9
1000	5	60	13.9
1000	5	100	16.2
1000	10	60	17.6
1000	10	100	17.0

*Base line is 20 lbs. average breaking load of as-received material = 20.0 lbs.

TABLE 3

Apparent Tensile Strength of 2450 MHz Plasma Treated Thornel 50 at a 10/90 Ratio of N_2/C_2; 60 and 100 watts; traverse rates of 5 ft/min; and precursor pressures of 250 μ and 500 μ.

Precursor Pressure (μ)	Traverse Rates (ft/min)	Power (watts)	Breaking Load* (lbs)
250	5	60	23.7
250	5	100	23.6
250	10	60	23.6
250	10	100	24.9
500	5	60	22.5
500	5	100	21.1
500	10	60	22.5
500	10	100	21.3

*Average Breaking Load of as-received material = 20.0 lbs.

TABLE 4

Apparent Tensile Strength of 450 KHz Plasma Treated Thornel 50 at a 70/30 ratio of N_2/O_2; traverse rates of 1 ft/min; 5 ft/min, and 10 ft/min; precursor pressures of 250 μ, 500 μ and 1000 μ. Power levels indicated as Plate Current (0.16 or 0.30 amps).

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs)
250	1	0.16	19.6
250	1	0.30	20.1
250	5	0.16	21.7
250	5	0.30	21.1
250	10	0.16	20.2
250	10	0.30	20.6
500	1	0.16	20.5
500	1	0.30	20.3
500	5	0.16	21.4
500	5	0.30	19.2
500	10	0.16	20.6
500	10	0.30	20.4
1000	1	0.16	19.9
1000	1	0.30	20.1
1000	5	0.16	20.1
1000	5	0.30	21.1
1000	10	0.16	21.1
1000	10	0.30	19.8

*Average Breaking Load of as-received material = 21.5 lbs.

TABLE 5

Apparent Tensile Strength of 450 KHz Plasma Treated Thornel 50 at a 30/70 ratio of N_2/O_2; traverse rates of 1 ft/min, 5 ft/min, and 10 ft/min; precursor pressures of 250 μ, 500 μ and 1000 μ Power levels indicated as Grid Current (o.16 or 0.30 amps).

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs)
250	1	0.16	20.2
250	1	0.30	19.2
250	5	0.16	19.6
250	5	0.30	18.8
250	10	0.16	20.9
250	10	0.30	16.2
500	1	0.16	19.5
500	1	0.30	18.1
500	5	0.16	19.1
500	5	0.30	19.5
500	10	0.16	19.3
500	10	0.30	19.3
1000	1	0.16	19.6
1000	1	0.30	20,0
1000	5	0.16	19.6
1000	5	0.30	19.3
1000	10	0.16	19.6
1000	10	0.30	19.2

*Average Breaking Load of as-received material = 21.5.

TABLE 6

Apparent Tensile Strength of 450 KHz Plasma Treated Thornel 50 at a 10/90 ratio of N_2/O_2; traverse rates of 1ft/min, 5ft/min, and 10ft/min; precursor pressures of 250 μ, 500 μ and 1000 μ. Power levels indicated as Grid Current (0.16 or 0.30 amps).

Precursor Pressure (u)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs.)
250	1	0.16	20.5
250	1	0.30	20.4
250	5	0.16	20.4
250	5	0.30	20.9
250	10	0.16	20.3
250	10	0.30	19.8
500	1	0.16	20.4
500	1	0.30	20.8
500	5	0.16	21.0
500	5	0.30	21.8
500	10	0.16	21.5
500	10	0.30	19.9
1000	1	0.16	20.0
1000	1	0.30	18.6
1000	5	0.16	19.4
1000	5	0.30	19.9
1000	10	0.16	19.8
1000	10	0.30	20.1

*Average Breaking Load of as-received material = 21.5 lbs.

TABLE 7

Apparent Tensile Strength of 2450 MHz Thornel 50 Fiber Treated with Ethanolamine at pressures of 250 μ, 500 μ and 1000 μ, traverse rates of 1ft/min, 5ft/min, and 10ft/min, power levels of 60 and 100 watts (Fiber cleaned at N_2/O_2 rate of 10/90 and a pressure of 250 μ

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs)
250	1	60	11.0
250	1	100	14.7
250	5	60	17.5
250	5	100	18.6
250	10	60	18.9
250	10	100	19.2
500	1	60	15.8
500	1	100	16.1
500	5	60	18.8
500	5	100	18.8
500	10	60	19.9
500	10	100	19.0
1000	1	60	13.1
1000	1	100	15.0
1000	5	60	17.4
1000	5	100	17.3
1000	10	60	21.3
1000	10	100	20.6

*Average breaking load of as-received material = 21.5 lbs.

TABLE 8

Apparent Tensile Strength of 2450 MHz Thornel 50 Treated with Acetylene at pressures of 250 μ, 500 μ and 1000 μ traverse rates of 1ft/min, 5ft/min, and 10ft/min; power levels of 60 and 100 watts (Fiber cleaned at N_2/O_2 ratio of 10/90 and pressure of 250 μ.

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Power (watts)	Breaking Load* (lbs)
250	1	60	20.8
250	1	100	20.9
250	5	60	20.5
250	5	100	21.1
250	10	60	21.3
250	10	100	20.8
500	1	60	21.0
500	1	100	20.3
500	5	60	19.4
500	5	100	21.1
500	10	60	20.5
500	10	100	21.2
1000	1	60	19.7
1000	1	100	19.1
1000	5	60	17.6
1000	5	100	18.3
1000	10	60	20.4
1000	10	100	19.2

*Average value of ten strand tensile strength specimens.
Average breaking load of as-received material = 21.5 lbs.

TABLE 9

Apparent Tensile Strength of 450 KHz Thornel 50 treated with ethanolamine at pressures of 250 μ, 500 μ and 1000 μ; traverse rates of 1ft/min, 5ft/min, and 10ft/min; power levels of 0.16 and 0.30 amps. (Fibers cleaned at N_2/O_2 ratio of 10/90 and pressure of 250 u).

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Fower (amps)	Breaking Load* (lbs)
250	1	.21	18.2
250	5	.21	19.0
250	10	.21	19.0
250	1	.48	17.3
250	5	.48	19.1
250	10	.50	19.6
500	1	.21	18.3
500	5	.22	19.5
500	10	.21	19.8
500	1	.50	18.4
500	5	.49	17.8
500	10	.48	18.5
1000	1	.22	17.9
1000	5	.21	19.7
1000	10	.22	19.9
1000	1	.49	18.9
1000	5	.50	19.3
1000	10	.51	19.0

*Average breaking load of as-received material = 20.0 lbs.

TABLE 10

Apparent Tensile Strength of 450 KHz Thornel 50 treated with acetylene at pressures of 250 μ, 500 μ and 1000 μ traverse rates of 1ft/min, 5ft/min, and 10ft/min; power levels of 0.16 and 0.30 amps. (Fibers cleaned at N_2/O_2 ratio of 10/90 and pressure of 250 μ).

Precursor Pressure (μ)	Rate of Traverse (ft/min)	Power (amps)	Breaking Load* (lbs)
250	1	.21	18.8
250	5	.21	20.3
250	10	.21	20.5
250	1	.33	18.6
250	5	.34	20.2
250	10	.33	18.6
500	1	.21	20.7
500	5	.21	20.6
500	10	.21	19.9
500	1	.33	19.5
500	5	.33	20.1
500	10	.33	19.0

*Average breaking load of as-received material = 20.0 lbs.

TABLE 11

Conditions for Winding NOL Rings Using optimum 2450 MHz Plasma Cleaning Procedure (NOL Rings were prepared in a matrix of Union Carbide ERLA/2256 ZZL-0820).

Ring #	N_2/O_2 Ratio	Pressure (μ)	Power (watts)	Traverse Rate (ft/min)
*1	Vacuum	10^{-3}	0	10
2	10/90	250	60	5
3	30/70	500	100	10
4	70/30	500	100	10

TABLE 11-A

Interlaminar Shear Strengths Obtained from NOL Rings wound under Condition Described in Table 11, and in accordance with ASTM D2344-67.

	Apparent Interlaminar Shear Strength (psi)	
Ring #	Average	Highest
*1	4523	4615
2	5445	5830
3	5232	5376
4	4639	4792

*Ring 1 was prepared from as-received, PVA coated fiber.

TABLE 12

Condition for Winding NOL Ring using Ethanolamine as Coupling Agent. (Cleaning Condition: N_2/O_2 Ratio of 10/90 at Pressure of 250 μ). (Matrix: Union Carbide ERLA-2256/ZZL-0820).

Ring #	Frequency	Precursor Partial Pressure (μ)	Power	Traverse Rate (ft/min)
1*	None	Standard	None	10
2	2450 MHz	1000	100 watts	10
3	2450 MHz	500	100 watts	10
4	450 KHz	1000	.21 amps	10

TABLE 12-A

Interlaminar Shear Strengths Obtained from NOL Ring wound under Conditions Described in Table 12 and in accordance with ASTM D2344-67.

	Apparent Interlaminar Shear Strength (psi)	
Ring #	Average	Highest
1*	4523	4615
2	5530	5610
3	4705	4825
4	4310	4450

*Ring 1 was prepared from as-received, PVA coated fiber.

TABLE 13

Condition for Winding NOL Rings Using Acetylene as Coupling Agent. (Cleaning Condition: N_2/O_2 ratio of 10/90 at Pressure of 250 μ. (Matrix: Union Carbide ERLA-2256/ZZL-0820).

Ring #	Frequency	Precursor Partial Pressure	Power	Traverse Rate (ft/min)
1 *	None	Standard	None	10
2	2450 MHz	1000μ	100 watts	10
3	2450 MHz	500 μ	100 watts	10
4	450 KHz	250 μ	.21 amps	10
5	450 KHz	500 μ	.21 amps	10

TABLE 13-A

Interlaminar Shear Strengths Obtained from NOL Rings wound under conditions described in Table 13 and in accordance with ASTM D 2344-67.

	Apparent Interlaminar Shear Strength (psi)	
Ring #	Average	Highest
1*	4523	4615
2	4825	5200
3	5259	5616
4	4935	4950
5	6287	6490

*Ring 1 was prepared from as-received, PVA coated fiber.

TABLE 14

Conditions for Winding NOL Rings Using 2-Phenethylamine as the Coupling Agent, a 2450 MHz Cleaning Plasma and a 450 KHz Coupling Agent Plasma. (Traverse Rate of Fiber Constant at 10ft/min). Matrix ERLA2256/0820.

Ring #	Cleaning Frequency	N_2/O_2 Ratio	N_2/O_2 Pressure (μ)	Power
1	None	None	None	None
2	2450 MHz	10/90	250	100
3	2450 MHz	10/90	250	100

Ring #	Coupling Frequency	Precursor Partial Pressure (μ)	Power (Plate Current)
2	450 KHz	250	0.5 amps
3	450 KHz	500	0.5 amps

TABLE 14-A

Interlaminar Shear Strengths Obtained from NOL Rings Wound under conditions described in Table 14 and in accordance with ASTM-D-2344-67.

Ring #	Apparent Interlaminar Shear Strength (psi)	
	Average	Highest
1	4523	4615
2	4813	5050
3	4544	4725

Ring 1 was prepared from "as-received" PVA coated fiber.

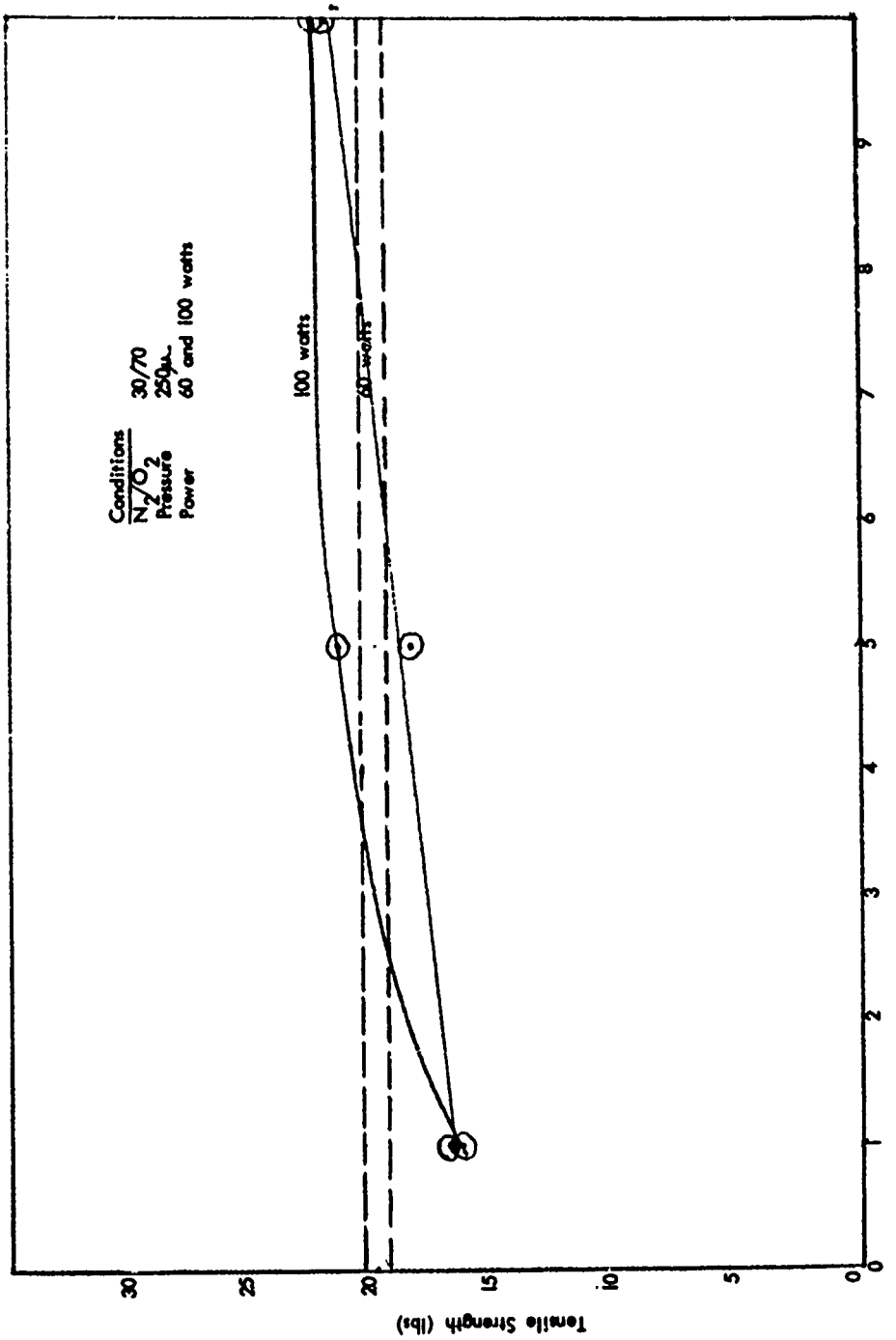

Fig. 3 - Tensile Strength vs Process Rate (ft/min)

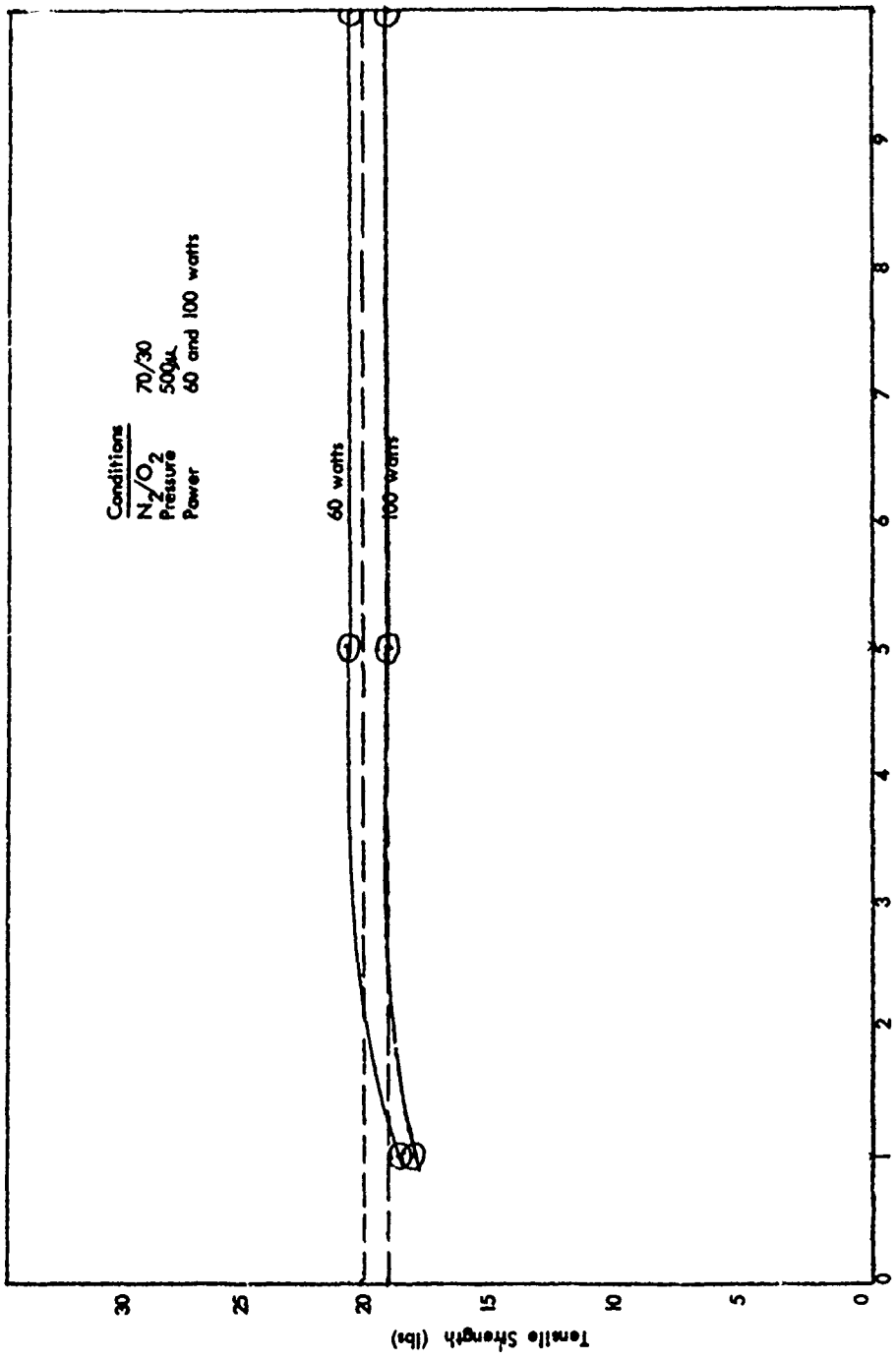

Fig. 4 - Tensile Strength vs Process Rate (ft/min)

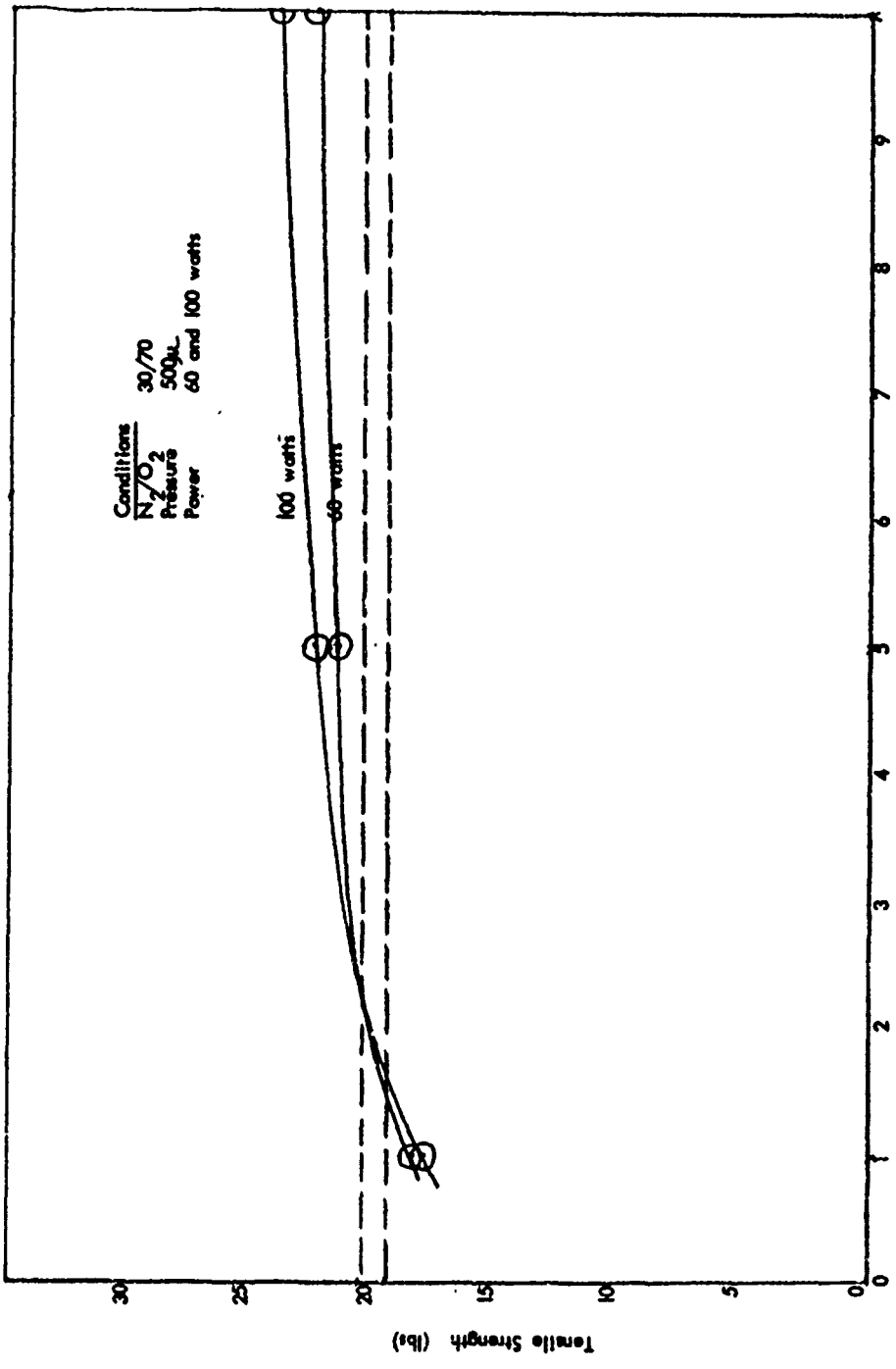

Fig. 5 - Tensile Strength vs Process Rate (ft/min)

