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Effects of Some Commercial Enzymes in the Deinking of Newsprint

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EFFECTS OF SOME COMMERCIAL ENZYMES IN THE DEINKING OF NEWSPRINT

by

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ABSTRACT

The trend of industry, in general, today is one of recycling. This is brought about as a means of conserving our dwindling natural resources and to help abate the pollution problem.

The design of this paper is to see if enzymes can be used successfully and economically in the deinking process of newsprint. Varying concentrations of enzymes, both an amylase and a protease, and a biodegradable detergent were used in a handsheet study. Temperature and pH were controlled so as to not denature the enzymes. It was found that the brightness increase was only minimal with a protease and the brightness actually decreased with an amylase. The physical strength characteristics were also found to decrease with the addition of the enzymes.

Therefore, it was concluded that there is very little prospect of enzymes being used in the deinking process to increase brightness or to strengthen the physical properties of newsprint.

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INTRODUCTION

In 1943, A.G. Wakeman (1) stated a need for 15 million tons of raw paper pulp but that only 8.5 million tons of virgin pulp was available. This would mean forcing the use of waste paper and other waste fibers up to the limit and further down-grading of paper quality. A similar idea was expressed this same year, 1943, by G.T. Jubb of the Kalamazoo Paper Company (1). Since then, this need has multiplied making it necessary to find new methods for facilitating the recycling of waste paper.

One such direction has been with the use of enzymes in various paper making processes. In particular, the use of enzymes in the deinking of waste paper.

Very little research work has been done in this field. In 1961, the effects of enzymes on coated magazine stock was studied by E.E. Moore (2) but yielded only negative results. In 1971, a study of enzymes and deinking of newsprint was conducted by Peter Alyward (3). But due to a lack of proper controls, the results are considered rather inconclusive. There has been no other published work on this subject that could be found.

Therefore, virtually no previous guidelines existed with which to judge the merits of these experiments. With the use of enzymes being relatively new to the paper industry and still not completely understood,

it was decided to use both a commercial amylase and protease to find the effects, if any, of each.

Deinking

Deinking is the removal of non-fibrous constituents from waste paper (4). These non-cellulosic materials comprise 1% to 50% of the total weight of waste paper of which ink is but 1% to 2%.

Today's printing news inks consist of limed rosin 12%, refined kerosene 47%, mineral oil 15%, industrial grade grease 20%, carbon black 3%, furnace black 3% (10). This combination gives a quick drying, cheap ink. But in the same sense is one of the hardest inks to remove due to its tackiness.

There are six things necessary in the deinking process: (1) alkali to saponify ink vehicle, (2) detergent, (3) dispersing agent to prevent agglomeration, (4) softening agent to dissolve synthetic resins, (5) agent for selective adsorption to prevent redisposition and, (6) agent to prevent formation of calcium soaps. It is hoped that the enzymes can help facilitate steps (1) and (4).

The presently accepted method of deinking newsprint is with hot alkali. This is done at 170° - 180° fahrenheit for about 1 hour. A lower temperature is more desirable but takes much longer to soften and remove the ink. Another important factor is agitation. Constant mixing is essential so as to be able to remove all of the ink and to avoid redeposition of the liberated ink.

The major disadvantage of this type of deinking is that the pH is lowered due to the formation of sodium hypocarbonate:

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

This in turn raises the oxidation potential and results in poorer deinking. Also, these hot weak alkalis tend to dissolve cellulose and in general darken lignin in groundwood. Therefore, zinc hydrosulphite must be added to raise the brightness.

With the use of enzymes, no caustic will be present and the experiment will be done at a much lower temperature, thus hoping to eliminate the bad features of deinking mentioned above; darkening of the lignin, use of zinc hydrosulphite, dissolving the cellulose. The lower temperature cook could also indicate a steam cost savings.

Enzymes

In 1870 (5) two schools of thought had arisen concerning enzymes: the vitalism theory by Pasteur which assumed that enzymatic reactions required the presence of living cells. The other was proposed by Liebig which assumed that enzymes were just complex chemicals. In 1878 Kuhne gave the name "enzyme" to biological catalysts which comes from the Greek words for "in yeast" since yeasts were the principle biological catalysts first studied (5).