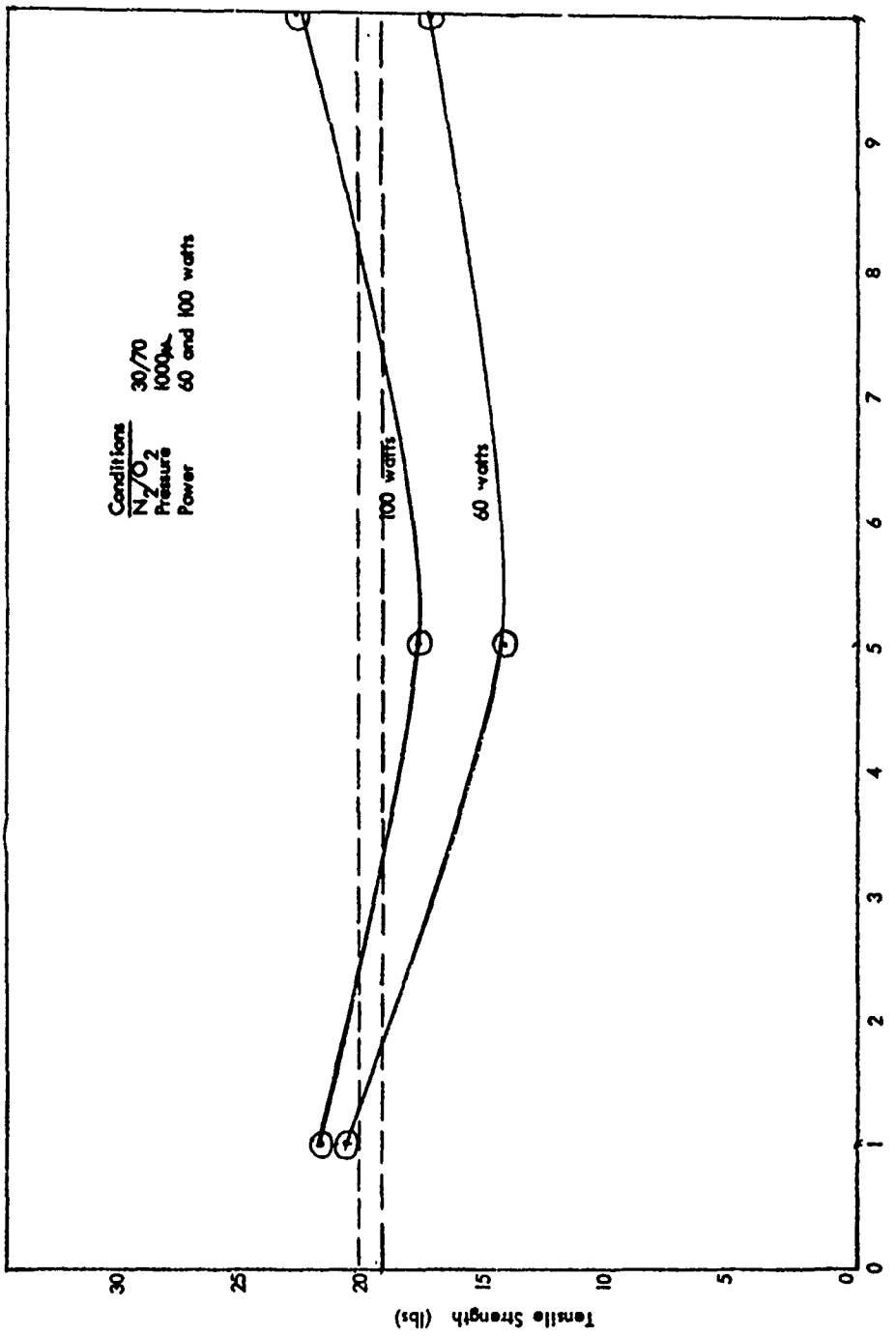

Fig. 6 - Tensile Strength vs Process Rate (ft/min)

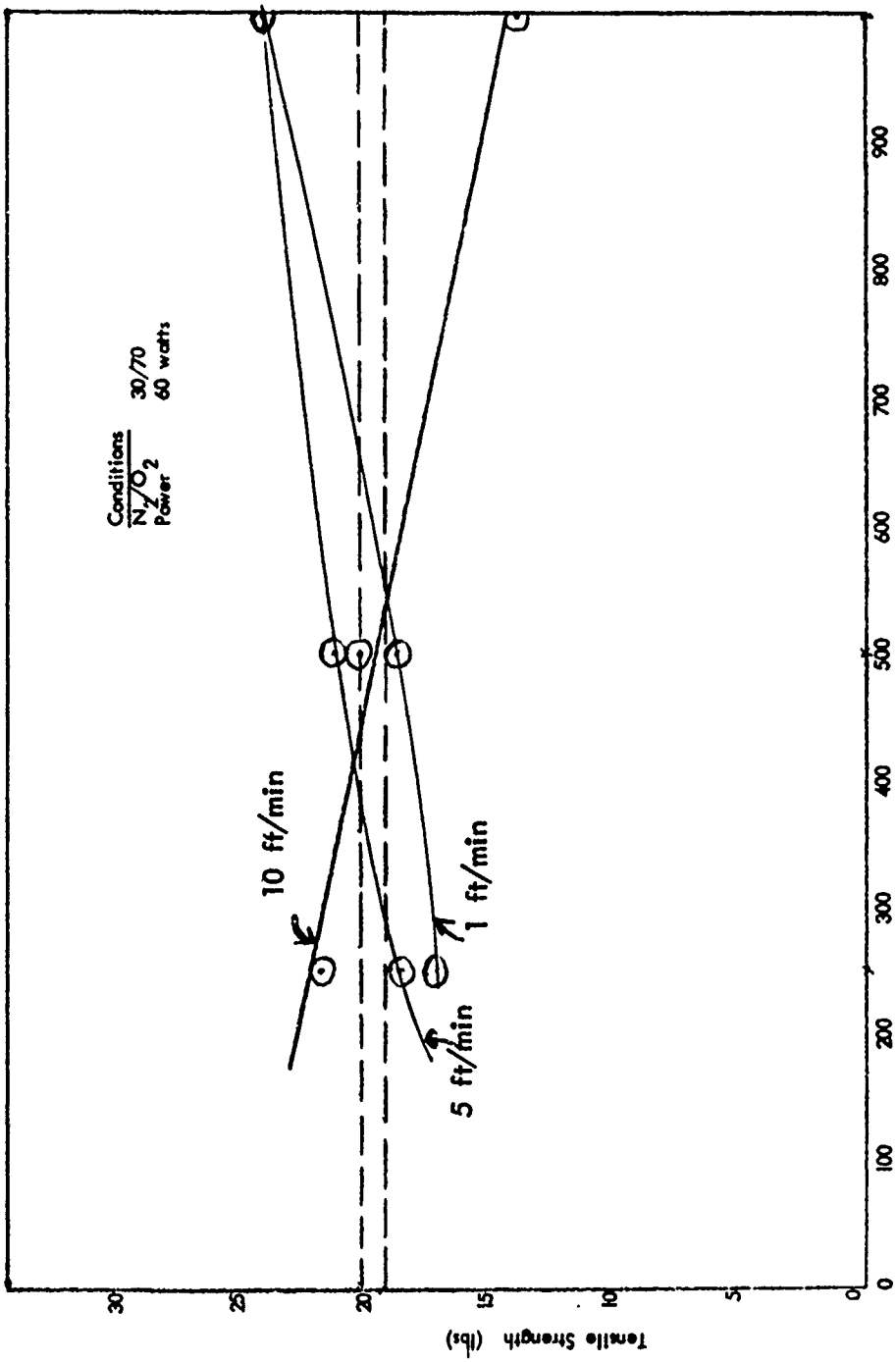

Fig. 7 - Tensile Strength vs Precursor Pressure (60 watts)

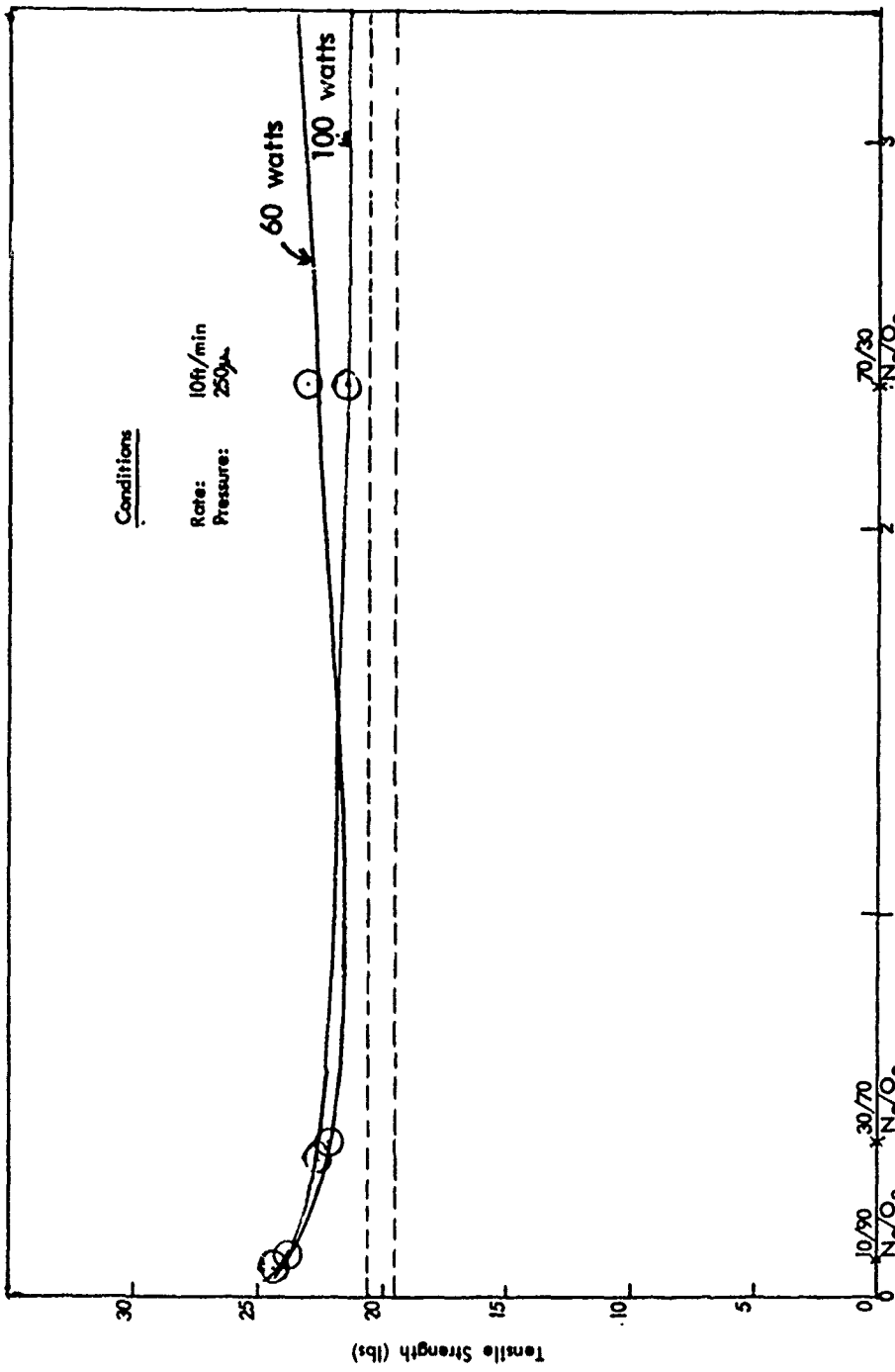

Fig. 8. Tensile Strength vs Gas Ratio

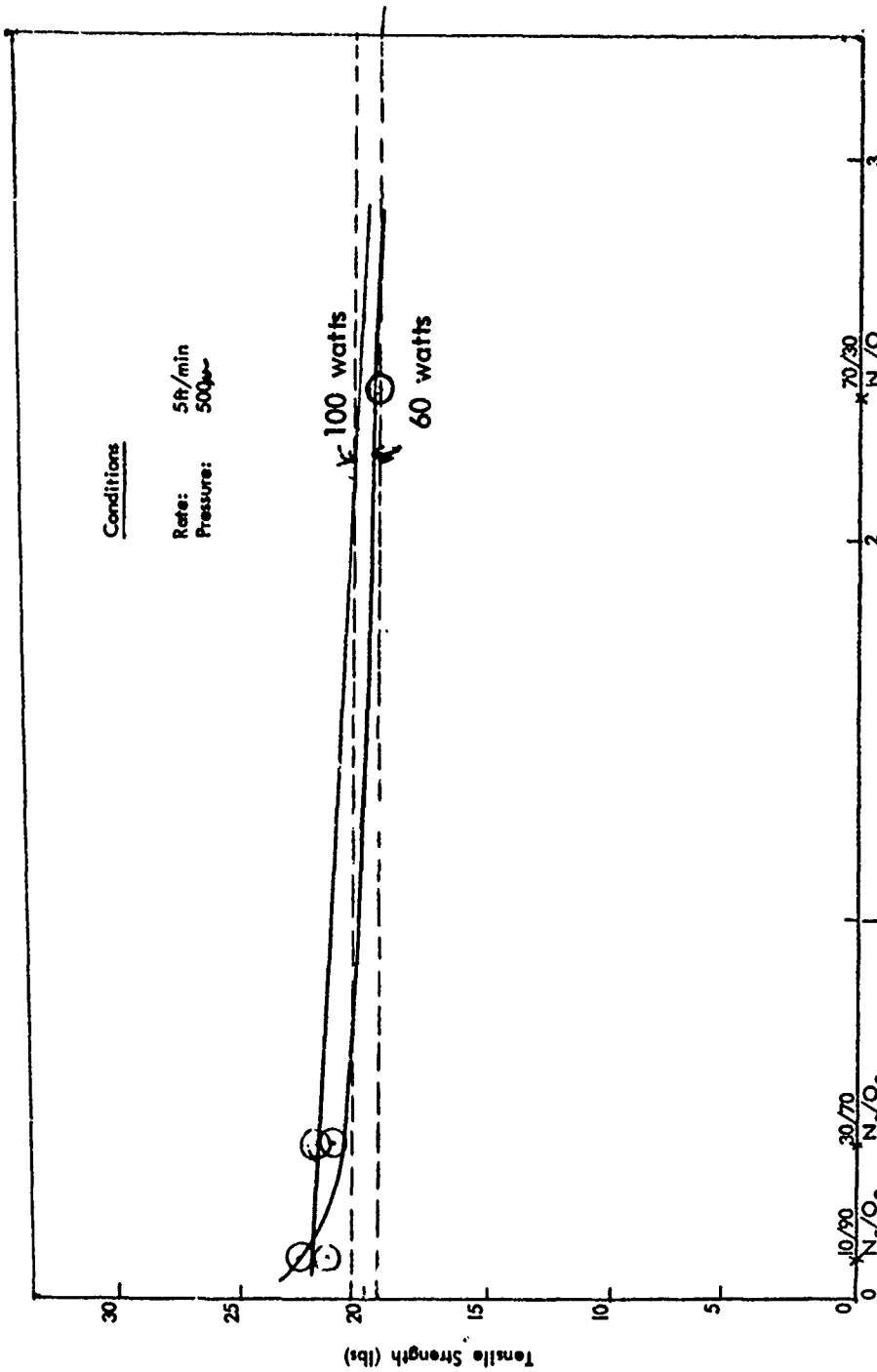

Fig. 9 - Tensile Strength vs Gas Ratio

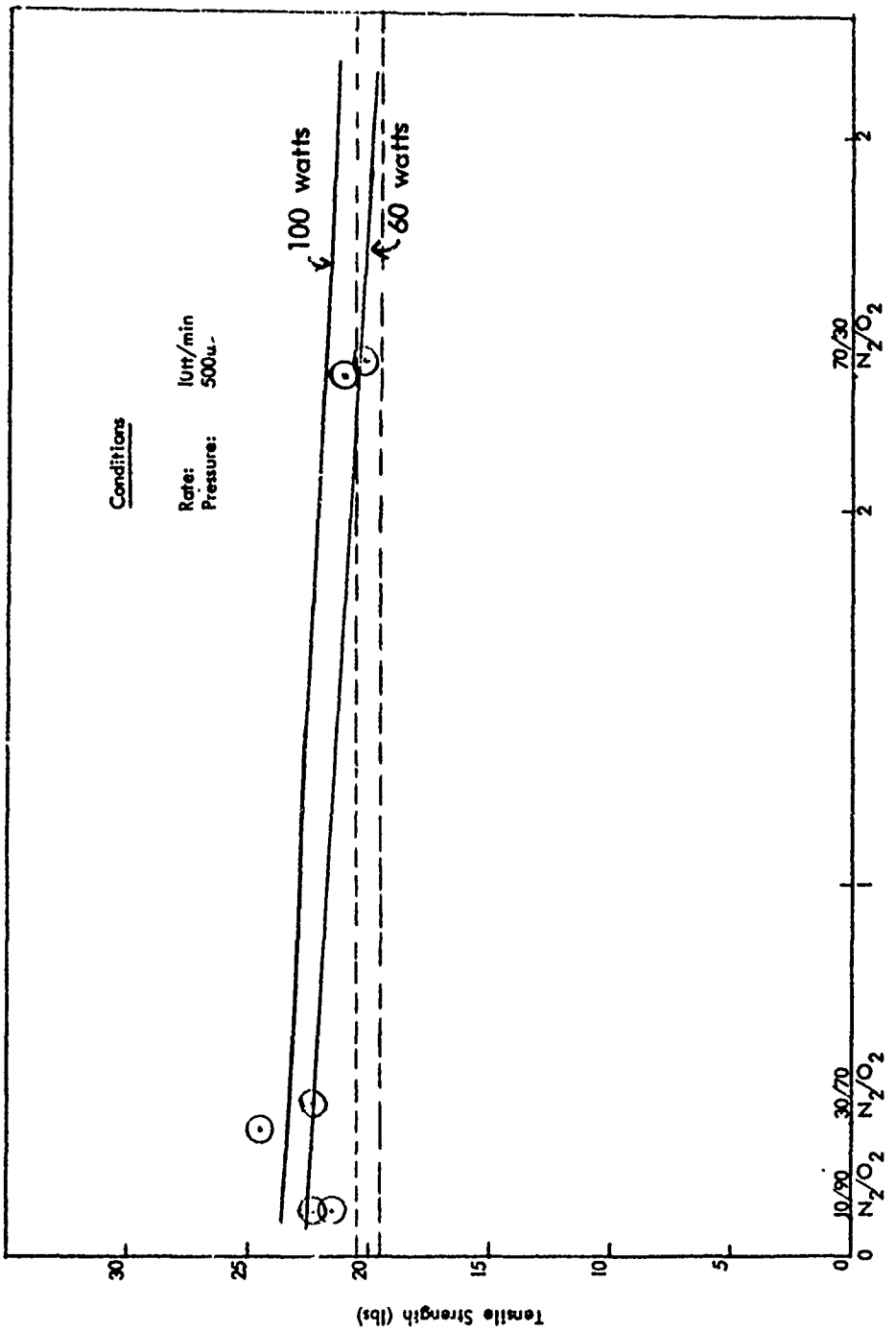

Fig.10 - Tensile Strength vs Gas Ratio

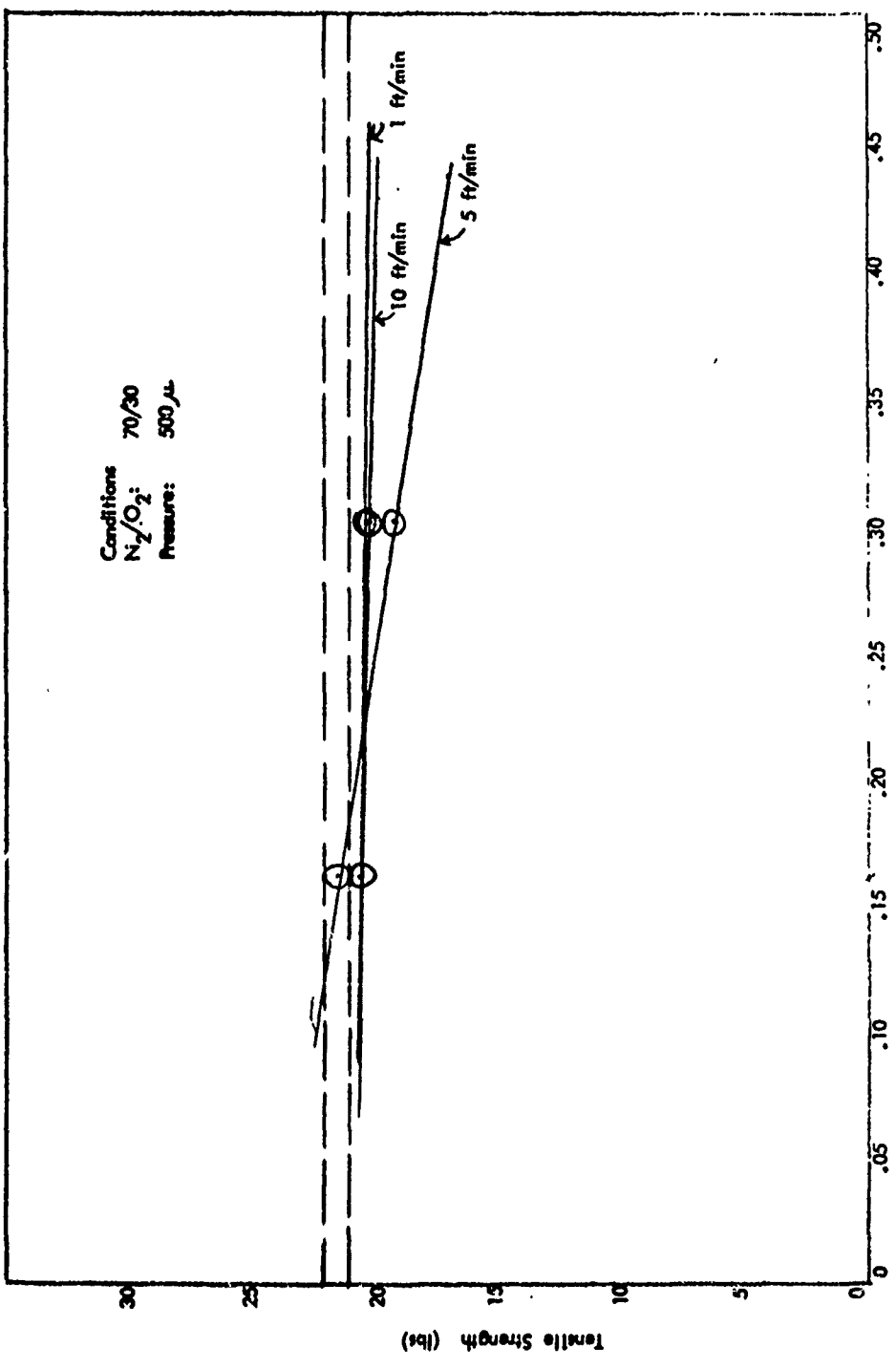

Fig. 11 - Tensile Strength vs Power (Plate Current)

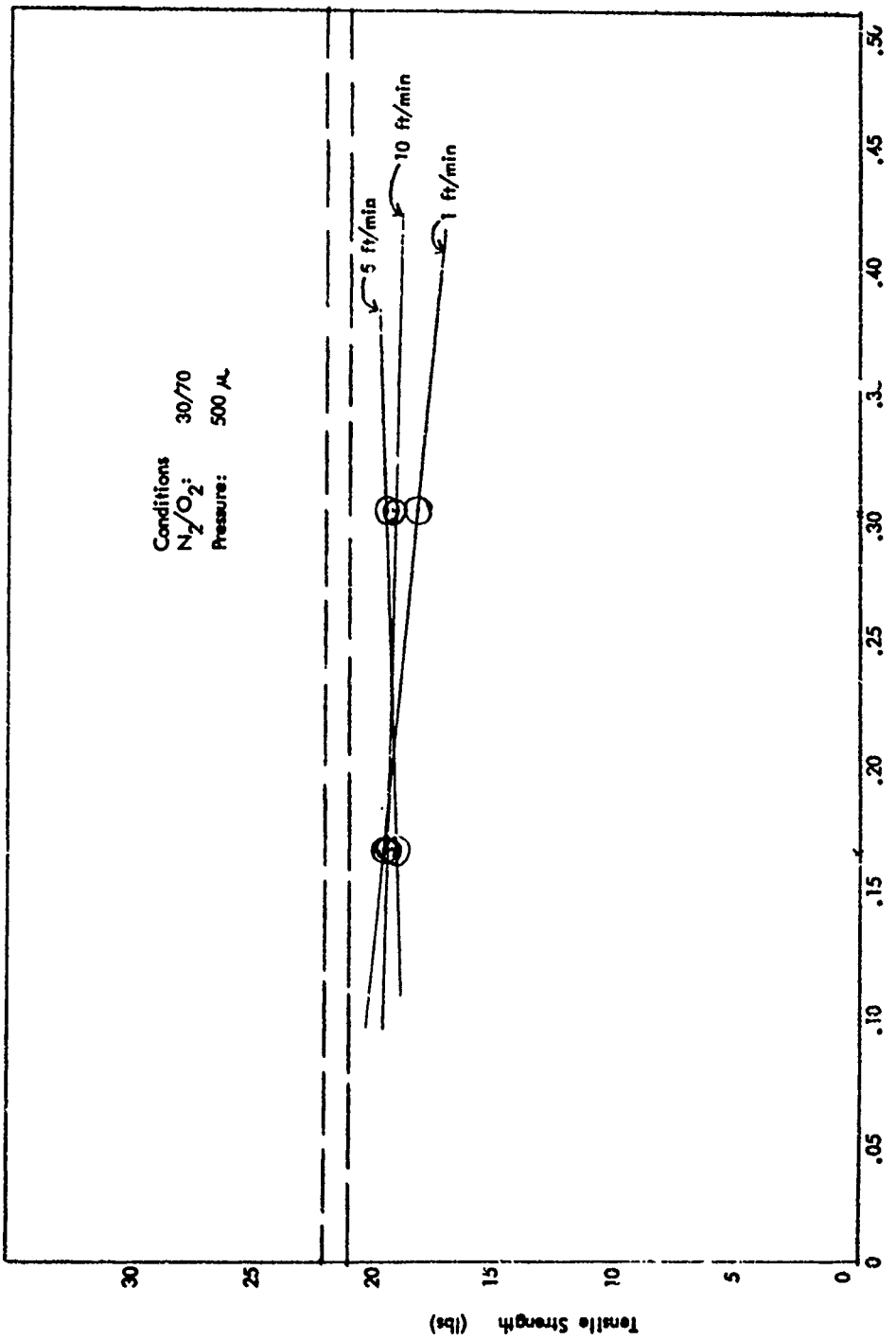

Fig.12 - Tensile Strength vs Power (Plate Current)

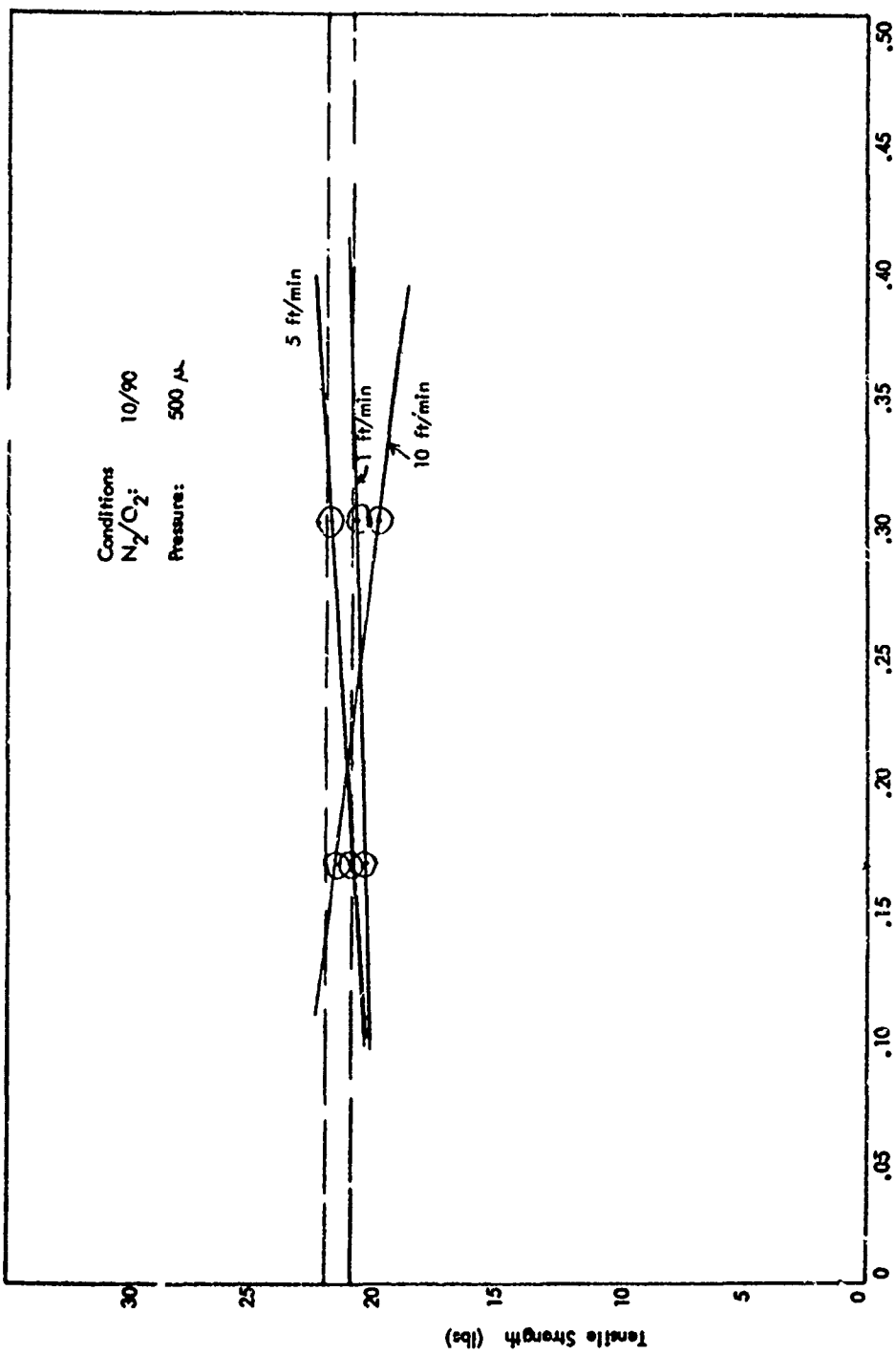

Fig. 13 - Tensile Strength vs Power (Plate Current)

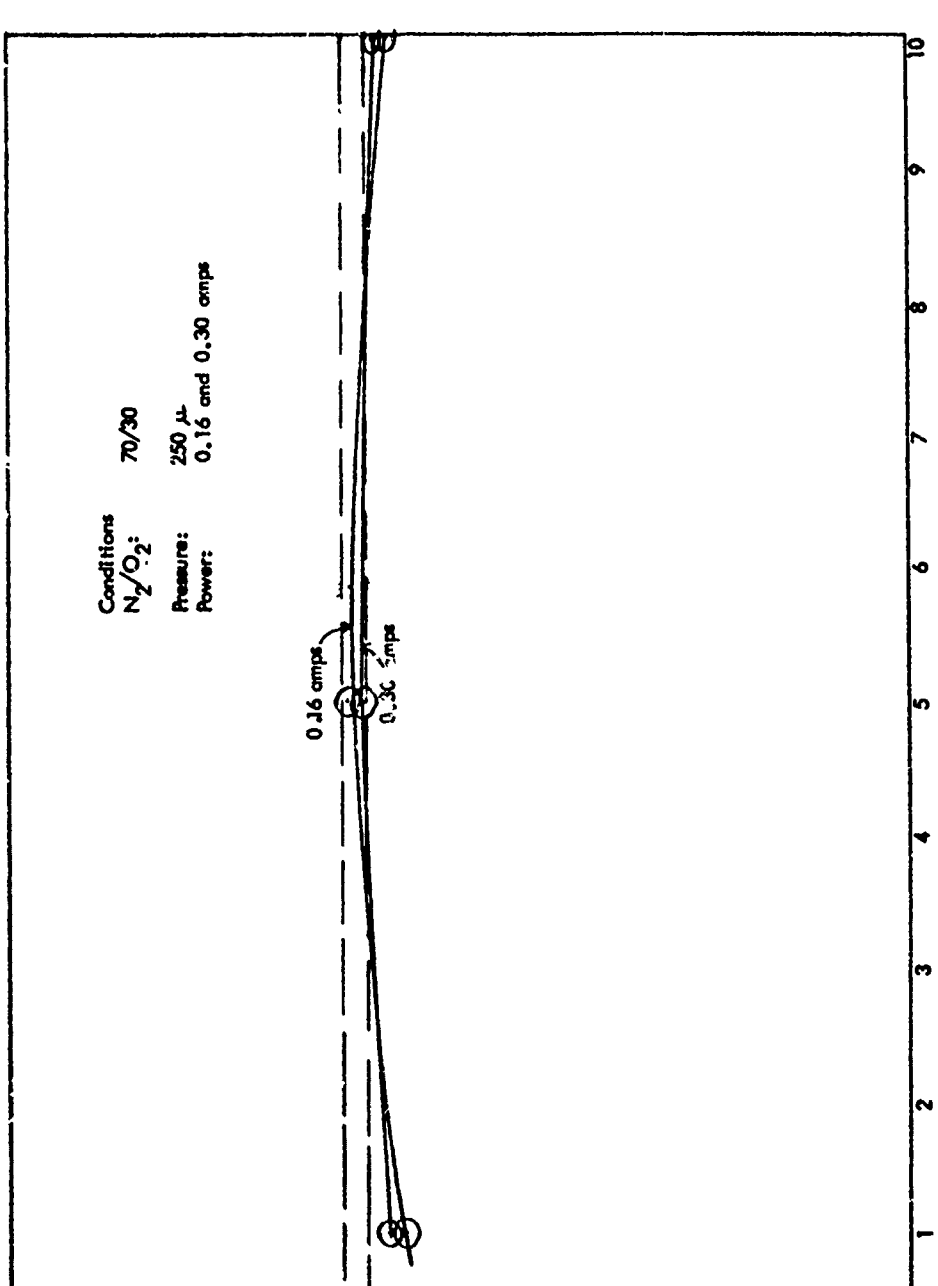

Fig. 14- Tensile Strength vs Process Rate (ft/min)

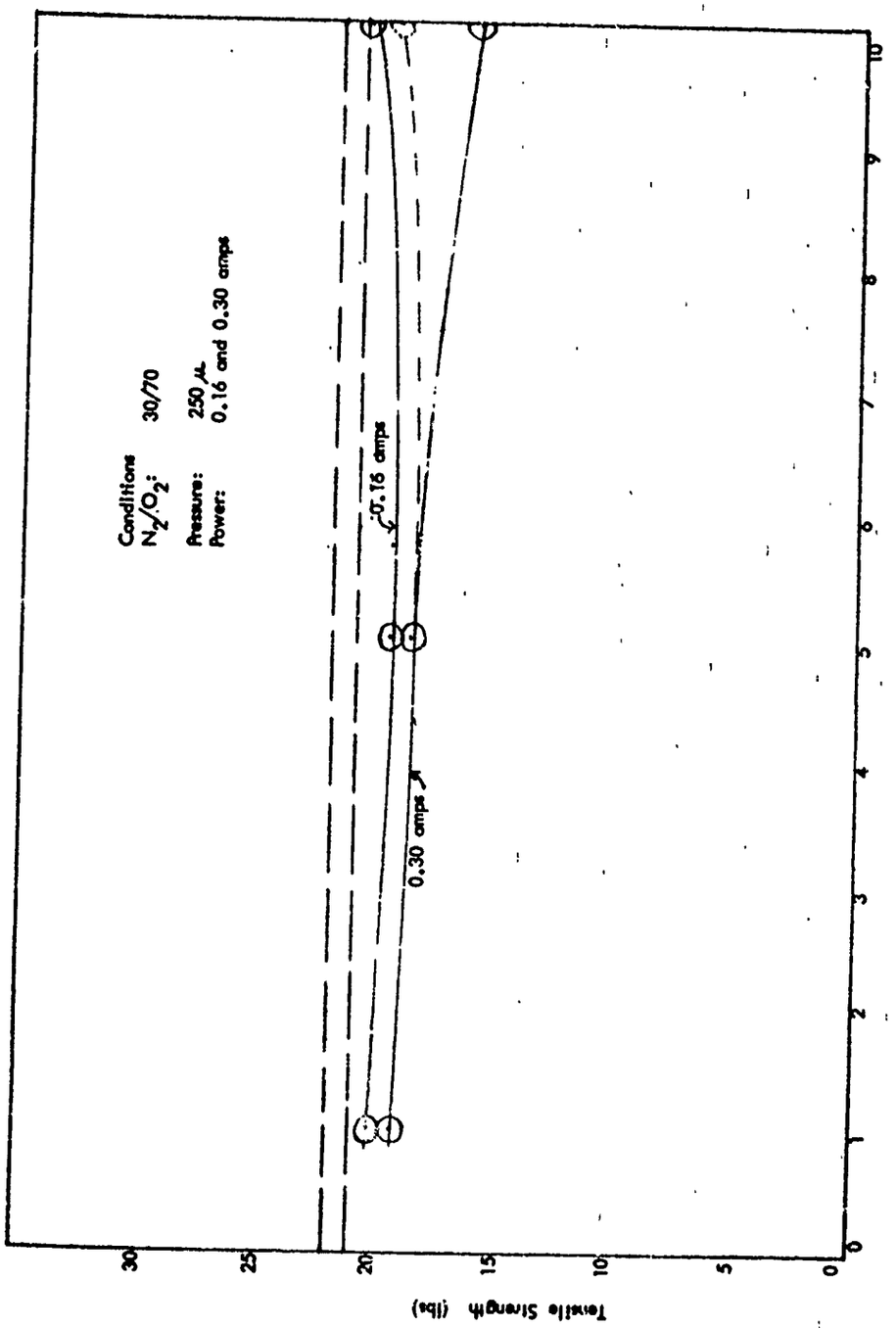

Fig. 15- Tensile Strength vs Process Rate (ft/min)

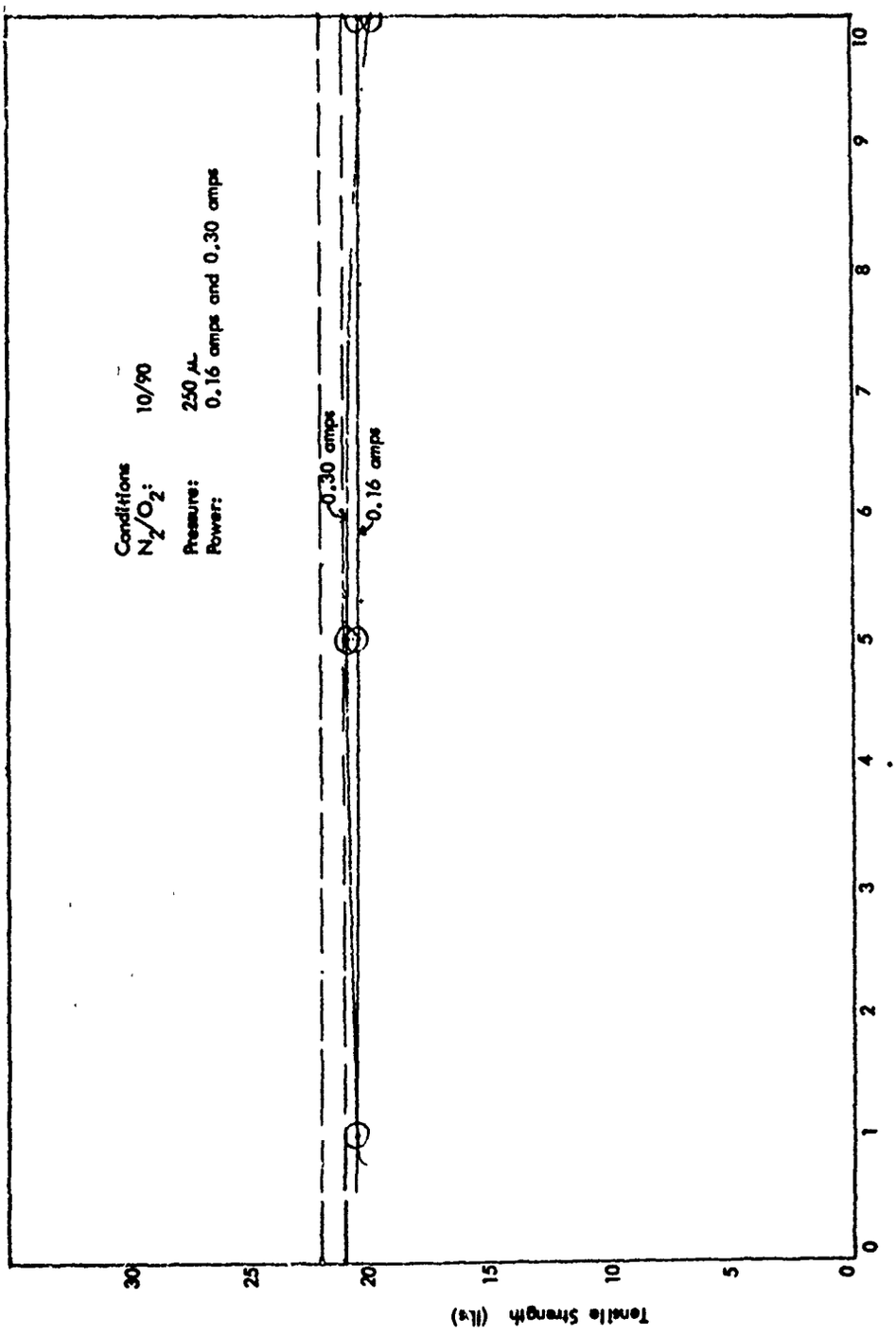

Fig. 16 – Tensile Strength vs Process Rate (ft/min)