A big break-through came with the experiments of Buchner in 1897 (5). Buchner ground and filtered yeast cells and was then able to ferment sugar with the filtrate. Upon microscopic examination, he determined the filtrate contained no cellular constituents thus disproving

the vitalism theory. In 1894 Emil Fischer formulated a theory, that the substrate for an enzyme fitted into a cavity on its surface, like a key fits into a lock. Once the "key" is in the lock (6) then groups on the enzyme would catalyse the reactions. There are three concepts implied by this theory. The first, that compounds of a different shape from the substrate will not fit into the lock of the enzyme and the reaction will not be catalyzed. This is an explanation of specificity. The second being that compounds of similar shape and size to the substrate will fit into the "lock" and prevent any catalyzed reactions. This idea of inhibitors was later verified by Armstrong in 1904 (6). The third implied concept is that there is an active site on the enzyme surface where the catalyzed reaction occurs.

There is a complexing between the substrate and the enzyme prior to reaction which implies that there is a saturation effect on these active sites.

Enzymes have been defined as proteinacious catalysts used in biochemical processes. This definition has been slightly altered through the years since now enzymes can be used in processes other than biochemical processes. But they still remain a protein-type catalyst. A catalyst being a substance which can speed up a reaction but remain unchanged at the end of the process although it may first form an activated Eyring complex, followed by a thermodynamically stable enzyme-containing compound before being regenerated into the enzyme and the final product. This definition was later restated by Bell in 1941 (5), a

catalyst is that substance whose concentration occurs in the velocity expression to a higher power than it does in the stoichiometric equation.

A catalyst functions by formulating a more efficient pathway by which substrates can be converted into products. There are two basic reasons behind this lower energy of activation for an enzymatically catalyzed reaction. They are classified as proximity and orientation effects (6). The proximity effect is the attraction between a catalyst and two or more substrates which increases the concentrations of the two substrates relative to each other. This in turn increases the chance of a reaction. The orientation effect is a binding of the substrates to the enzyme which orients the substrates relative to one another. This tends to form the proper spatial arrangement for interaction between the substrates. It should not be misunderstood that these are the only forces acting during the reaction but that these are the two basic forces acting on the substrates by the enzyme during the entire reaction.

A convenient method for studying reactions which are enzymatic in nature is to study their rate reaction constants and their orders. For enzymatic reactions it was found frequently that the rate was dependent upon the substrate concentration [S] according to the law, $v = \frac{a\,[S]}{1 + b\,[S]}$. In this case the reaction cannot be said to have an order. At other conditions it was found that the reactions were of the zero-order or of the first-order type. The reaction order would depend on the

concentration range. Therefore, the rate of an enzyme reaction is usually proportional to the concentrations of the enzyme and the substrate but becomes independent of the concentration of the substrate as the substrate concentration increases (6).

The enzyme reaction which was first studied was that of a single substrate. It followed the general reaction path:

$$(1)\quad [E] + [S] \underset{K_2}{\overset{K_1}{\rightleftharpoons}} [ES] \xrightarrow{K_3} [E] + [P]$$

where [E] is the enzyme, [S] the substrate, [ES] the enzyme complex, and [P] the product. This equation is rewritten in the form:

$$(2)\quad [E] + [S] \xrightarrow{K_m} [ES] \xrightarrow{K_o} [E] + [P]$$

From this form, the Michaelis-Menten rate law is derived.

$$(3)\quad V = \frac{[E]\ Ko\ [S]}{[S] + K_m} \qquad \text{where } Km = \frac{[S]\ [E]}{[ES]}$$

where V is the initial rate of reaction and Km is a pseudo equilibrium constant equivalent to the concentration of the substrate which gives a rate equal to 1/2 V maximu. This Michaelis constant (6) can be re-written from equation (1) as:

$$(4)\quad Km = \frac{K_2 + K_3}{K_1}$$

The Michaelis-Menten equation which is also called the Henri equation gives a value of the variation of the rate with substrate concentration, at steady state conditions. This variation is again a function of concentrations and is directly proporational to what is termed the turnover, Ko, which is the number of moles of substrate changed per mole of enzyme per second. It should be noted at this point that the

Michaelis-Menten equation only holds true for reactions which follow the path of equations (1) or (2).

For enzyme reactions which involve two substrates, the reaction path is as follows:

$$[S_1] + [E_o] \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [E_1] \qquad [S_2] + [E_o] \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} [E_2]$$

$$[S_2] + [E_1] \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} [E_3] \qquad [S_1] + [E_2] \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} [E_3]$$

$$E_3 \xrightarrow{K_5} E_o + [P]$$

The stead-state equation for this type of reaction is:

$$V = \frac{a(X)^2 + bX + c}{f(X)^2 + gX + h}$$

where X can refer to either $[S_1]$ or $[S_2]$ with the coefficients depending on which X is chosen. With the addition of more substrates, the rate of reaction increases in complexity but still remains a functions of the concentration of substrates.