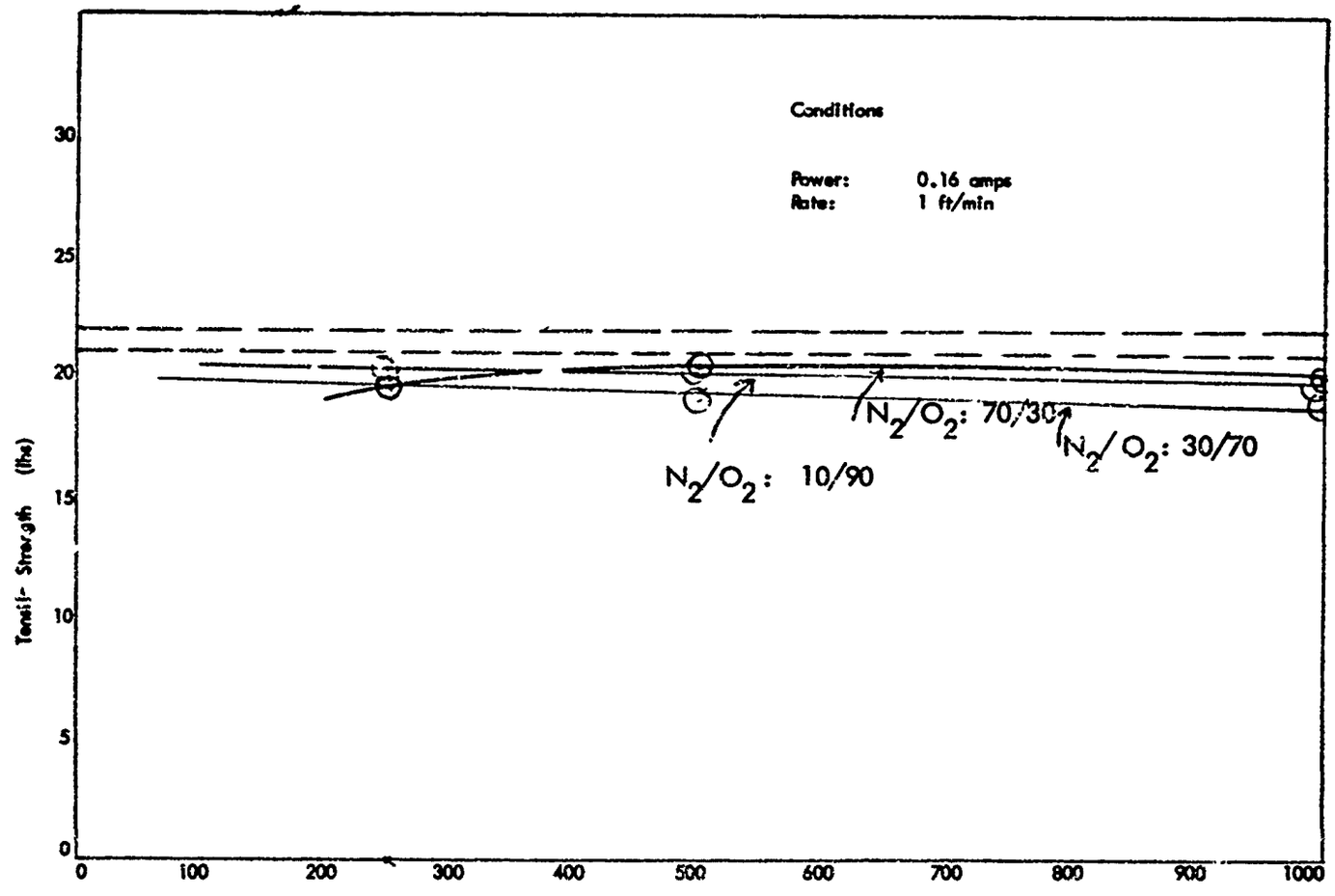

Fig.17 - Tensile Strength vs Precursor Pressure (0.16 amps)

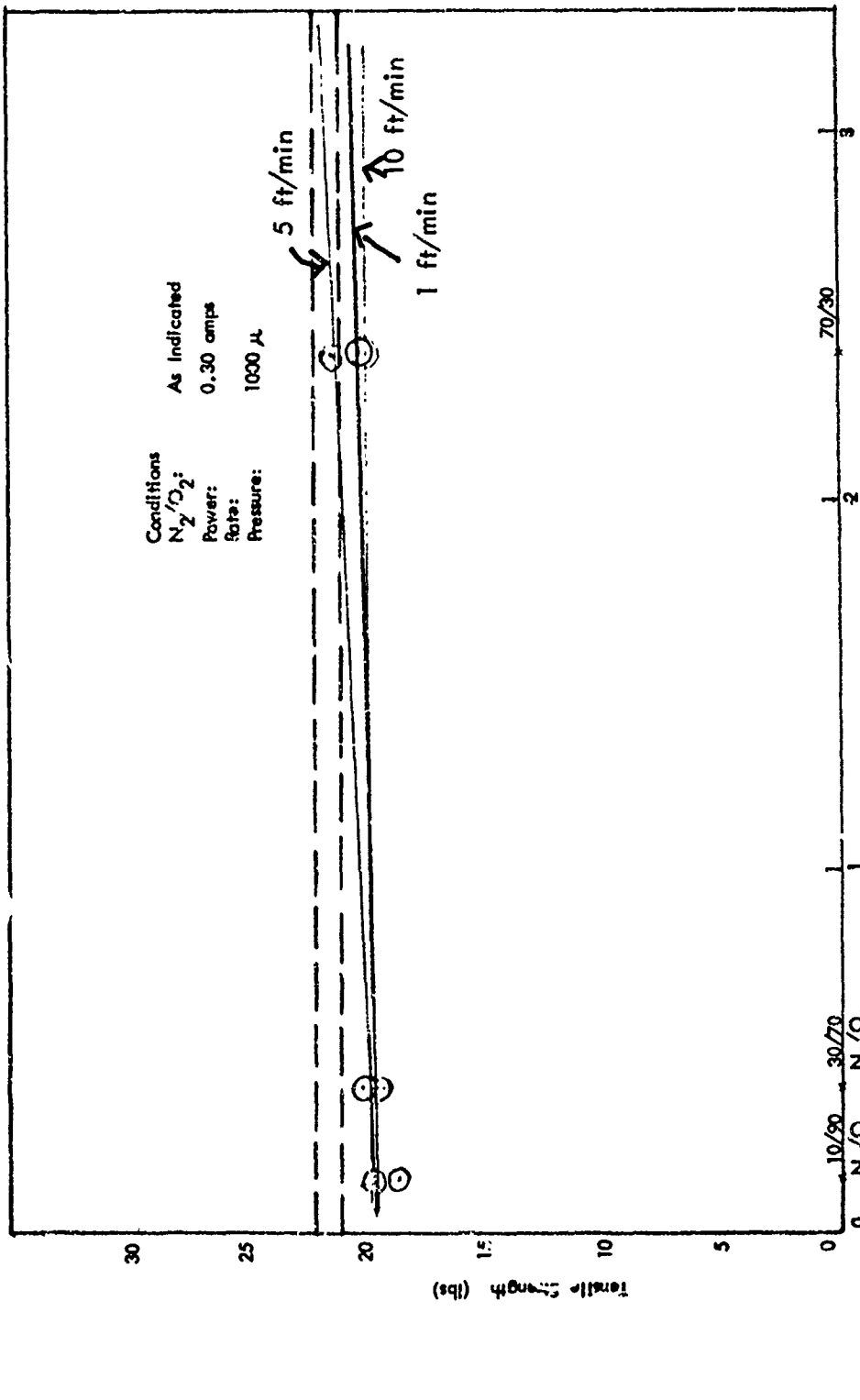

Fig. 18 - Tensile Strength vs Gas Ratio

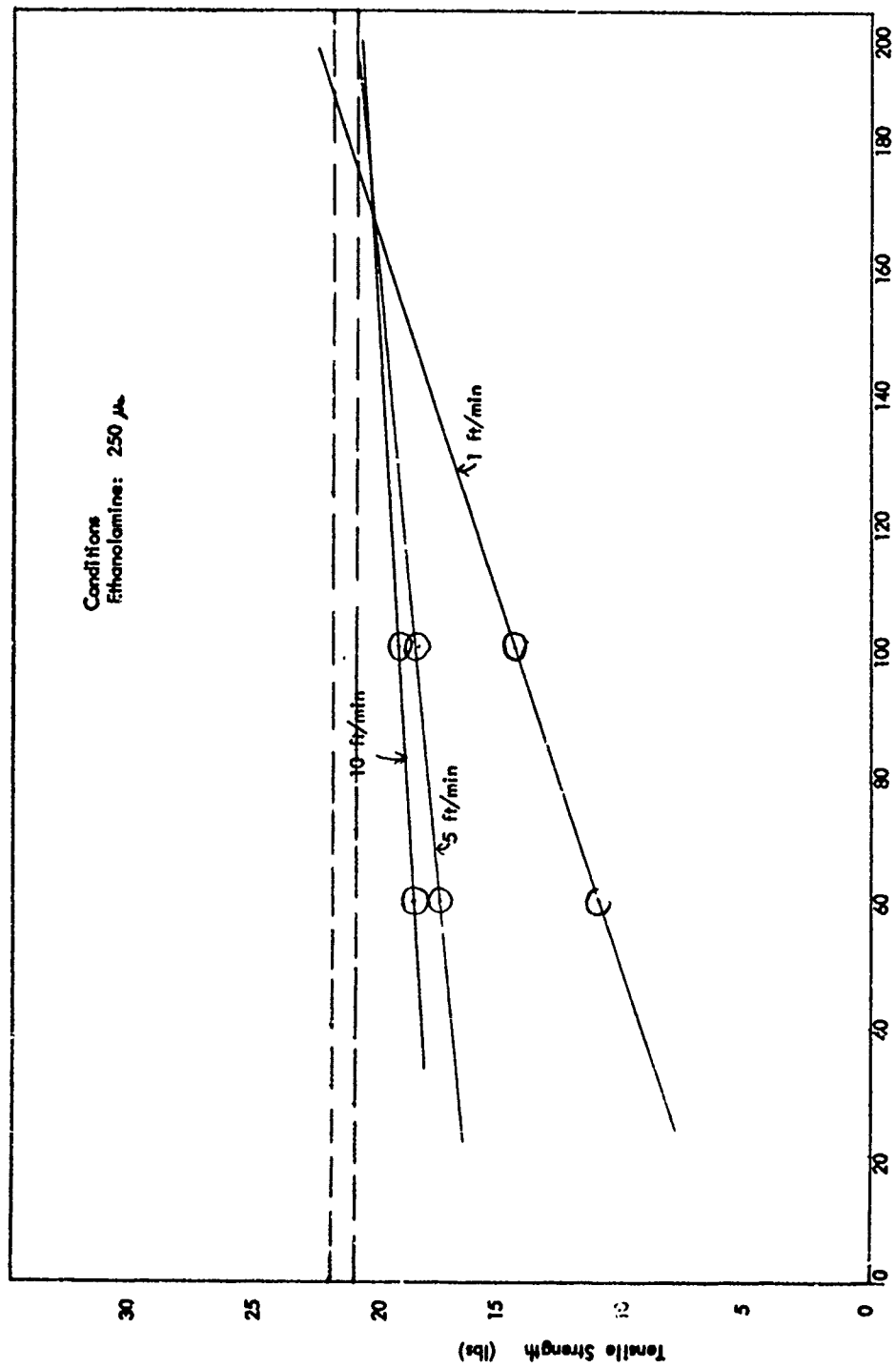

Fig. 19 - Tensile Strength vs Power (Watts)

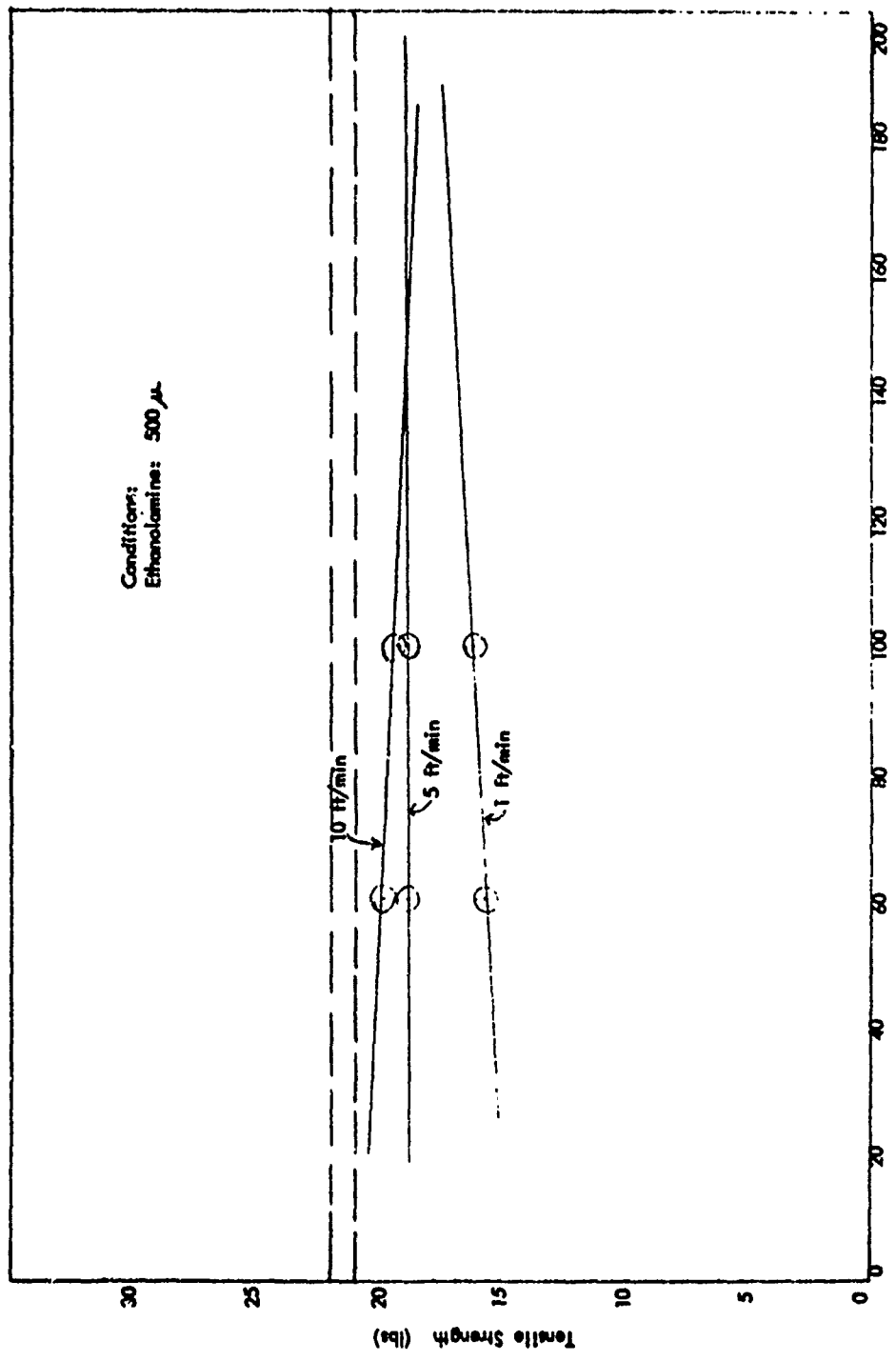

Fig. 20 - Tensile Strength vs Power (Watts)

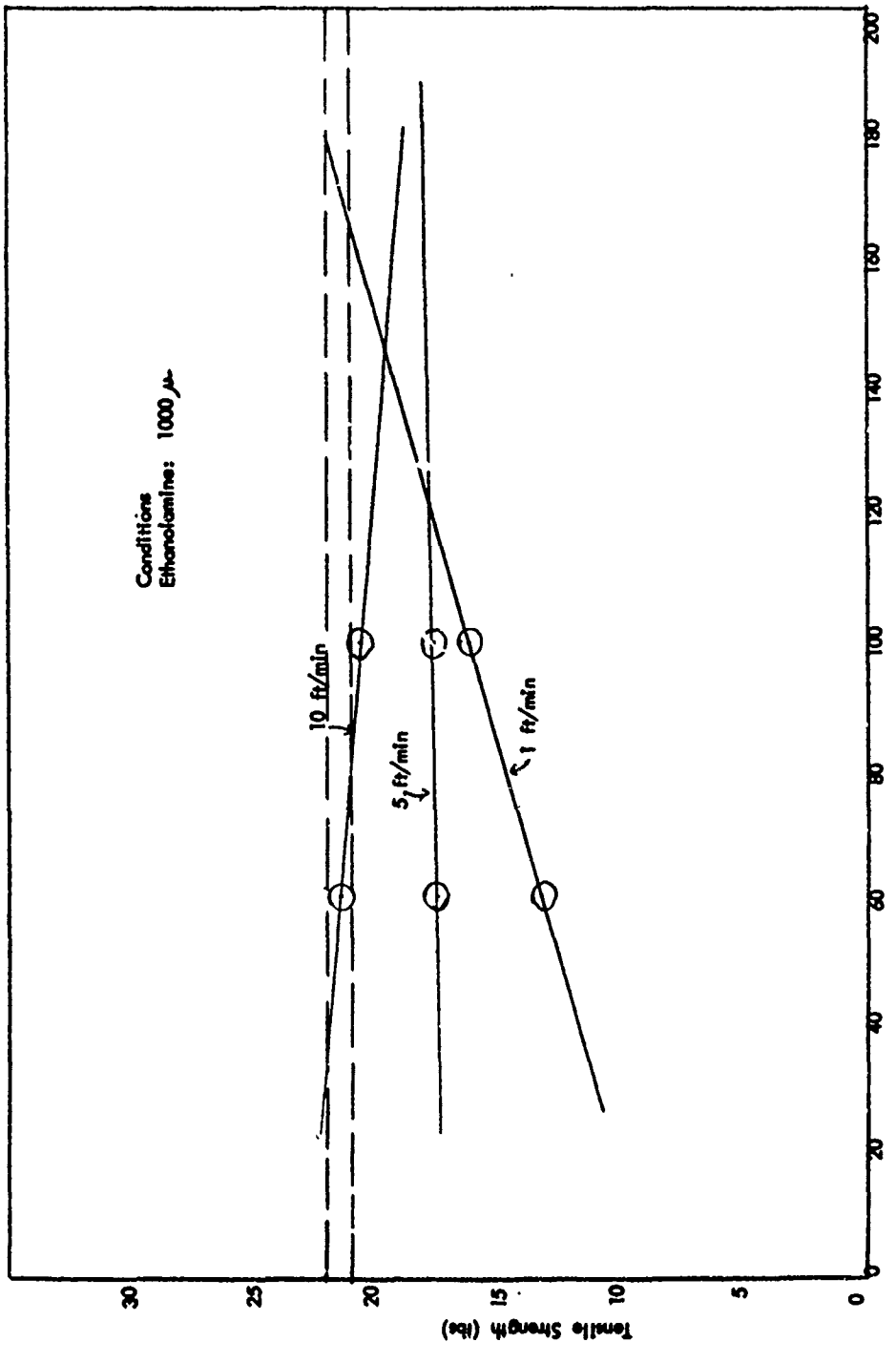

Fig-21 - Tensile Strength vs Power (Watts)

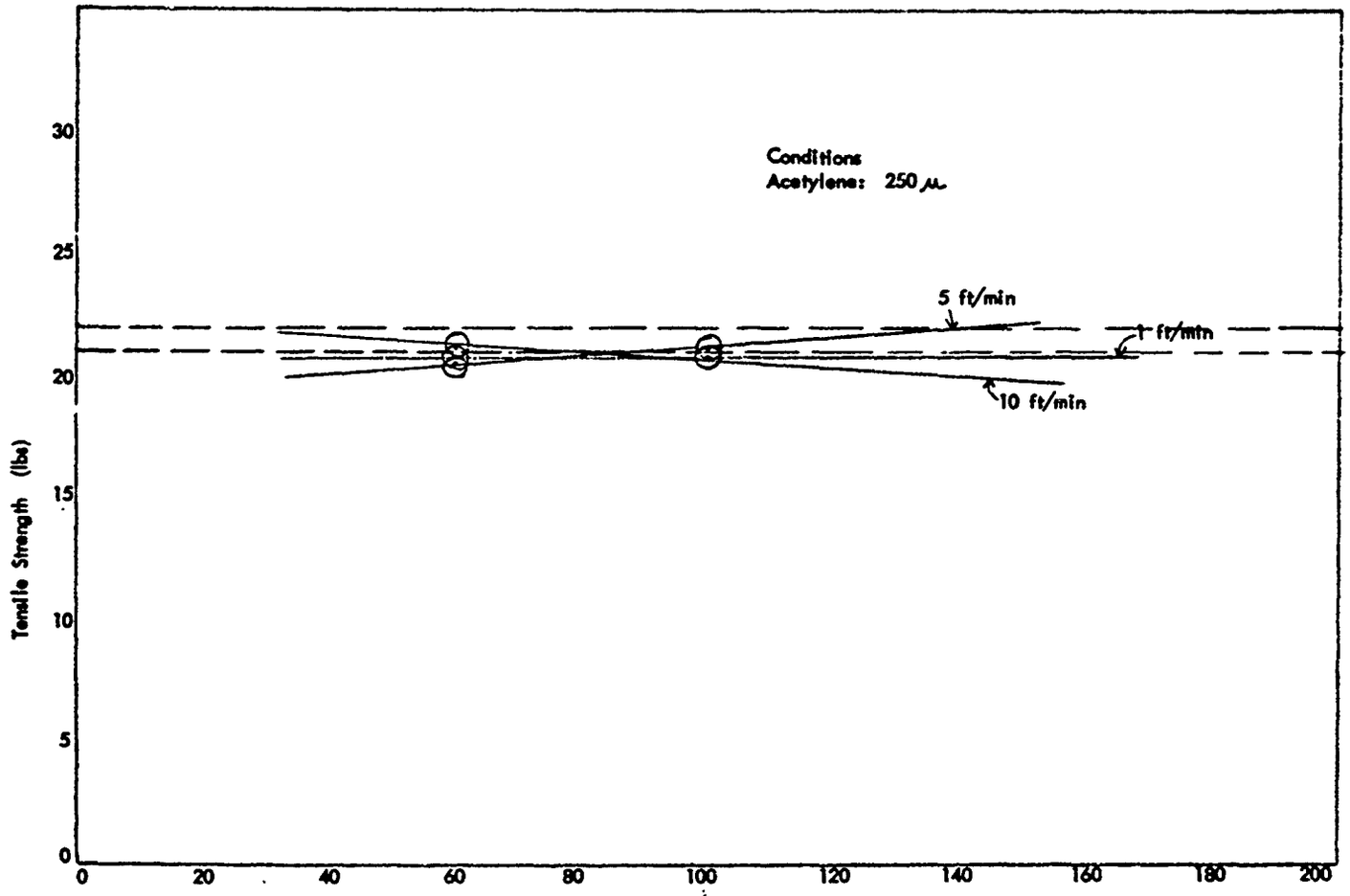

Fig. 22 - Tensile Strength vs Power (watts)

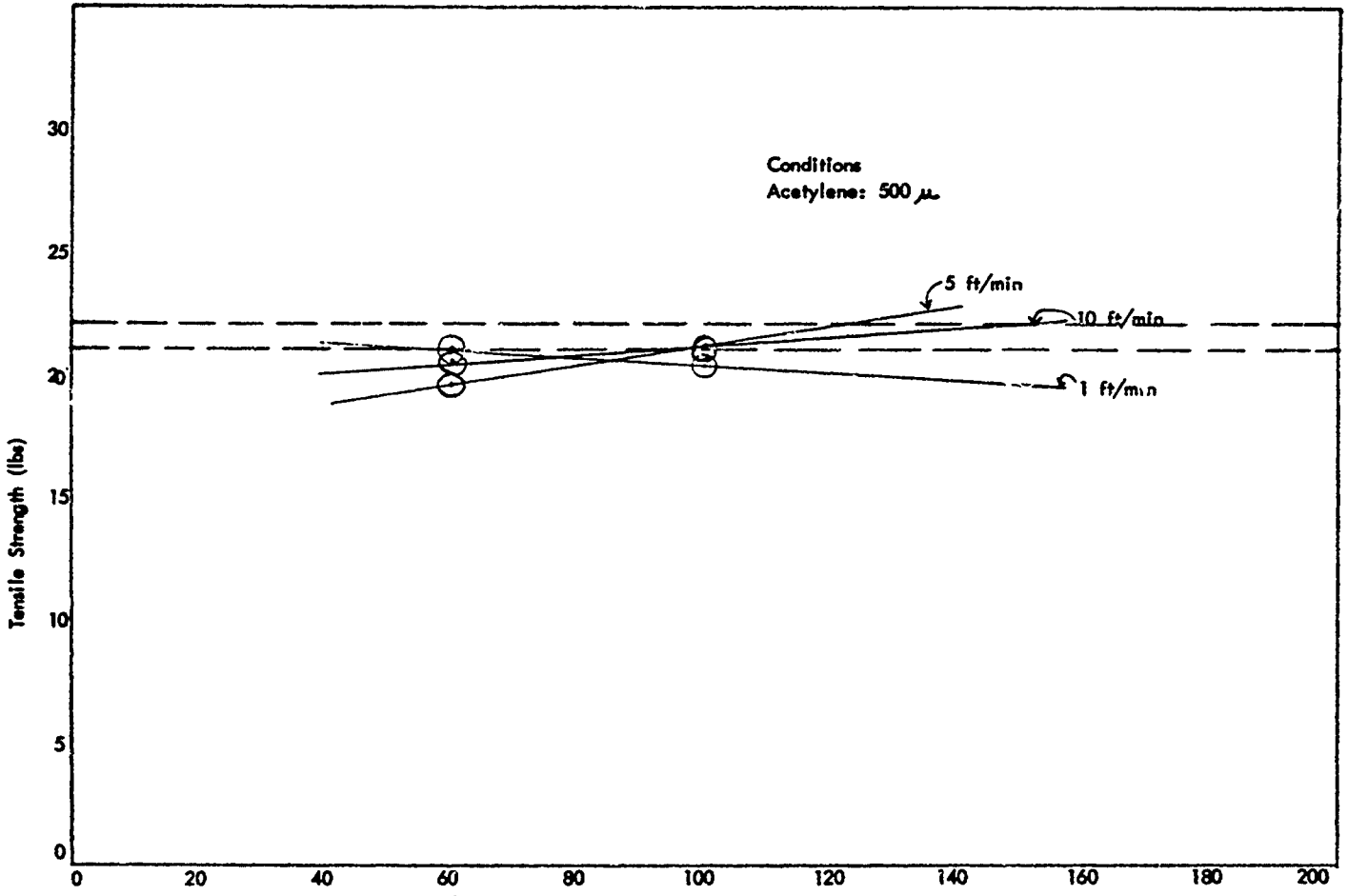

Fig. 23 - Tensile Strength vs Power (watts)

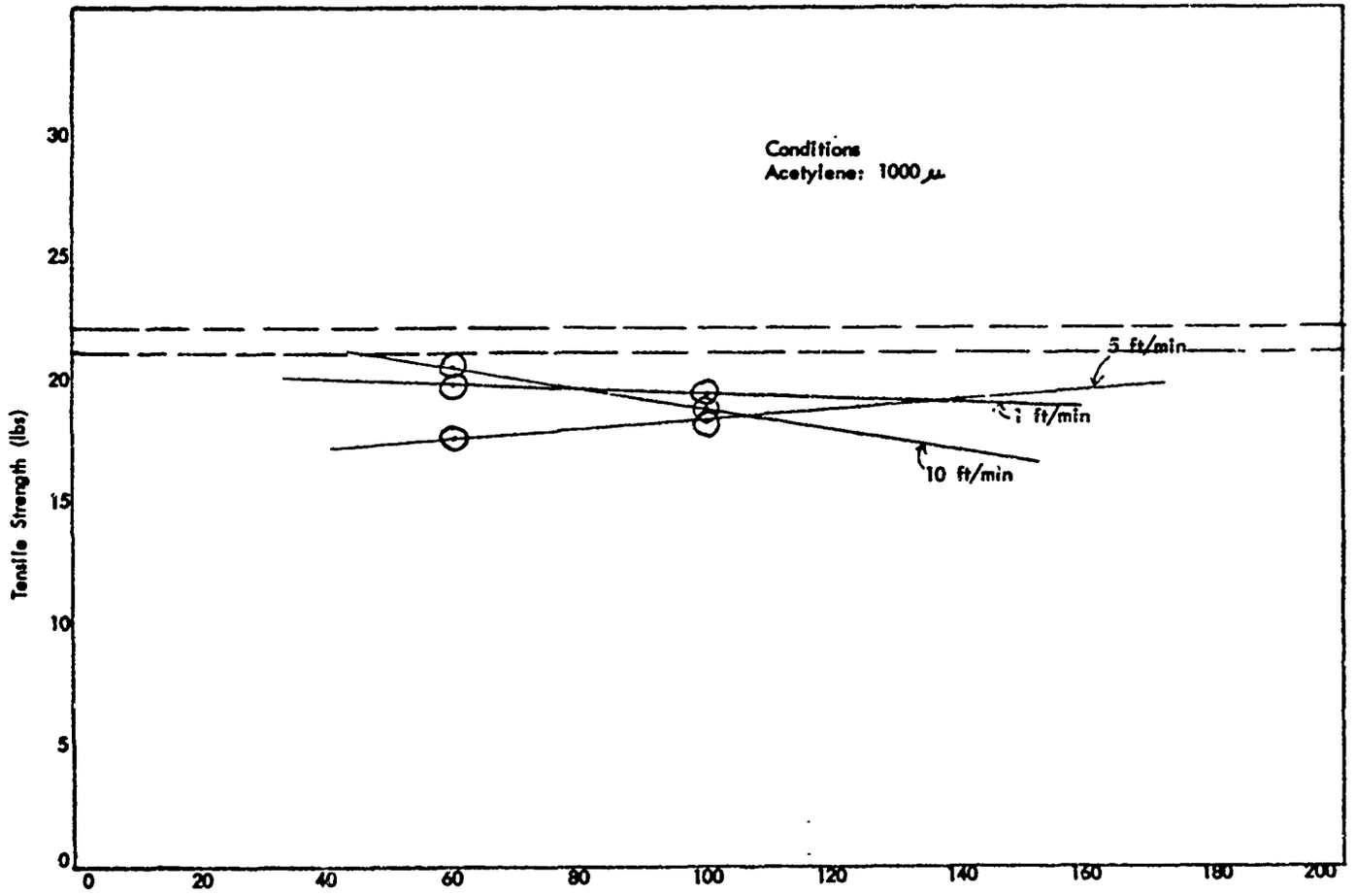

Fig. 24- Tensile Strength vs Power (watts)

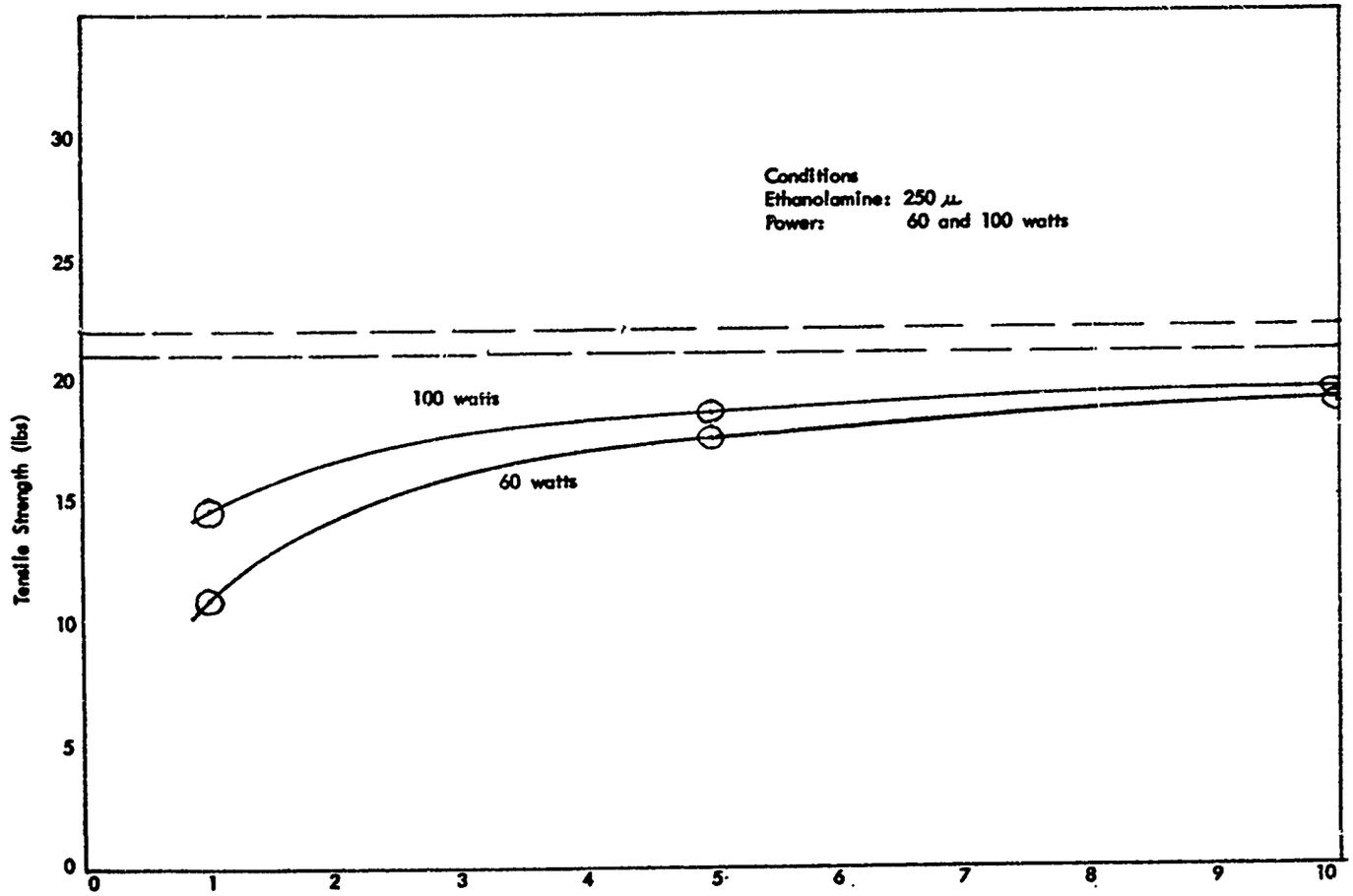

Fig.25 - Tensile Strength vs Process Rate (ft/min)

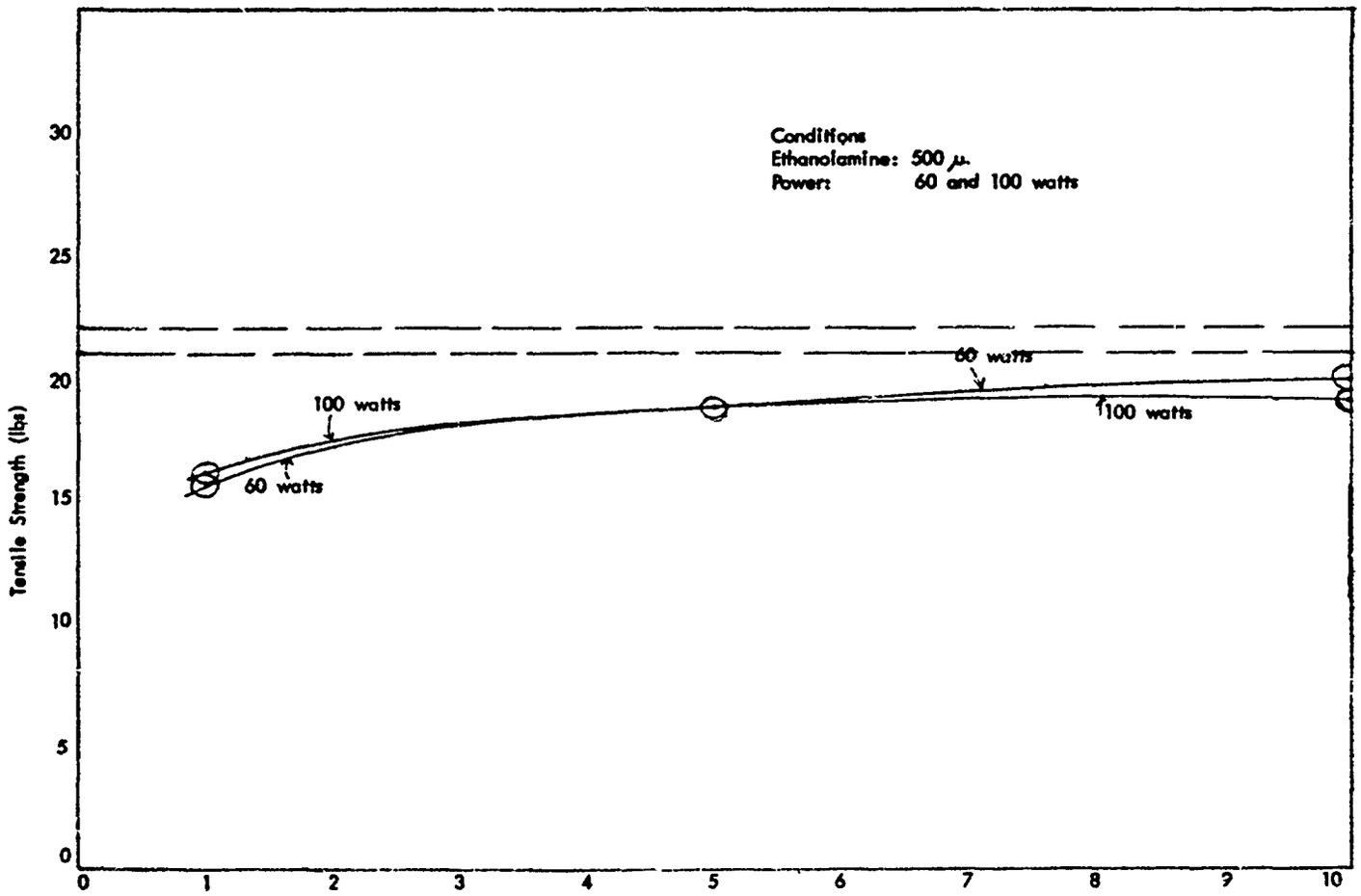

Fig. 25- Tensile Strength vs Process Rate (ft/min)

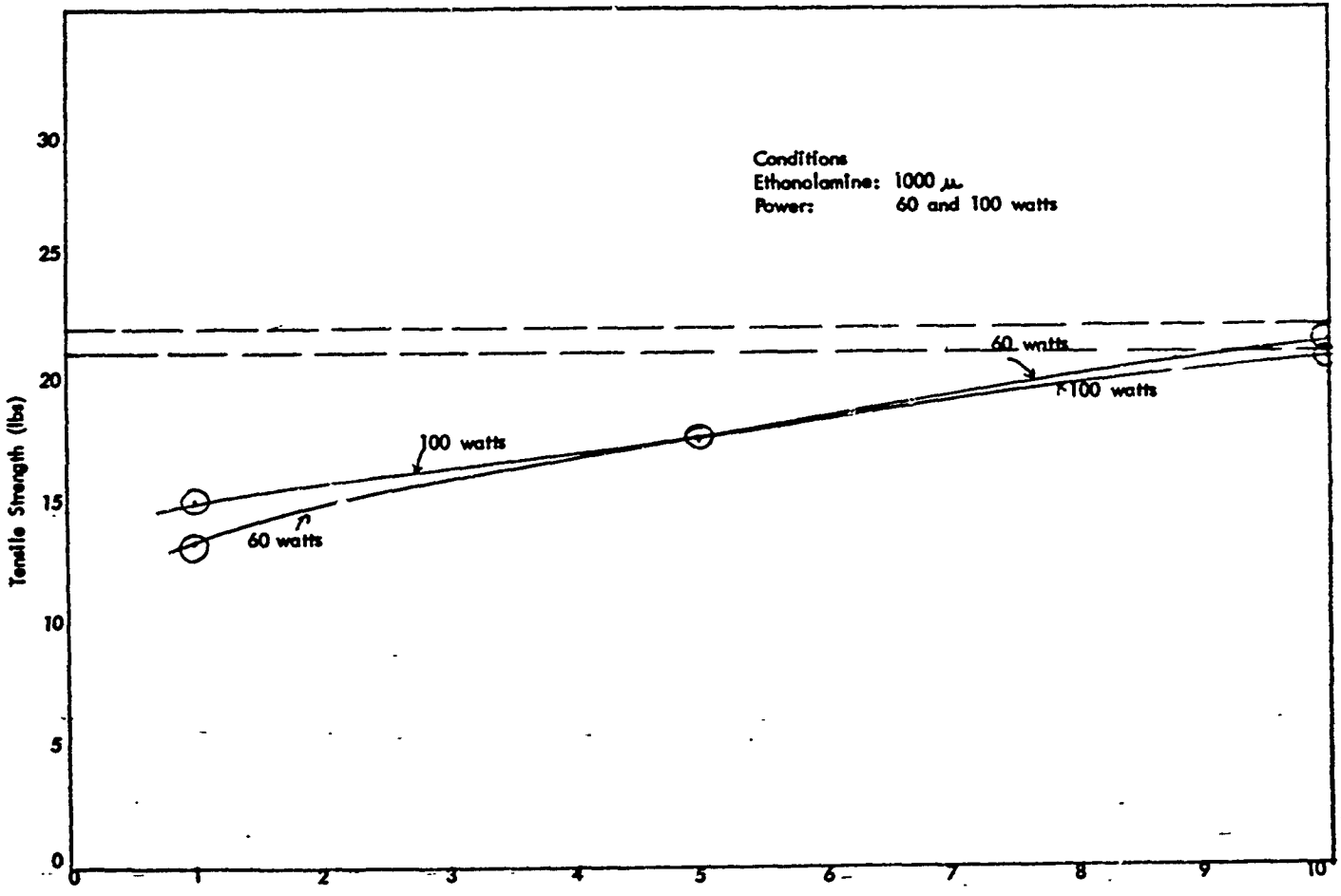

Fig. 27 - Tensile Strength vs Process Rate (ft/min)

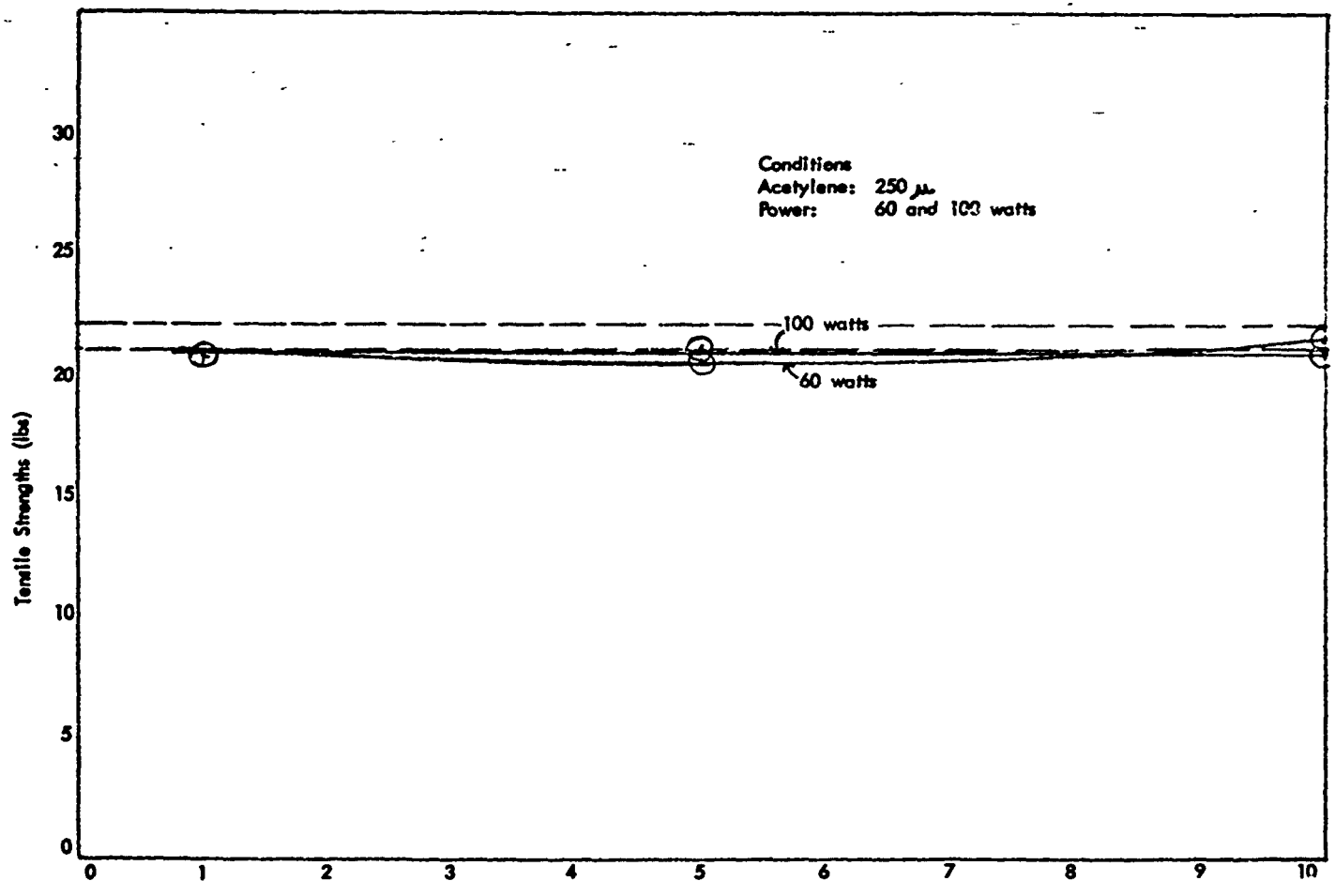

Fig. 28- Tensile Strength vs Process Rate (ft/min)