There are three major factors which influence the rates of enzymatic reactions. These are the pH of the solution, the temperature and the concentrations of any inhibitors present. Both temperature and pH are not well understood as to how they effect enzyme reactions except that there is an optimum value over a small range for each reaction. The two do appear to be interrelated. There are two types of effects by inhibitors. Noncompetitive, in which the fractional decrease in velocity is due only to the amount of inhibitor added and not on the concentration

of the substrate. The other is competitive, in which the decrease in velocity is in a direct proportion to the concentration of the inhibitor and an indirect proportion of the concentration of the substrate. This type of inhibitor saturates the reactive sites of the enzyme and has a dissociation constant K_I defined as:

$K_i = \frac{[E]\ [I]}{[EI]}$ where [EI] is the reaction product between the enzyme and the inhibitor.

There are six basic classifications of enzymes. Before mentioning these types, it should be made clear that these classifications are very general and that some enzymes fit several of these groups. The first are the hydrolytic enzymes which follow the reaction path; $AB + H_2O \rightarrow AOH + HB$. The subclassifications of this group are the proteolytic which catalyze the hydrolysis of the peptide linkage, the carbohydrases which catalyze the hydrolysis of the glycosidic linkage, the esterases which hydrolyze esters to their corresponding acid and alcohol, and deaminases which catalyze the hydrolysis of amines. The second general classification are the phosphorylases which are the phosphate analogues of the hydrolytic enzymes.

The third type, oxidative enzymes, are concerned with oxidative processes. These enzymes include the dehydrogenases, oxidases, and oxidative deaminases to name a few.

The adding enzymes, the fourth type, follow the reaction path: A + B AB. Since enzymes catalyze reactions equally in both directions, these enzymes are also known as splitting enzymes and reverse the

reaction; AB A + B. The fifth group, transferring enzymes, catalyze reactions in which groups are interchanged between molecules; AB + CD AC + BD.

The sixth group is the one of the isomerizing enzymes which catalyze various types of isomerization processes. This is by far not an exhaustive list but is merely a guideline of the types of enzymatically catalyzed reactions which are available today.

EXPERIMENTAL PROCEDURE

The purpose of this project was to determine the effectiveness of enzymes in the deinking of newsprint. The enzymes used were Vanzyme and Vanzyme 133, and amylase and a protease respectively, manufactured commercially by the R.T. Vanderbilt Company, Inc.

Three controls were maintained during the experiment. The pH was held at 8.0 which was recommended for the use of the enzymes; the temperature was held between 120° - 130° fahrenheit so as to not denature the enzymes; the same issue of newspaper was used so that the ink content did not vary.

Varying amounts of detergent and detergent with enzymes were then added to disintergrated news pulp where it was heated and agitated for 1/2 hours. Then the pulp was throughly washed and eight Noble and Wood handsheets were made. Physical and optical tests were then run to determine the effect of the enzymes.

Experimental Work

Materials

Detergent:	DRIVE - no enzyme, low phosphate, bio-degradable
Enzymes:	Vanzyme - amylase
	Vanzyme 133 - protease
Newsprint:	Western Herald - school newspaper

Equipment

Disperser: TAPPI disintegrator

Washing: 100 mesh filter screen

Sheet Making: Noble and Wood Sheet Machine

Experimental Method

The newsprint was torn into small strips and soaked in water for 1/2 hour. A TAPPI disintegrator was used to repulp the newsprint. A heating mantel and Variac were used to maintain a constant temperature. A blender was used for agitation during the 1/2 hour "cook" portion of the trial. Soap was added in amounts of 1%, 5%, 10% by weight of dry fiber in the sample. The two enzymes were added in amounts of .5%, 1%, 1.5% in combination with the soap. The enzymes were also by weight of dry fibers in the sample.

At the end of the 1/2 hour, the pulp was throughly washed on a 100 mesh filter screen. The pulp was then redispersed and eight three gram Noble and Wood handsheets were made. The handsheets were dried on a rotary drum dryer at 250° fahrenheit and then placed in a constant temperature and humidity room for three days before testing.

Testing

Brightness, printing opacity, tear, tensile, and mullen tests were conducted on the Noble and Wood handsheets. TAPPI standard tear and mullen tests were used. The INSTRON was used in the tensile testing. It was set at a 10 kilogram full scale load.

A digital read-out General Electric brightness meter set on filter #1 was used in the brightness test. This same brightness meter set on filter #15 was used to determine printing opacities.

DISCUSSION

As can be seen from Figure 1, with increasing amounts of protease enzyme added, there was a slight increase in brightness when compared to the control handsheet, no enzyme added. From Figure 2, it can be noted that with an increase in the amylose enzyme added, the brightness decreases. In both cases, neither change was of a significant amount.

The printing opacity (Figures 3 and 4) in both cases decreased slightly indicating the removal of the ink bodies from the interior of the handsheet. Again, nothing of great significance.

From Figure 5 through 10, it is evident that with the addition of either enzyme strength properties; tear, tensile, mullen, decrease. It is believed that the protease enzyme, which normally solubilizes proteins to peptides (9), is attacking the long carbon chain bonds of the cellulose and that the amylase enzyme, which acts upon starches by partially converting them to soluble dextrins (9), is attacking the inverted starch bonds between the cellulose molecules. In either case, it appears that the enzymes are attacking the cellulose instead of liberating the ink which causes the decrease in strength properties.

CONCLUSION

With only a minimal increase in brightness with the use of a protease and a decrease in brightness with the use of an amylase, which is probably caused by a complex formation between the enzyme and lignin, there is very little prospect of enzymes being used to advantage in a deinking process.

Also, with the decrease of the physical strength properties, which cannot be tolerated in newsprint, I can see no application of these two enzymes, Vanzyme and Vanzyme 133, in the specific use of deinking newsprint.

DATA *

	Brightness	Printing Opacity	Tear	Tensile	Mullen
1% soap	46.2	95.2	37.5	3.98	7.0
5% soap	49.5	95.8	40.2	3.85	7.6
10% soap	51.3	95.8	42.0	3.95	8.4
Vanzyme 133-Protease					
1% soap - .5% enz.	46.2	94.8	37.3	3.30	5.7
5% soap - .5% enz.	49.8	95.8	37.9	3.80	6.9
10% soap - .5% enz.	51.5	94.8	38.0	3.46	6.7
1% soap - 1% enz.	46.5	95.9	36.0	2.85	7.2
5% soap - 1% enz.	49.5	95.6	38.0	3.69	6.6
10% soap - 1% enz.	51.4	94.5	38.8	3.50	6.5
1% soap - 1.5% enz.	47.2	94.3	37.0	3.11	5.4
5% soap - 1.5% enz.	50.0	94.4	41.5	3.52	5.8
10% soap - 1.5% enz.	51.0	94.4	35.8	3.28	6.7
Vanzyme - Amylase					
1% soap - .5%	47.2	96.0	35.1	3.13	5.9
5% soap - .5%	49.5	94.2	35.3	2.97	4.8
10% soap - .5%	51.1	95.1	39.3	3.69	7.0
1% soap - 1%	47.5	95.9	41.0	4.33	8.5
5% soap - 1%	48.7	95.8	32.5	3.51	5.1
10% soap - 1%	50.4	94.0	35.5	2.71	4.2
1% soap - 1.5%	47.1	95.6	35.8	3.80	6.2
5% soap - 1.5%	49.9	94.6	37.2	3.25	5.9
10% soap - 1.5%	49.7	93.6	39.0	3.59	7.3