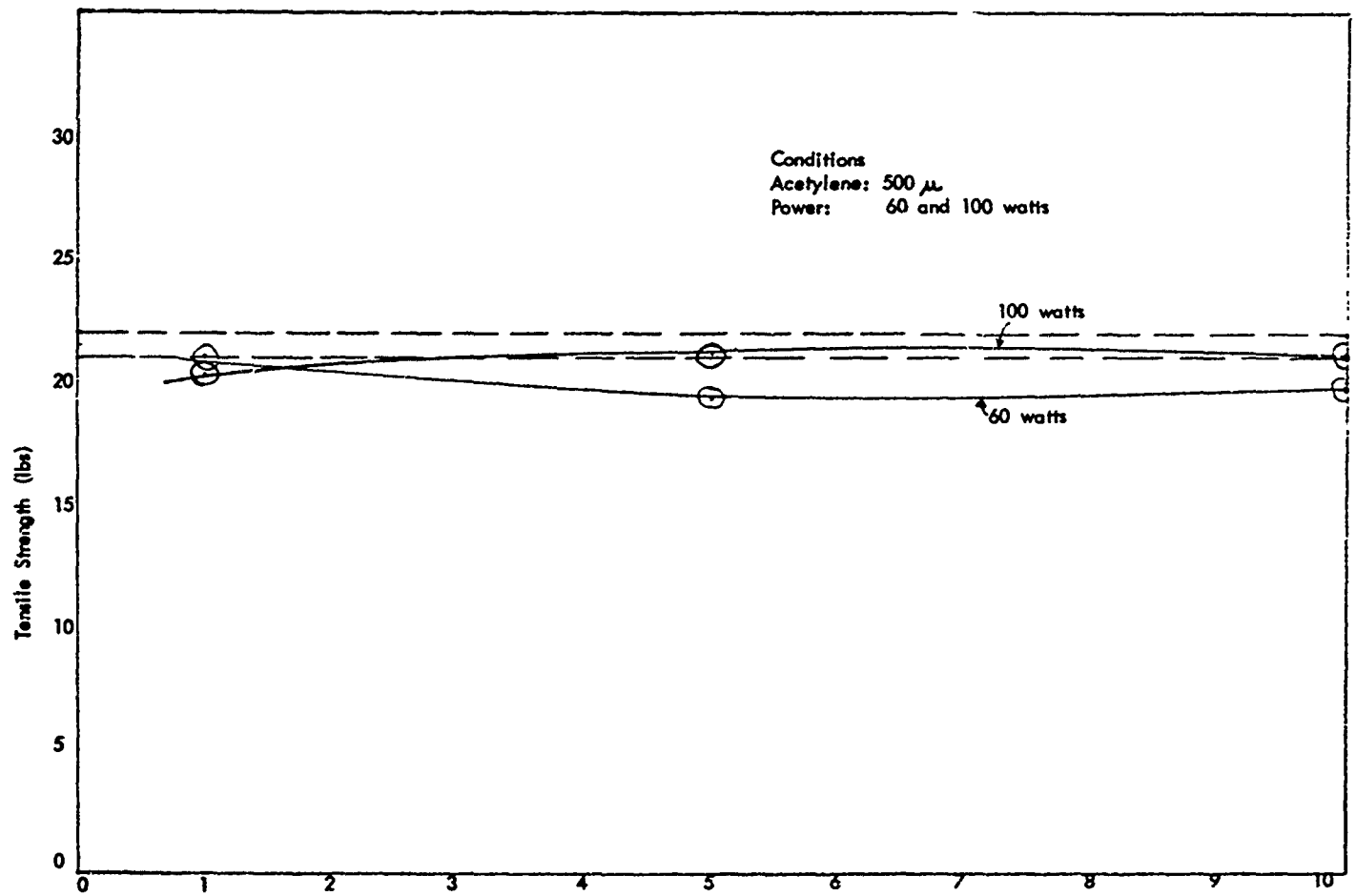

Fig. 29 Tensile Strength vs Process Rate (ft/min)

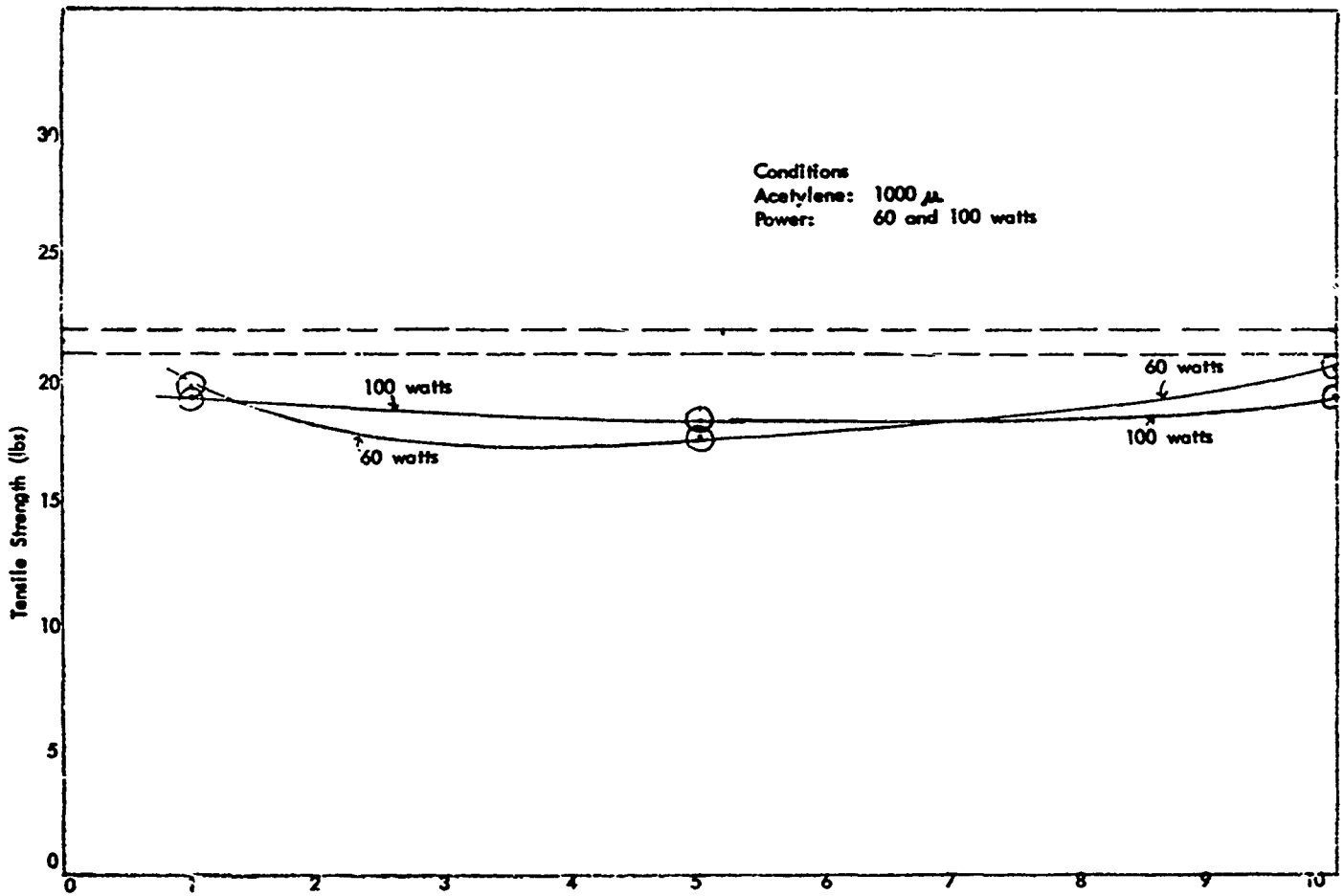

Fig. 30 - Tensile Strength vs Process Rate (ft/min)

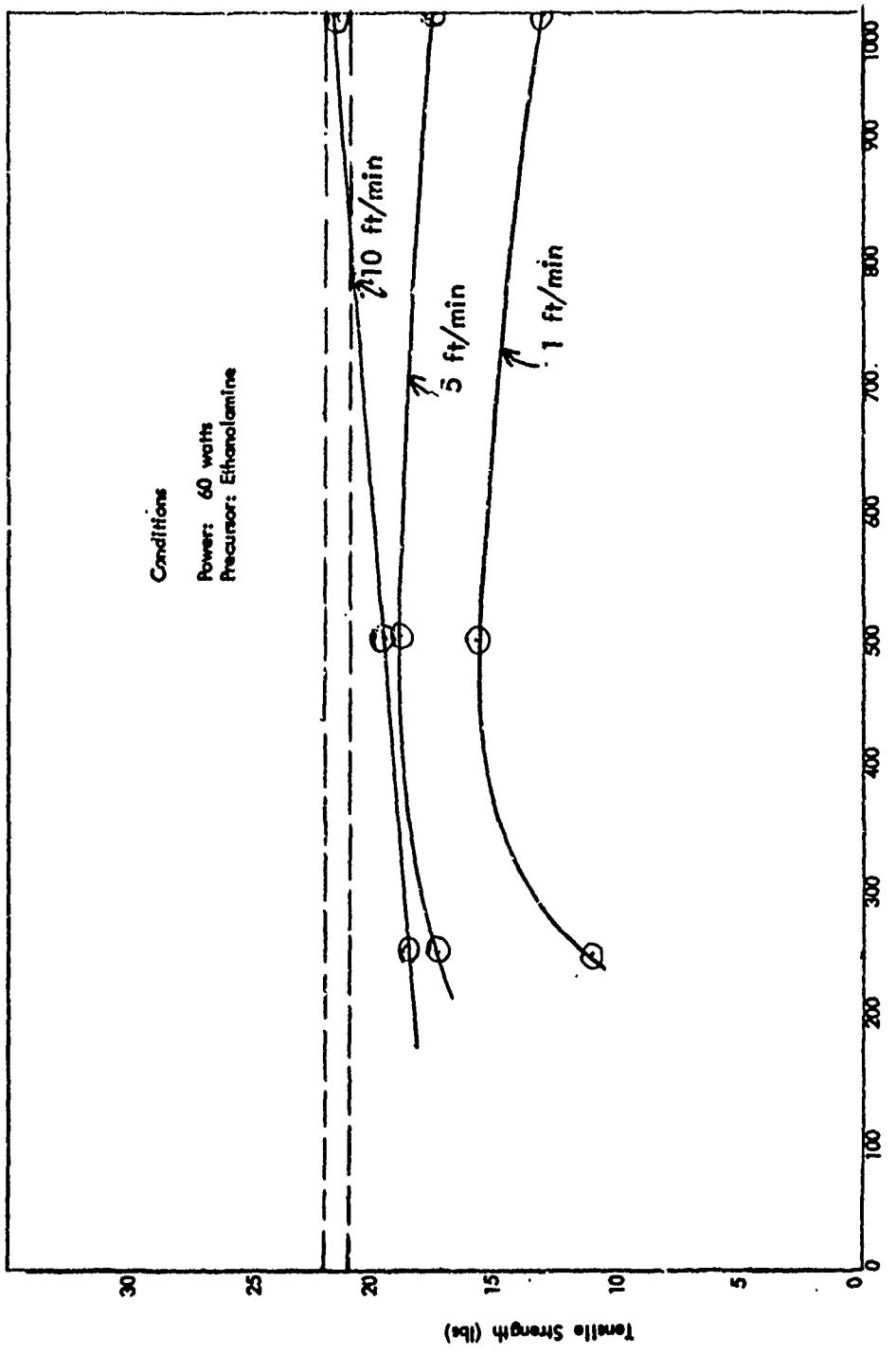

Fig. 31 - Tensile Strength vs Precursor Pressure (60 watts)

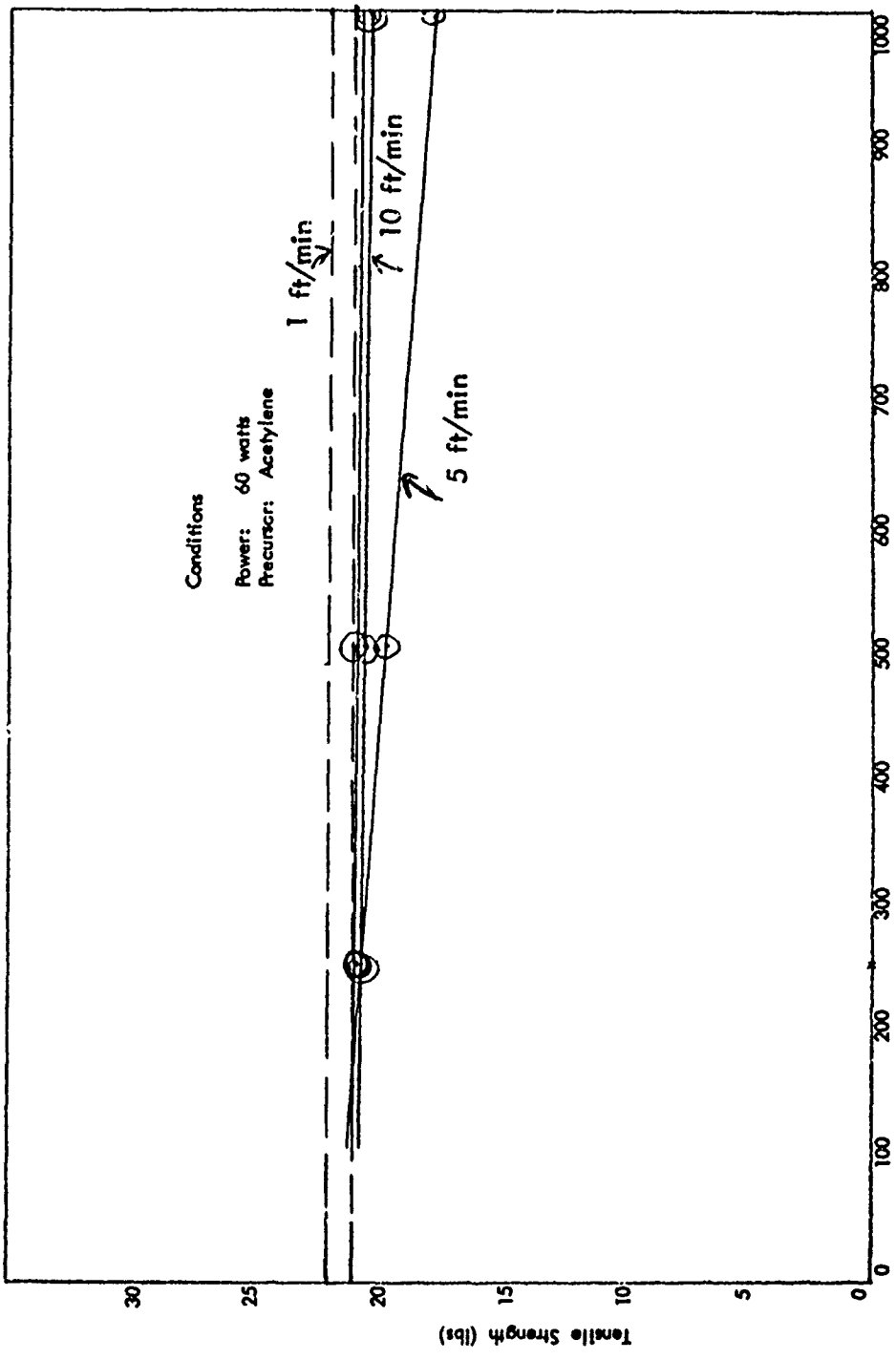

Fig 32 - Tensile Strength vs Precursor Pressure (60 watts)

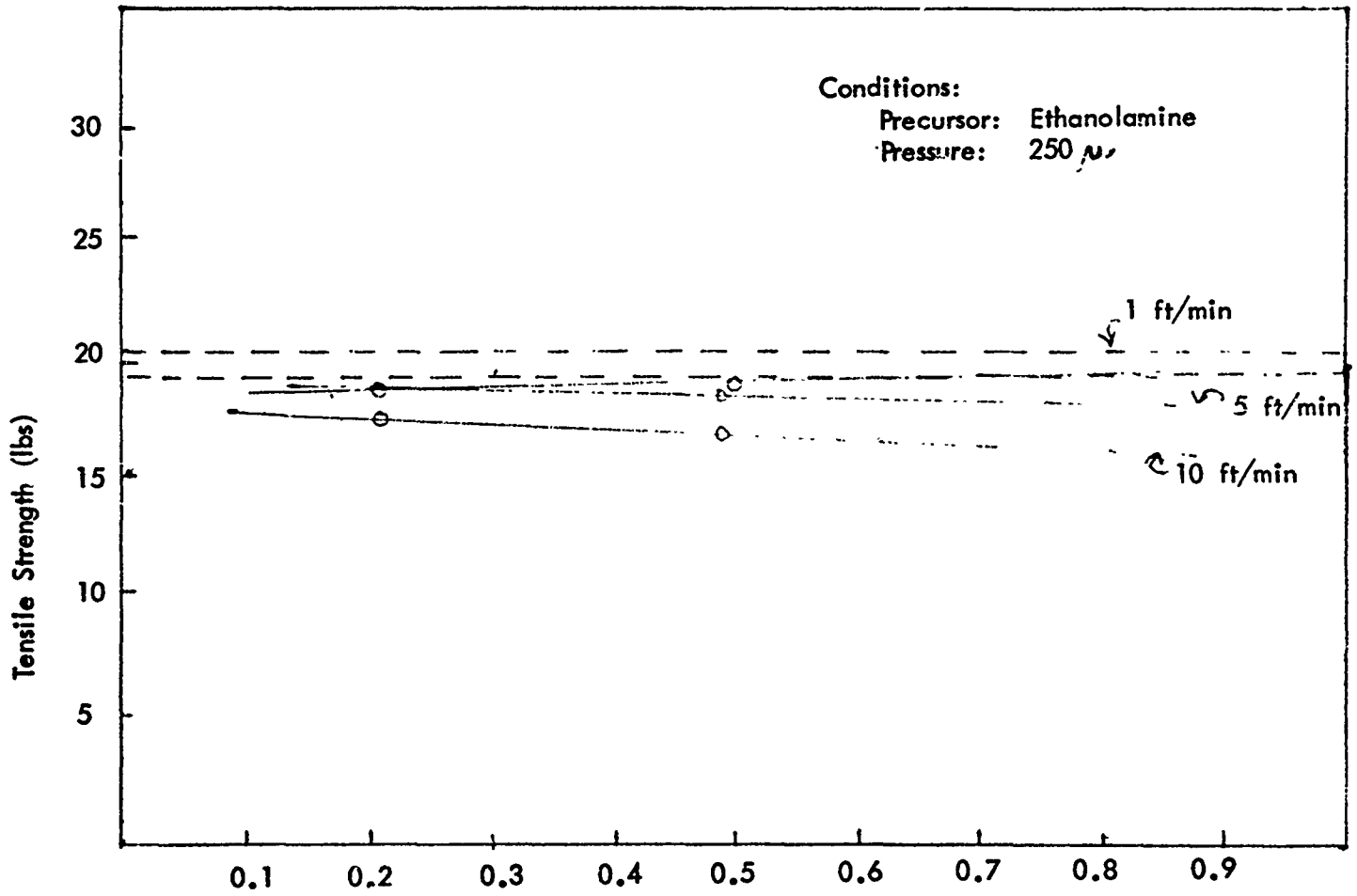

Figure 33 Tensile Strength vs Power (Plate Current)

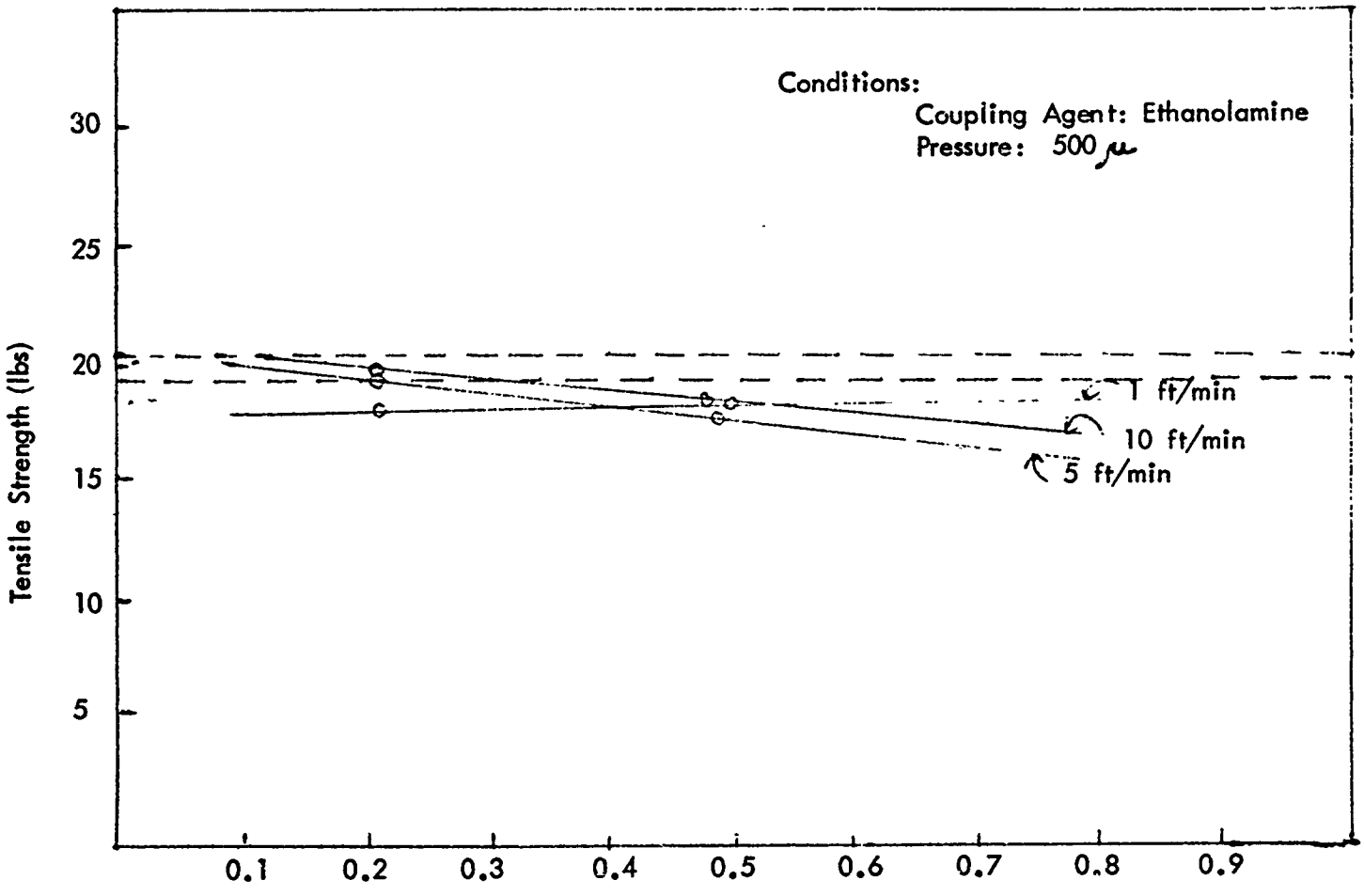

Figure 34 Tensile Strength s Power (Plate Current)