*Average of eight handsheets

FIGURE 1

BRIGHTNESS VS. % SOAP

VANZYME 133 - PROTEASE

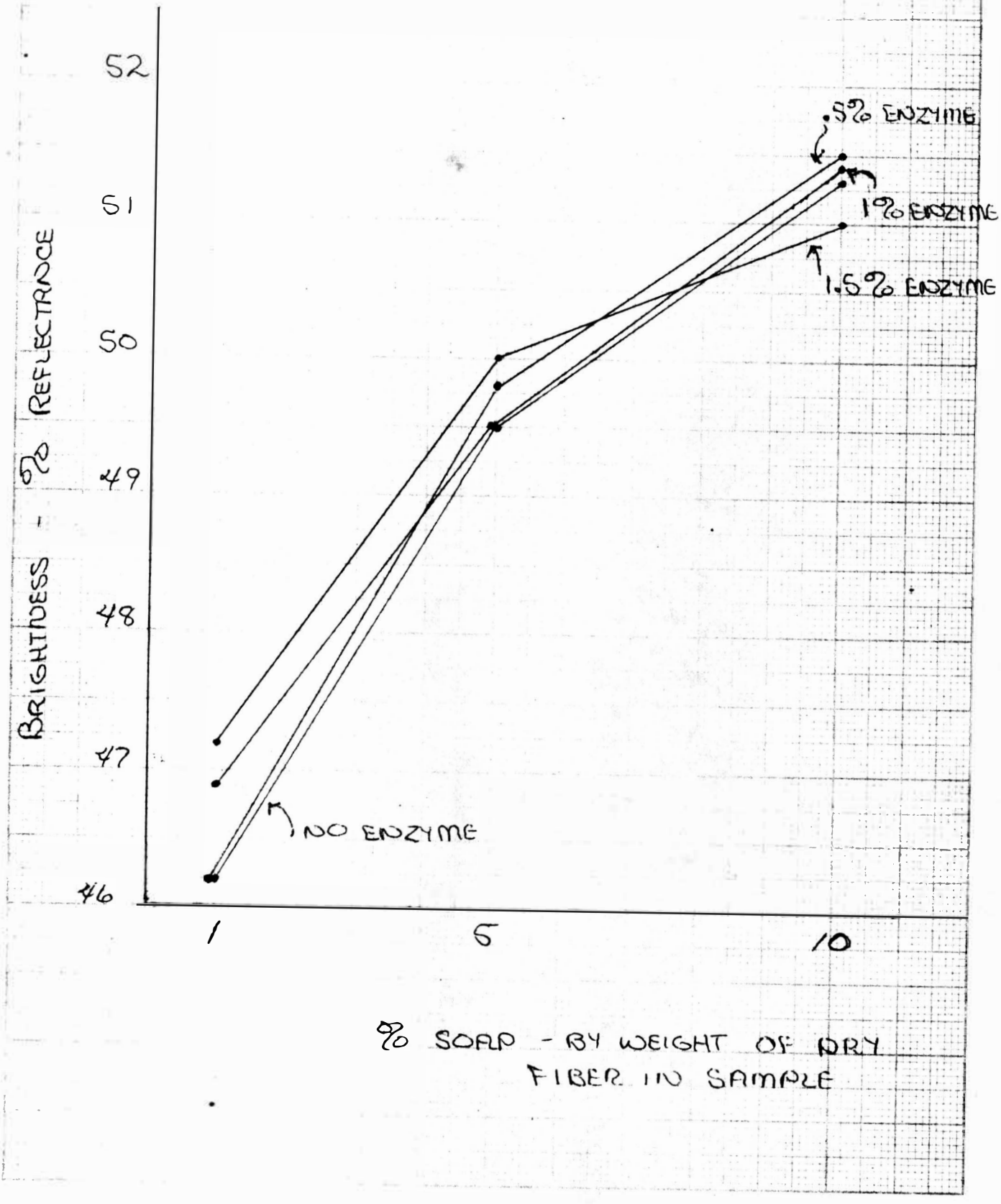


FIGURE 2

BRIGHTNESS VS. % SOAP

VARIOZYME - AMYLASE

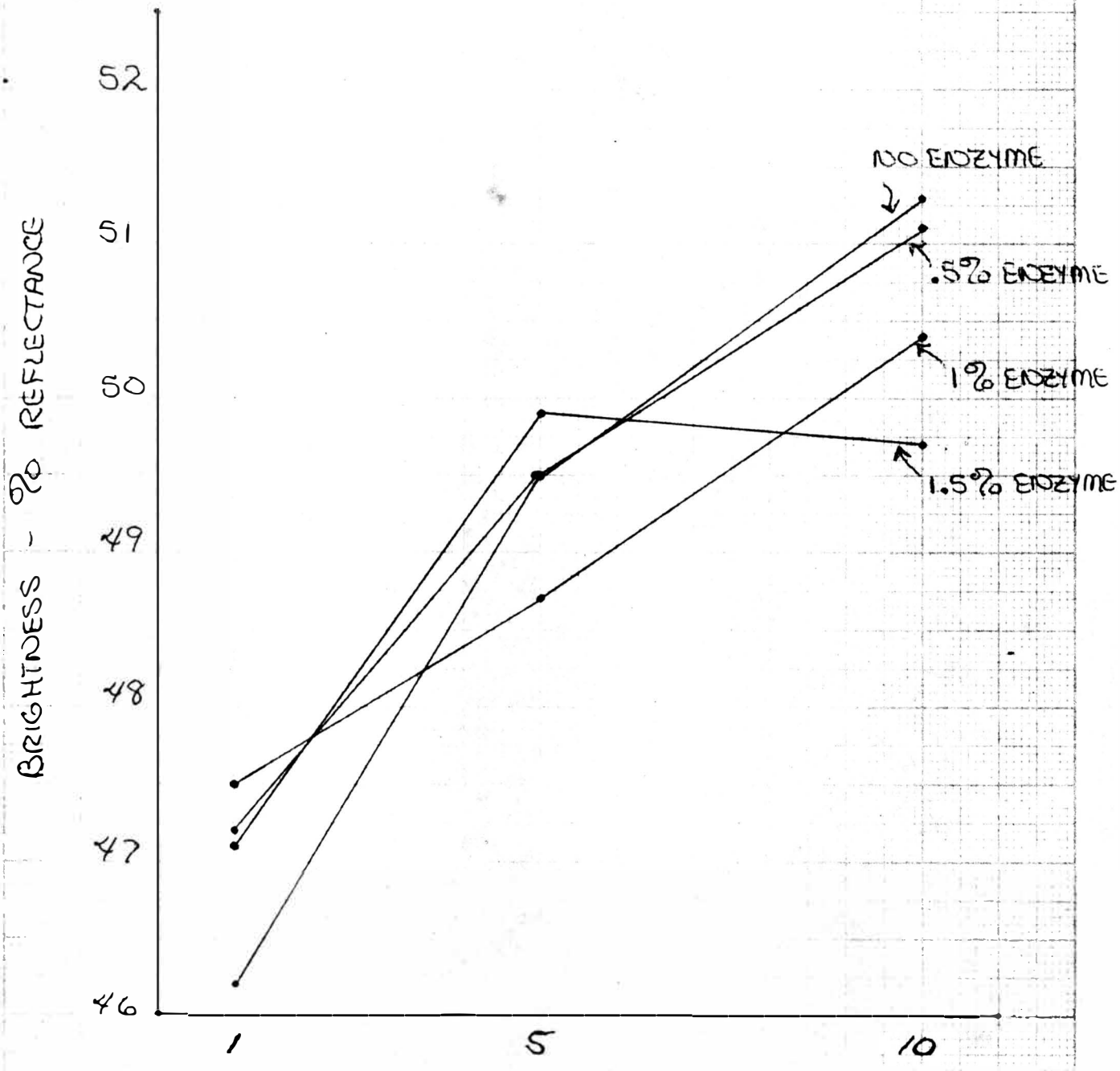


FIGURE 3

PRINTING OPACITY VS. % SOAP

VANZYME 133 - PROTEASE