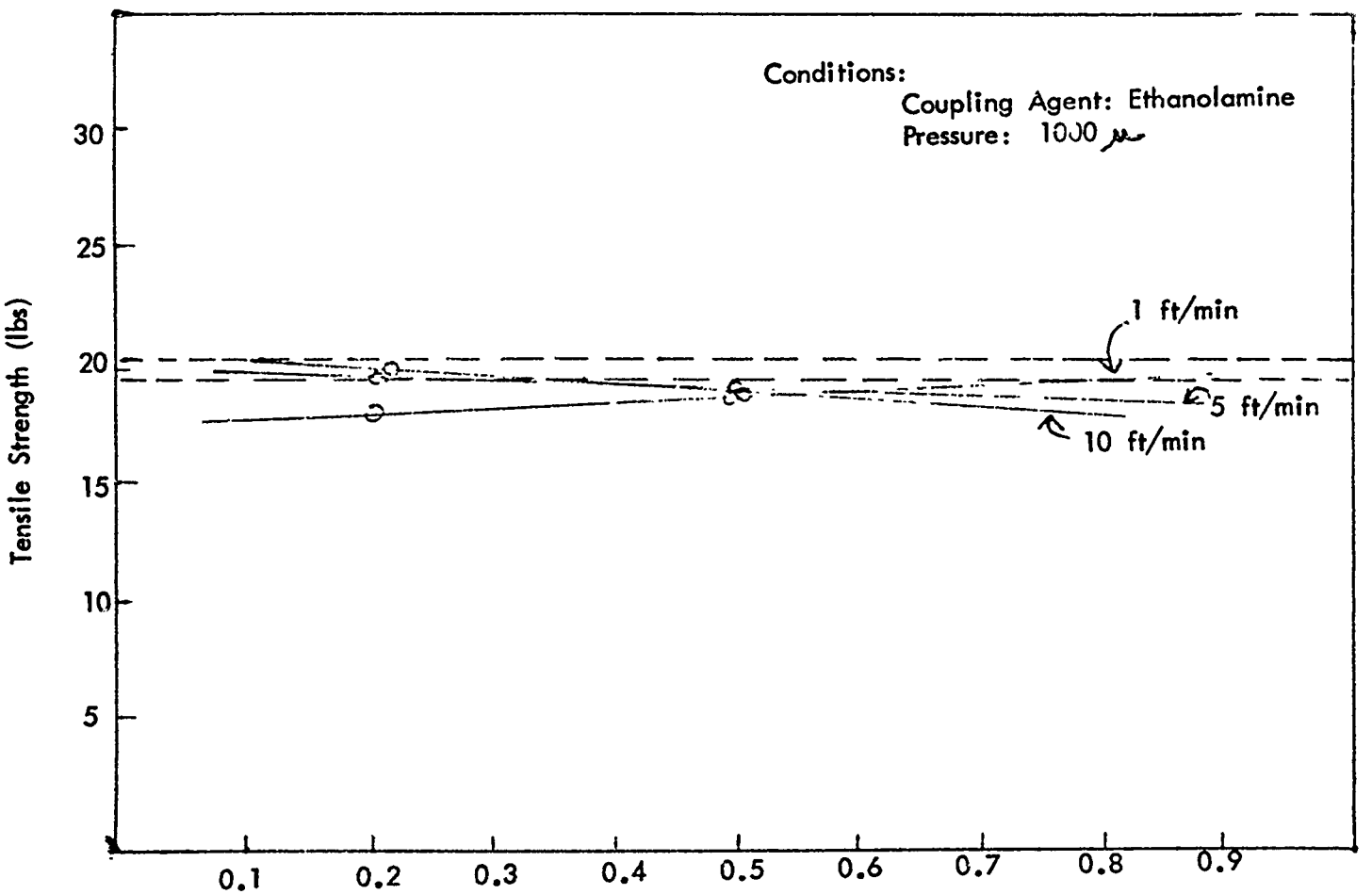

Figure 35 Tensile Strength vs Power (Plate Current)

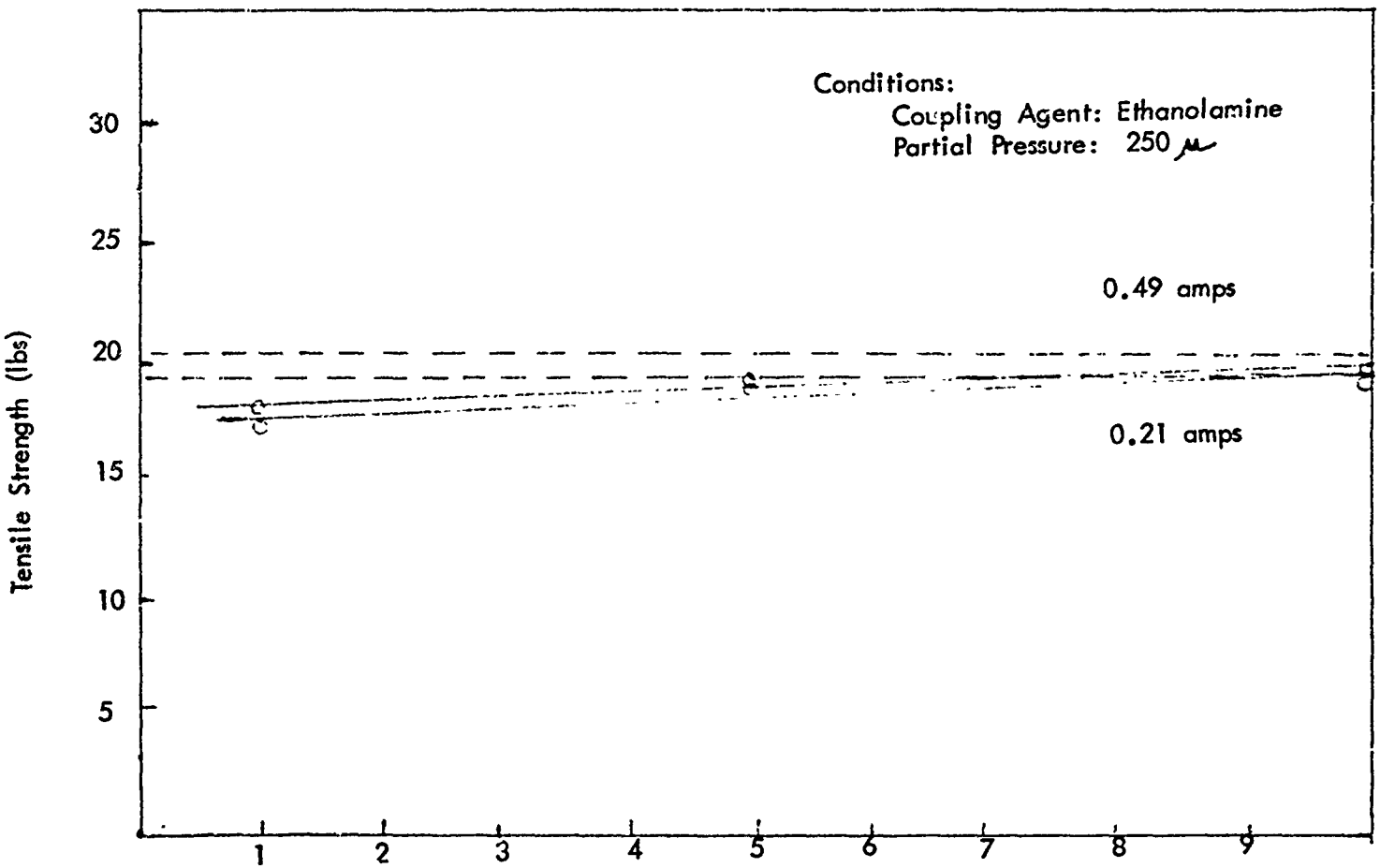

Figure 36 Tensile Strength vs Process Rate

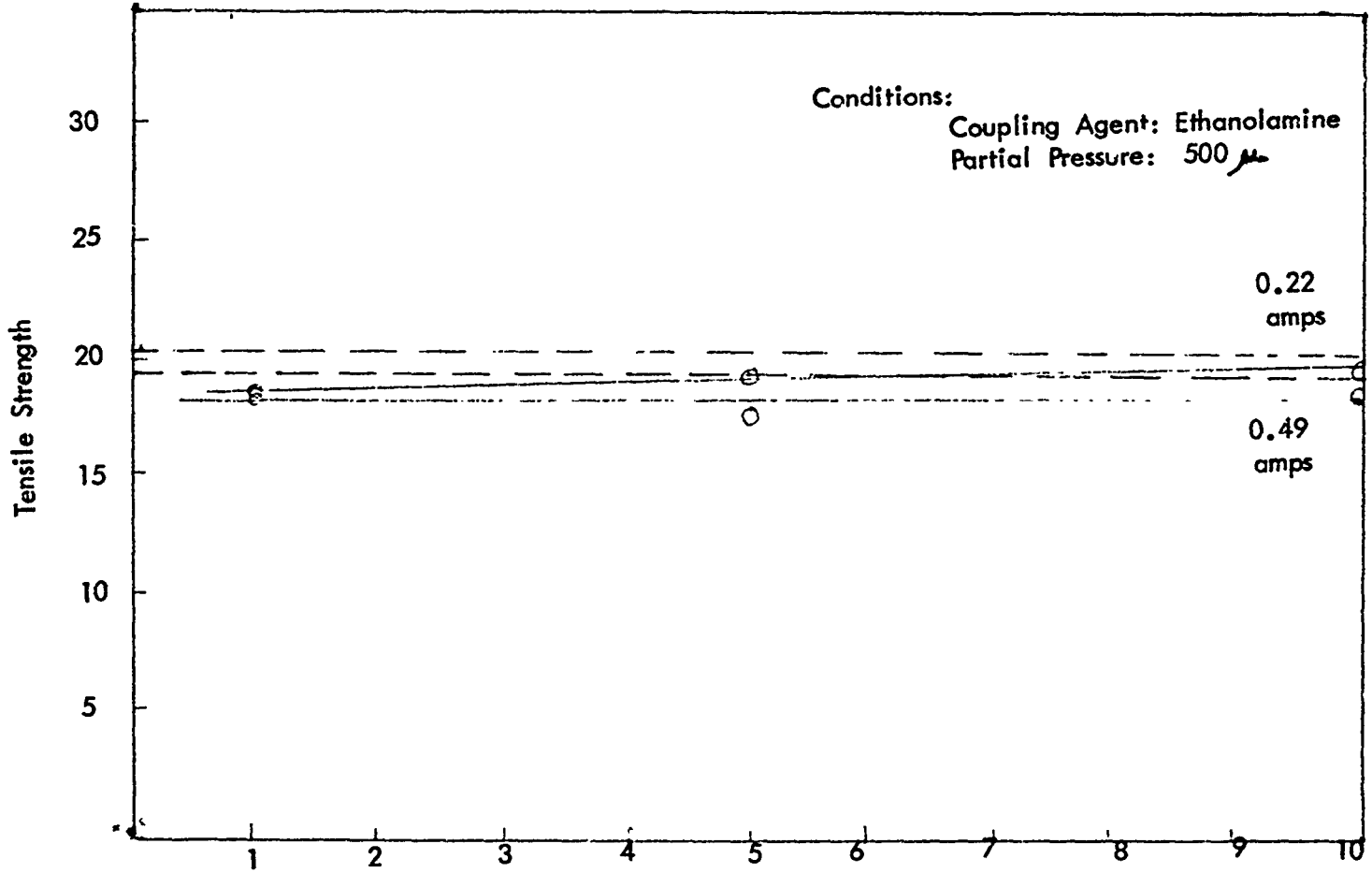

Figure 37 Tensile Strength vs Process Rate

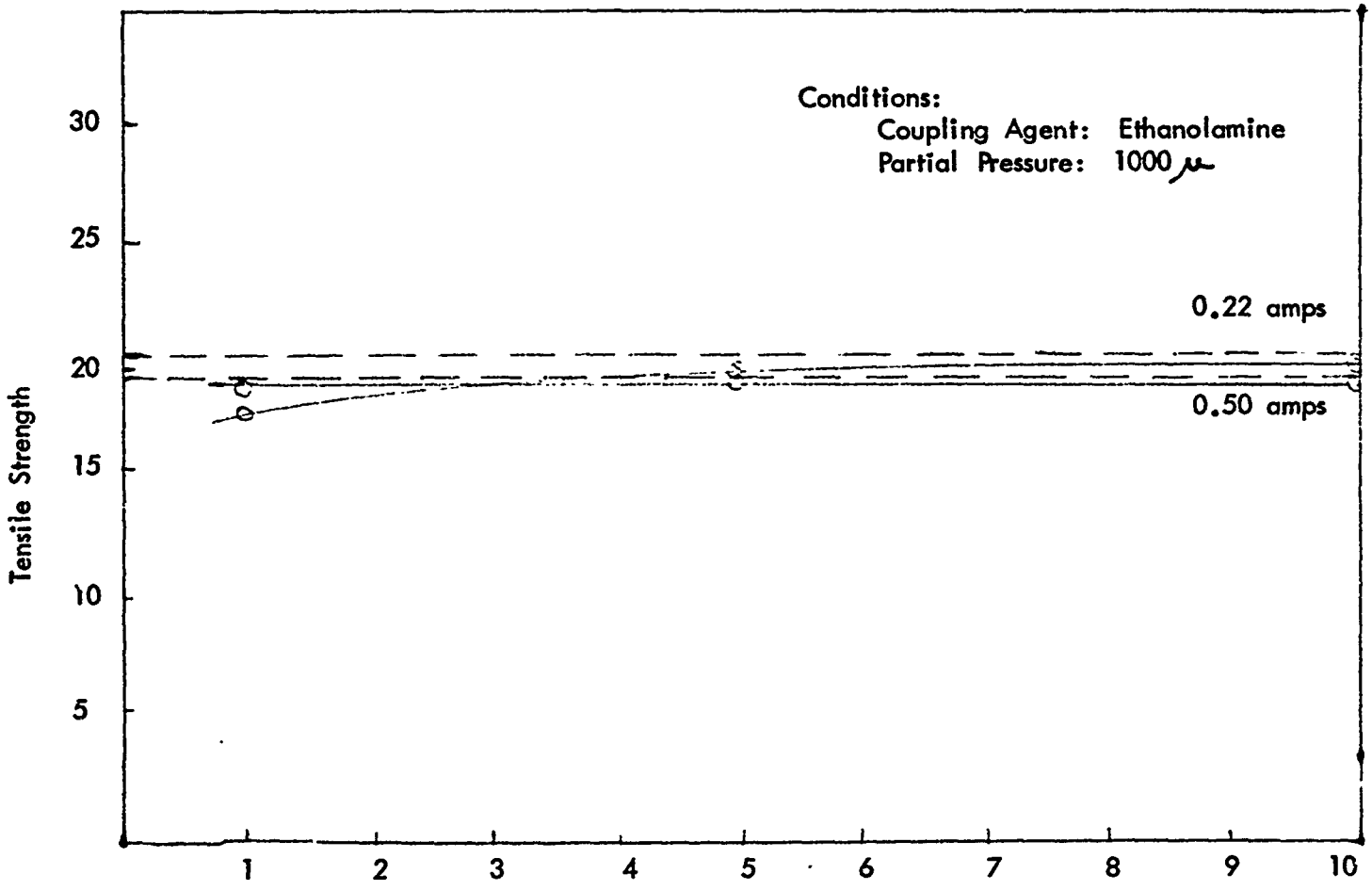

Figure 38 Tensile Strength vs Process Rate

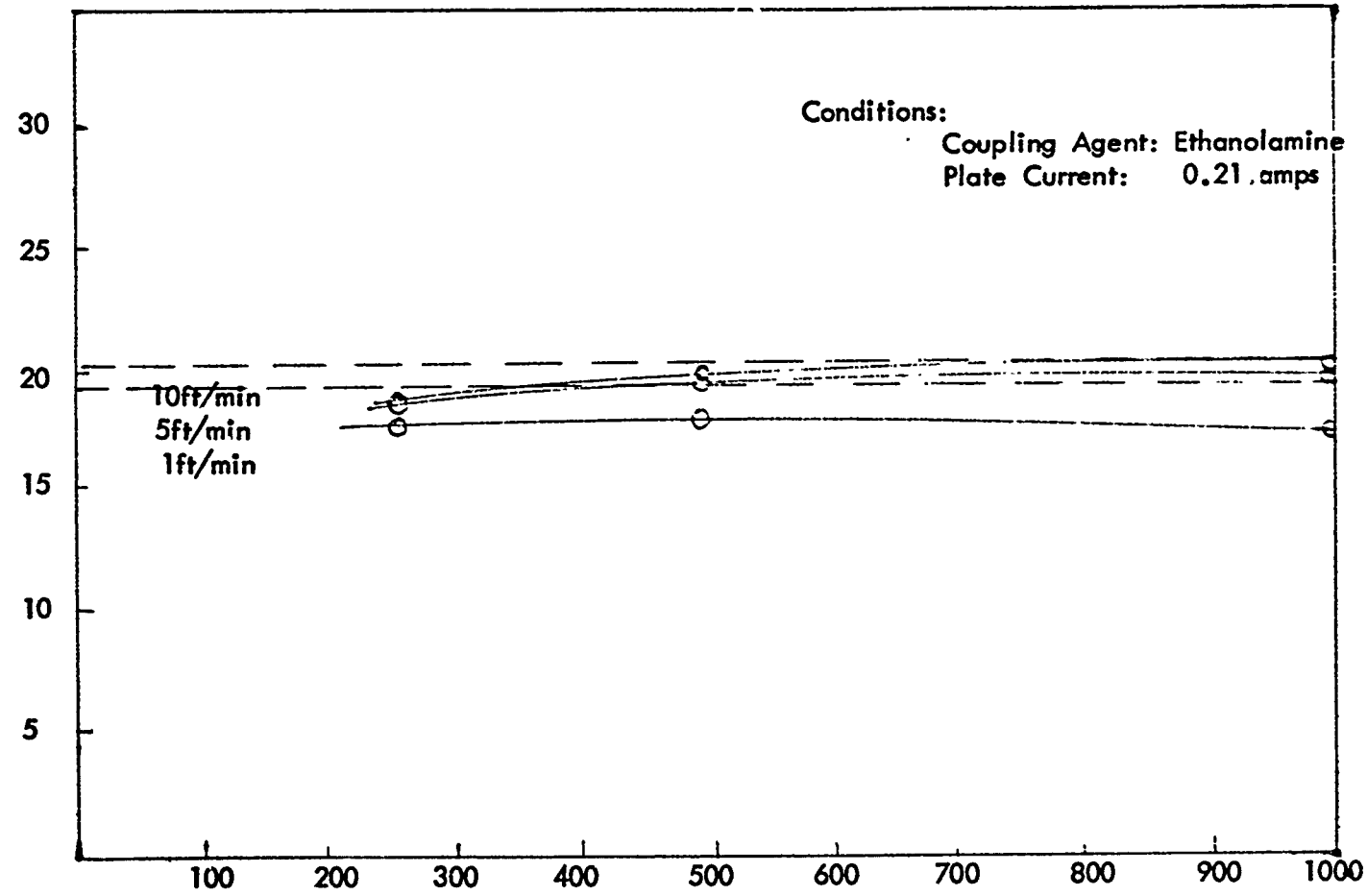

Figure 39 Tensile Strength vs Precursor Partial Pressure

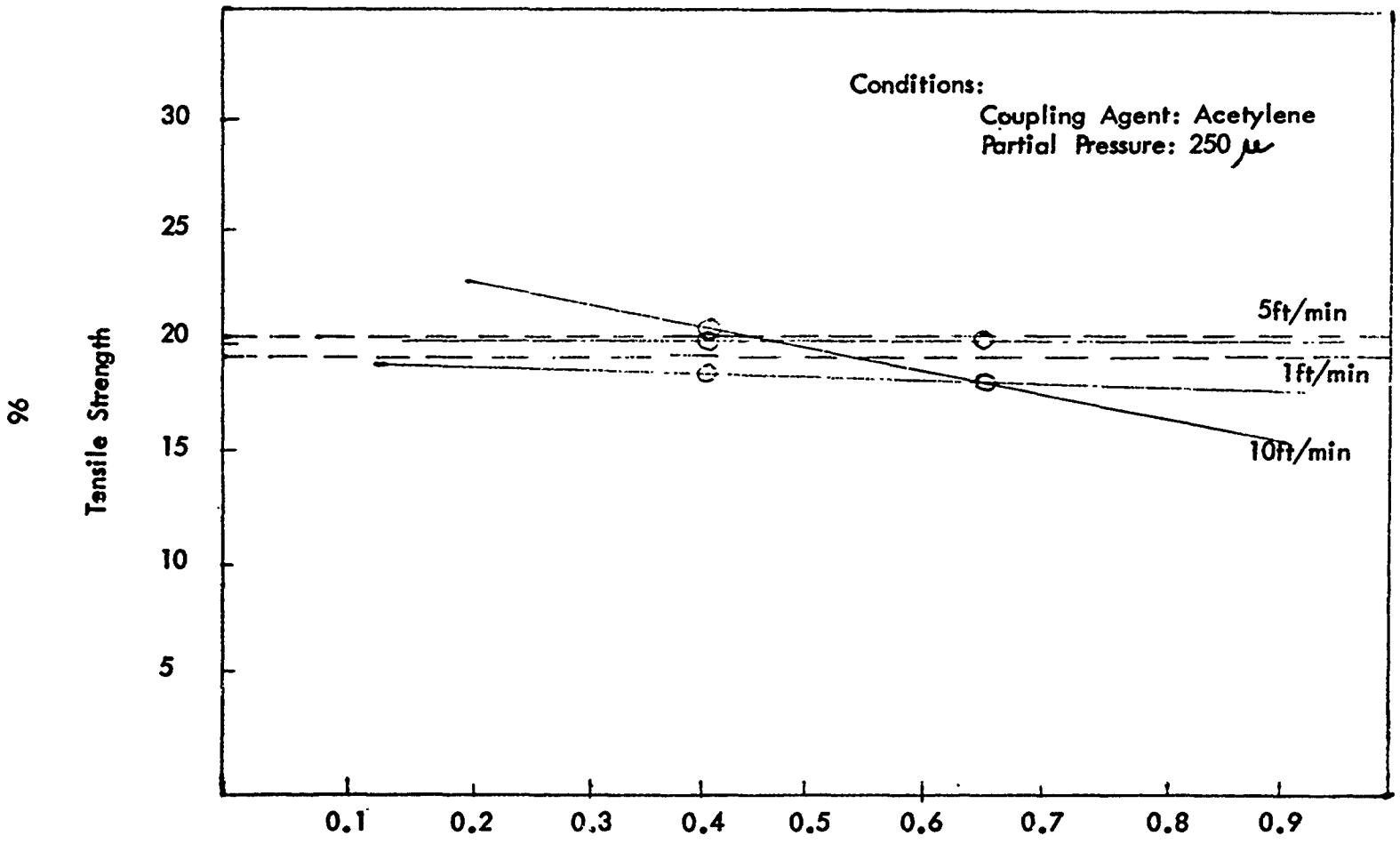

Figure 40 Tensile Strength vs Power (Plate Current)

Conditions:
Coupling Agent: Acetylene
Partial Pressure: 500 μ

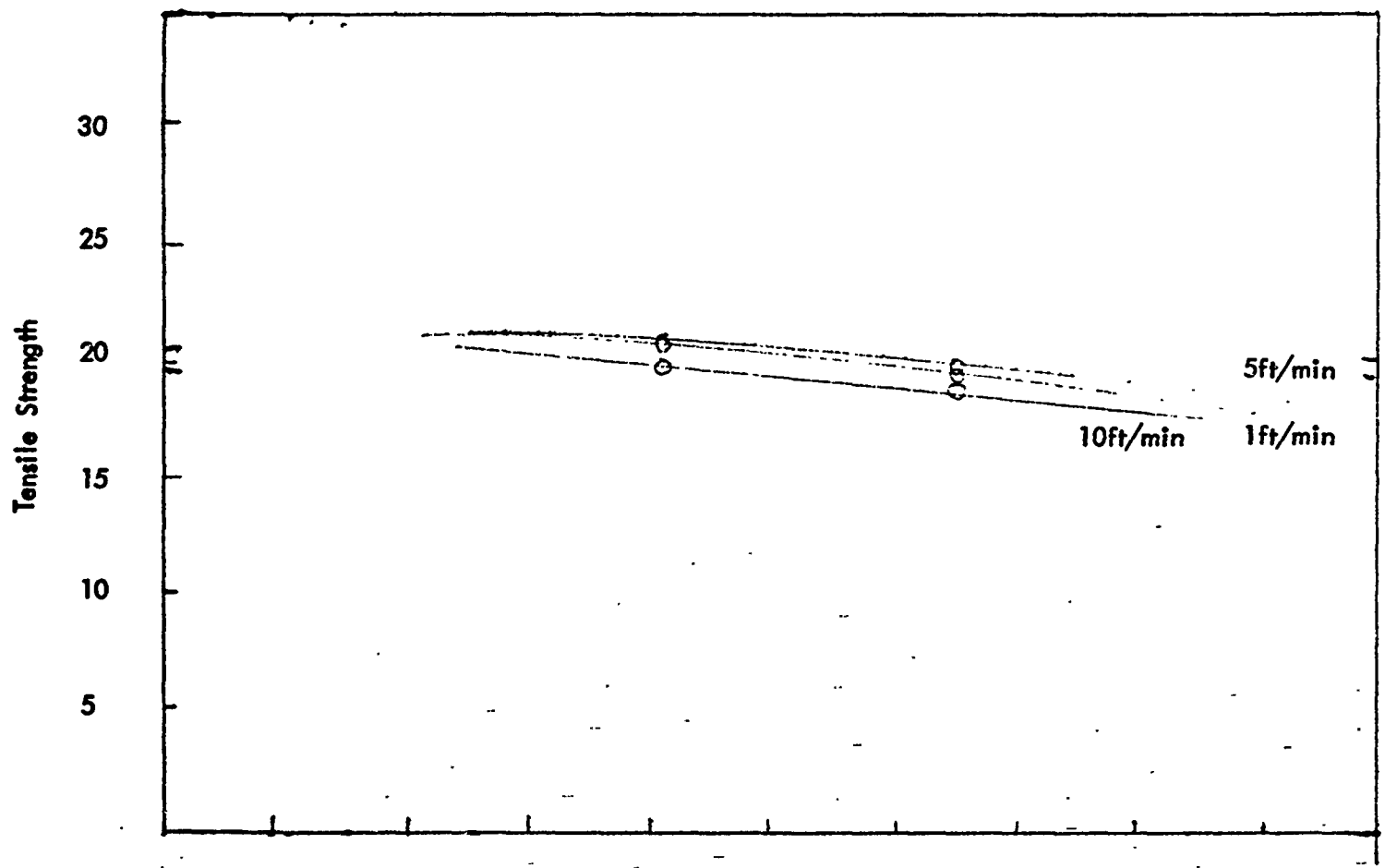

Figure 41 Tensile Strength vs Power (Plate Current)

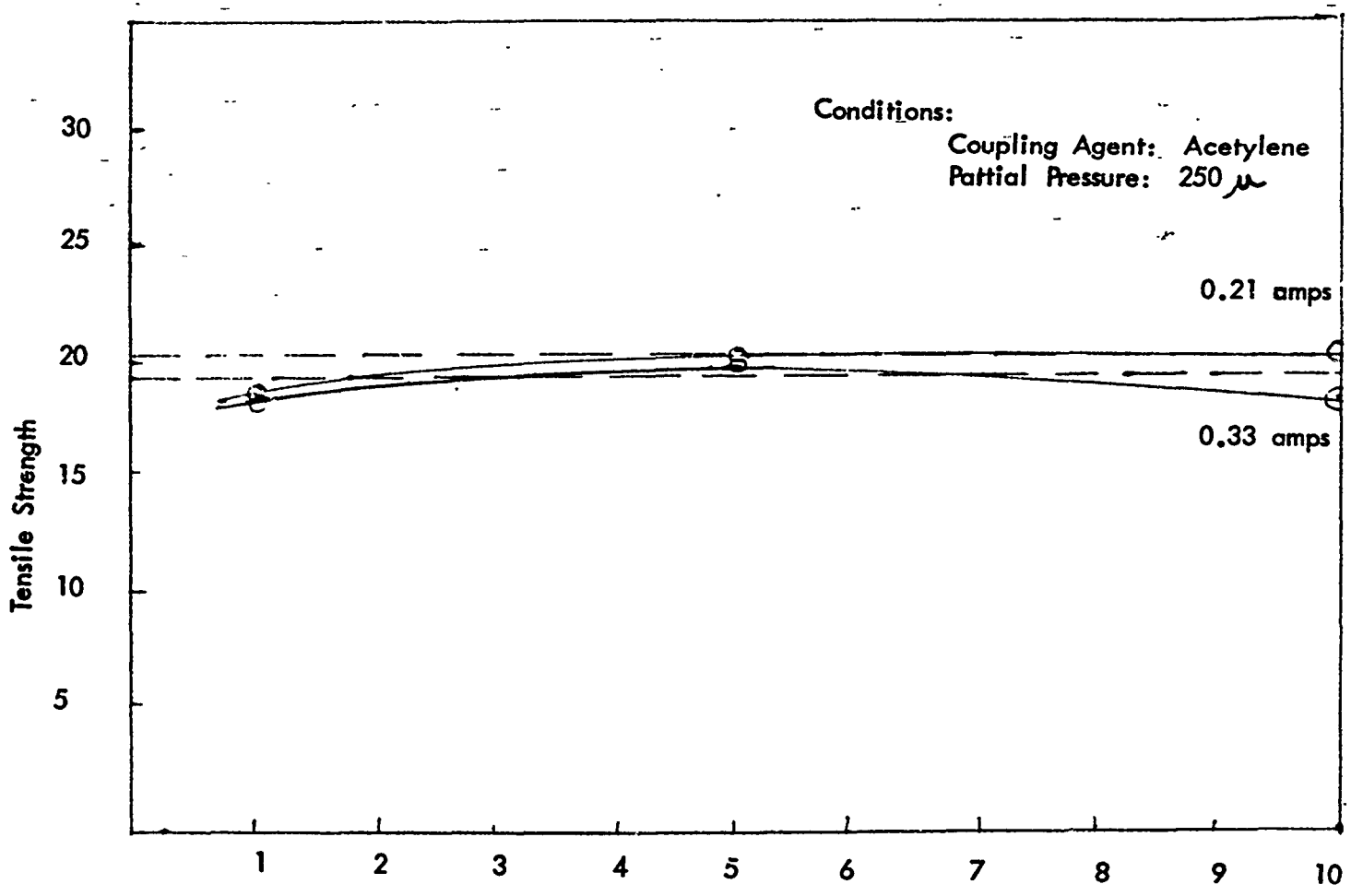

Figure 42 Tensile Strength vs Process Rate

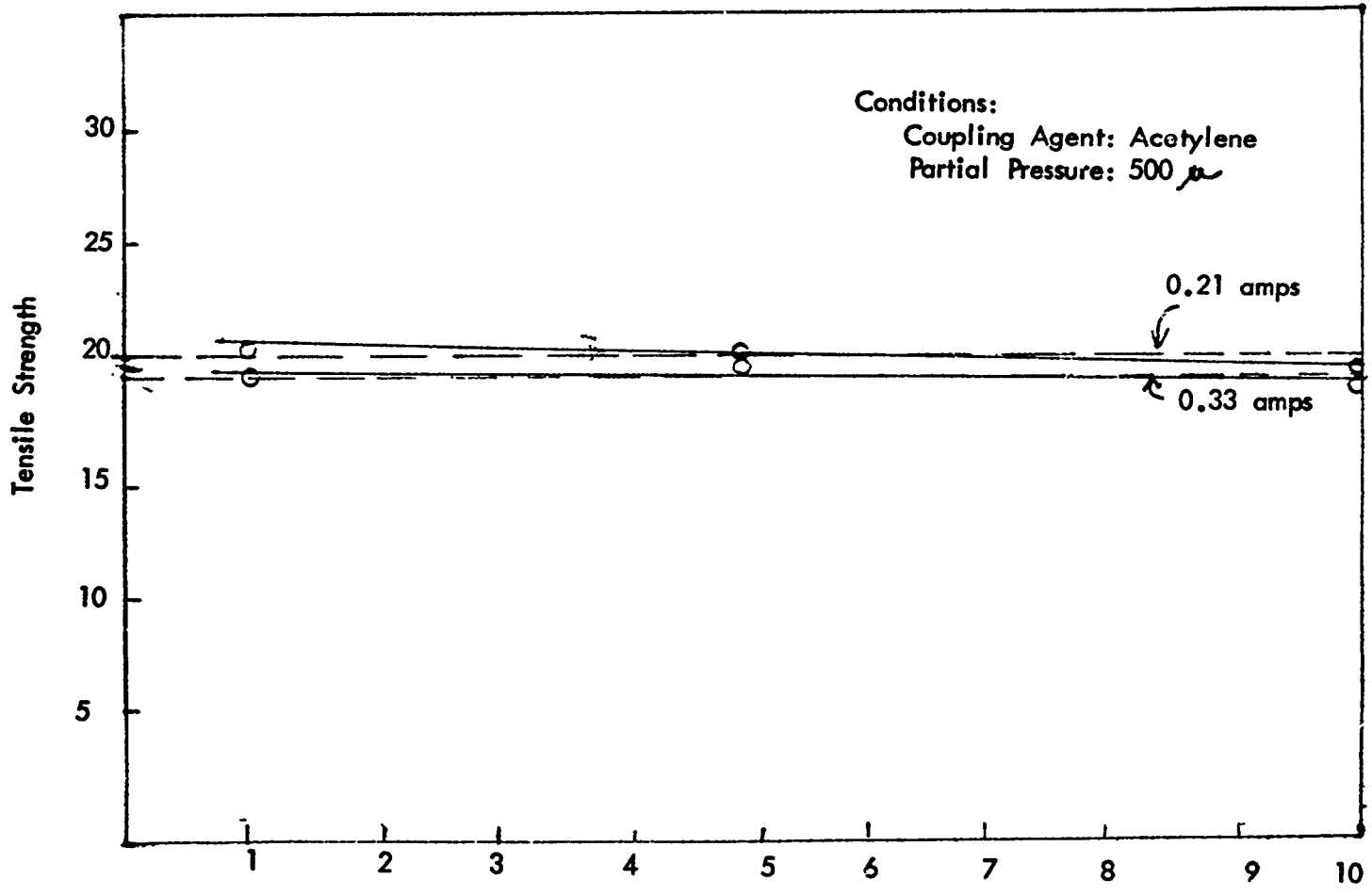

Figure 43 Tensile Strength vs Process Rate

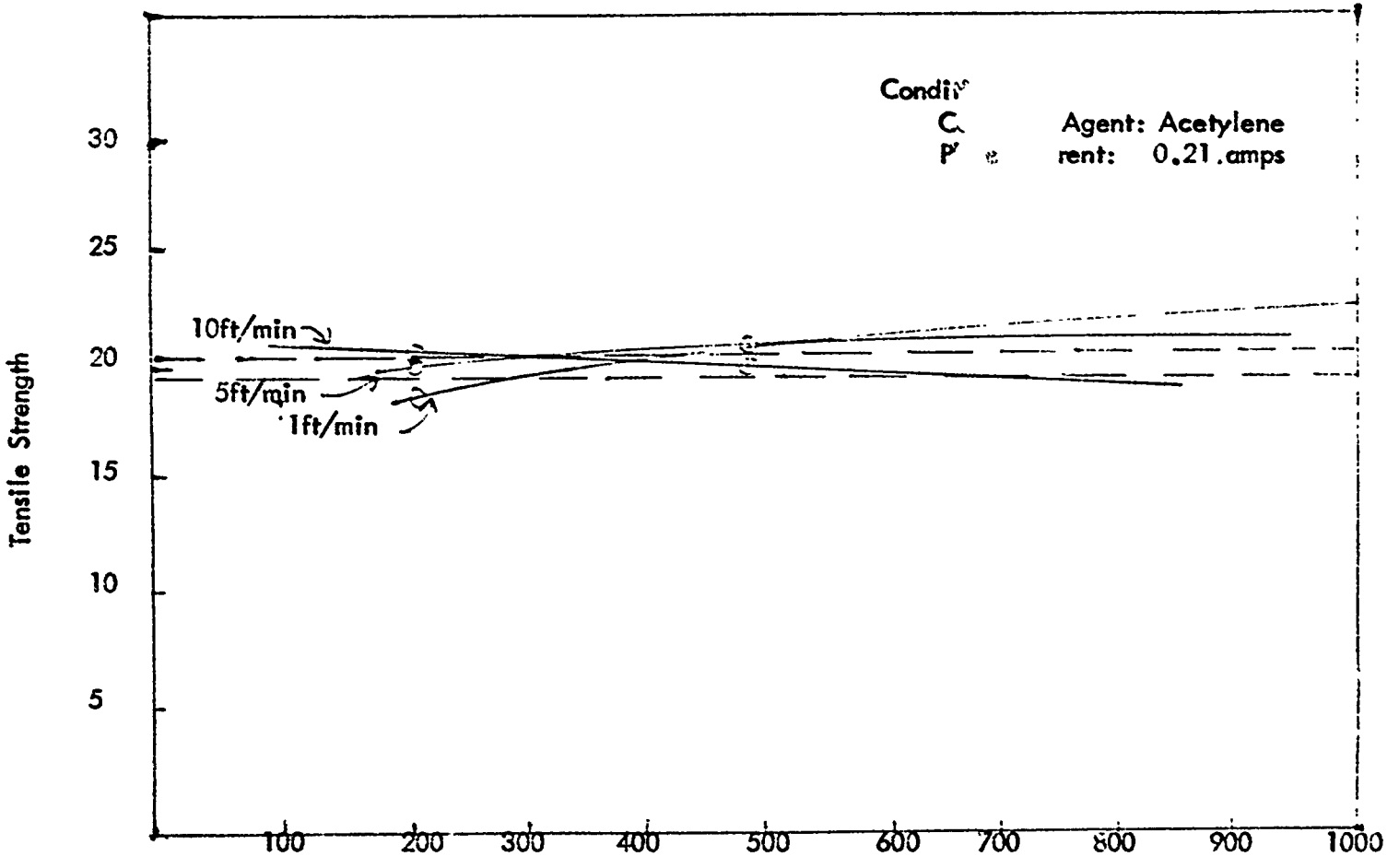

Figure 44 Tensile Strength vs Partial Pressure

6.0 TECHNOLOGICAL FORECAST & FUTURE WORK

The need for lighter, stronger, corrosion-resistant structural materials by the Navy is obvious. The material challenge is being met by the materials engineers through the Development of Composite materials. A composite material is in essence a two component system, the reinforcement which is to carry or support the load while the matrix is to transfer the load and permit fabrication. Such composite materials can be engineered to meet load specifications. An example of this is the design of deep submergence hulls utilizing graphite fiber reinforced plastics (GRP). As with the development of most new materials, certain problems arise which need to be answered.

In the use of GRP material in water under compressive load, one of the limiting factors is the strength of the bond between the graphite fiber reinforcement and the resin matrix. Poor or weak bonding at the interface results in shear failures along the interface of the fiber and resin. This is termed interlaminar shear failure, and it severely restricts a composite structure from obtaining its ultimate compressive strength, and results in premature buckling of the structure. The awareness of the Navy of this problem has led to a number of investigations to better understand the bonding mechanism and to develop methods for intermediate materials to serve as a coupling agent, i.e., a compound that will bond both to the fiber and to the epoxy. Methods have been developed for both cleaning and etching the fiber surface, such as the nitric acid bath, and for applying various agents to the surface of the fibers. These

agents are generally organic compounds containing methoxyl or halogen linkage to bond the surface of the fiber, and contain long alkyl side chains to react, or be compatible with the epoxy resin.

Using the aforementioned approaches, many agents have been developed, but none have been entirely successful as, the interlaminar shear strength of the composites have never realized their theoretical value. An anomaly in the whole process is that in the application of the coupling agent to fiber, water is often used as a solvent. Generally these solutions contain only a few percent of the coupling agents with the remainder being water with the pH adjusted for the compound being used. Though usually heated to dry the fiber, this is not enough to remove all the water from the fiber. In addition, graphite fibers are composed of many filaments in a bundle or strand (1440 ends/inch for Thornel 50, and 10,000 ends/inch for Modmor) and the penetration of the coupling agent solution into the bundle is difficult due to the surface tension effect. What is desired is a process to prepare more active coupling agents and to apply these agents in the absence of water by methods which insure complete coverage of all the filaments in the bundle.

By this Navy sponsored program it has been possible to demonstrate a new and radical approach to cleaning and micro-milling the fiber surface, and to the synthesis of coupling agents that can be deposited and polymerized directly from the vapor phase without the use of solvents. This approach also provides a means for easy diffusion of the coating material throughout the fiber tow. The results from tensile and interlaminar shear tests conducted in this program have conclusively verified the value of this process.

The coating technique has been adapted to impregnate the coated graphite fiber with resin while in the vacuum chamber before the fiber is wound on the mandrel. This modification drastically lowers the void content of the resin and reduces the likelihood of fiber contamination. With this coating process it is entirely feasible to handle and treat woven cloth as well as roving or yarn which provides the Navy with a large number of potential usages.

This work contributes to the understanding of the adhesion bonding of the graphite fiber to the organic matrices and particularly to the interface layer. Considerable effort has been expended on this program and it is felt that the following areas need more investigation to give pertinent information in this field.

(1) Investigation of the maximum traverse rates in the 2450 MHz plasma to make the plasma reactions more amenable for production purposes.

(2) Extensive effort should be directed towards the investigation of better coupling agents. Present work indicates that unsaturated compounds containing the amino-hydroxyl groups would yield polymeric materials which should be compatible with an epoxy resin matrix.

(3) Investigation should be made into the area of combining the 2450 MHz plasma and the 450 KHz plasma into one process since the 2450 MHz plasma has shown its ability to clean the fiber surface, and the 450 KHz has shown its ability to deposit amorphous polymeric materials from the respective monomers.

Additional work is needed as indicated above to move this process from the research phase to the development stage where production rates, quality control, operating costs can be ascertained and where small GRP structures can be prepared and tested. The use of Commonwealth Scientific Corporation's coating technology may also be considered as a possible means of grafting to polymeric films and for special protective coatings on conductors and non-conductors. Many of these potential users of the coating concept would encompass the electronic industry, the textile and printing industries, as well as the composite structure fabricator.

7.0 BIBLIOGRAPHY

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2. Duhamel, A. P., Nelson, L. D., Divecha, A. P. and Bazzarre, Frank D. "Improvement of Interlaminar Shear Strength in Organic Matrix Composites Utilizing Plasma Deposited Coupling Agents:" Fifth Quarterly Progress Report (Contract N) 17-70-C-4439) April 1, 1971 to July 1, 1971.

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