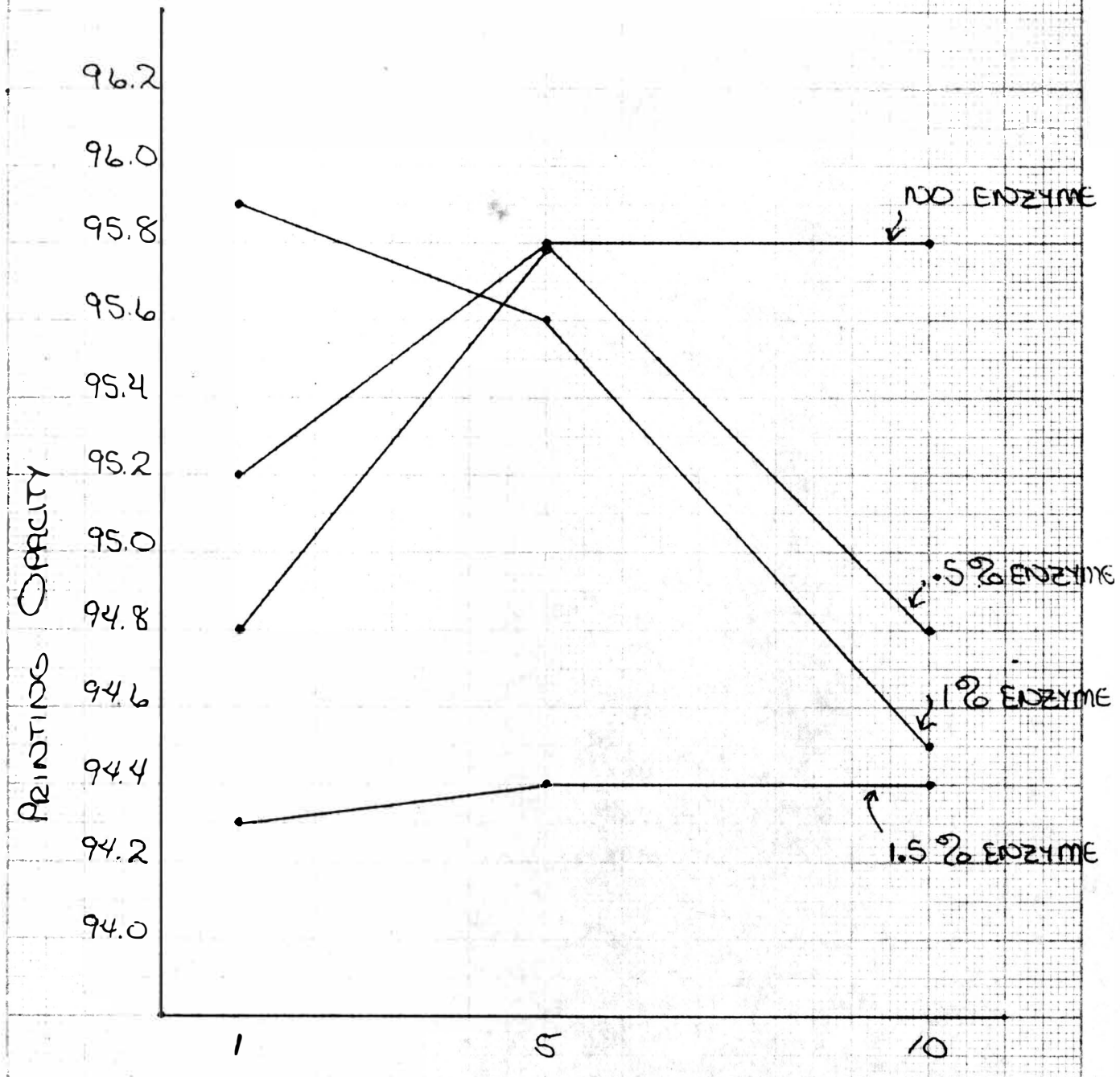


FIGURE 4

PRINTING OPACITY VS. % SOAP

VANZYME - AMYLASE

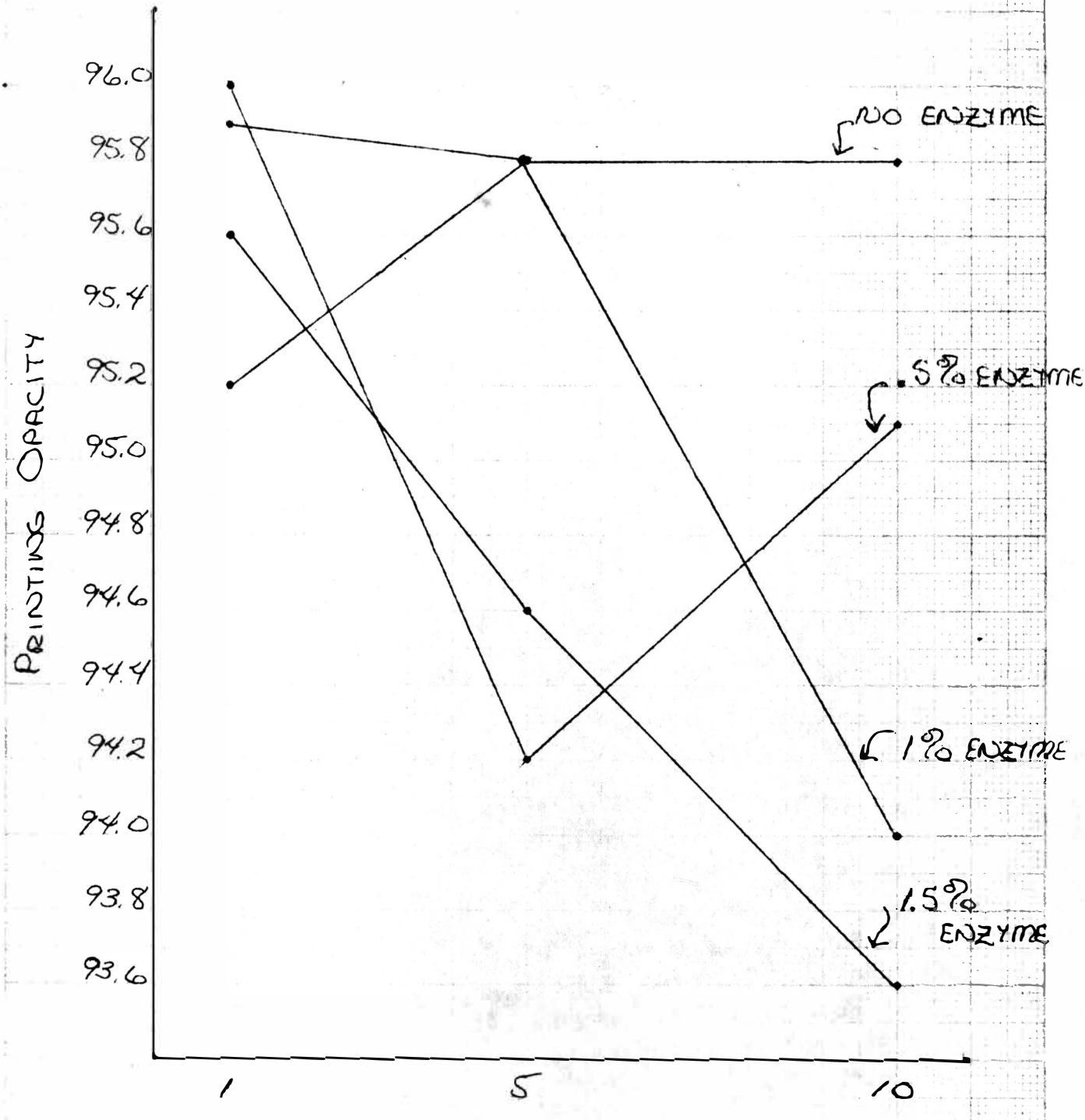
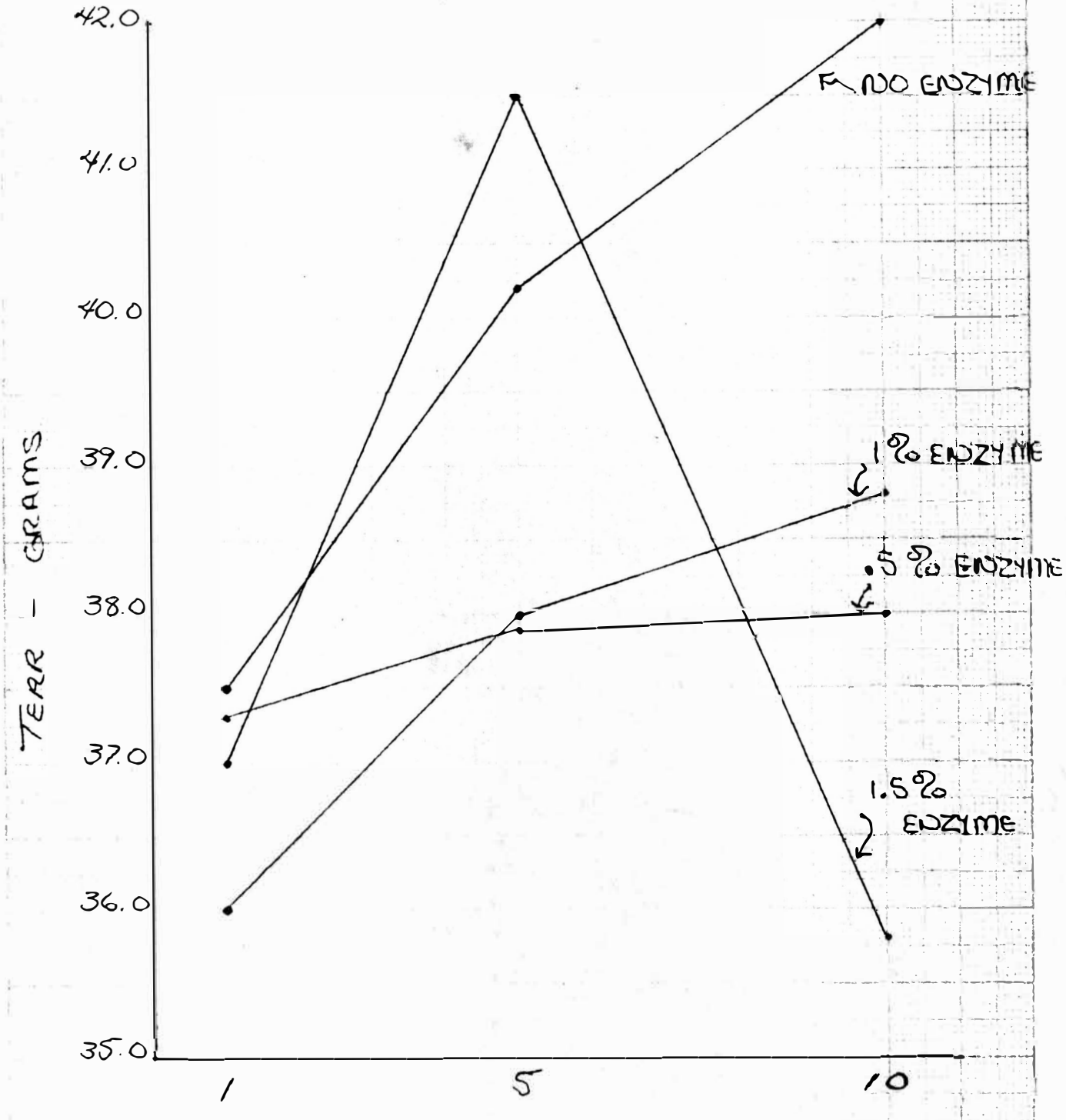


FIGURE 5

TERR VS. % SOAP

VANZYME 133 - PROTEASE



% SOAP - BY WEIGHT OF DRY FIBER IN SAMPLE

FIGURE 6

TERR VS. % SOAP

YANZYME - AMYLASE

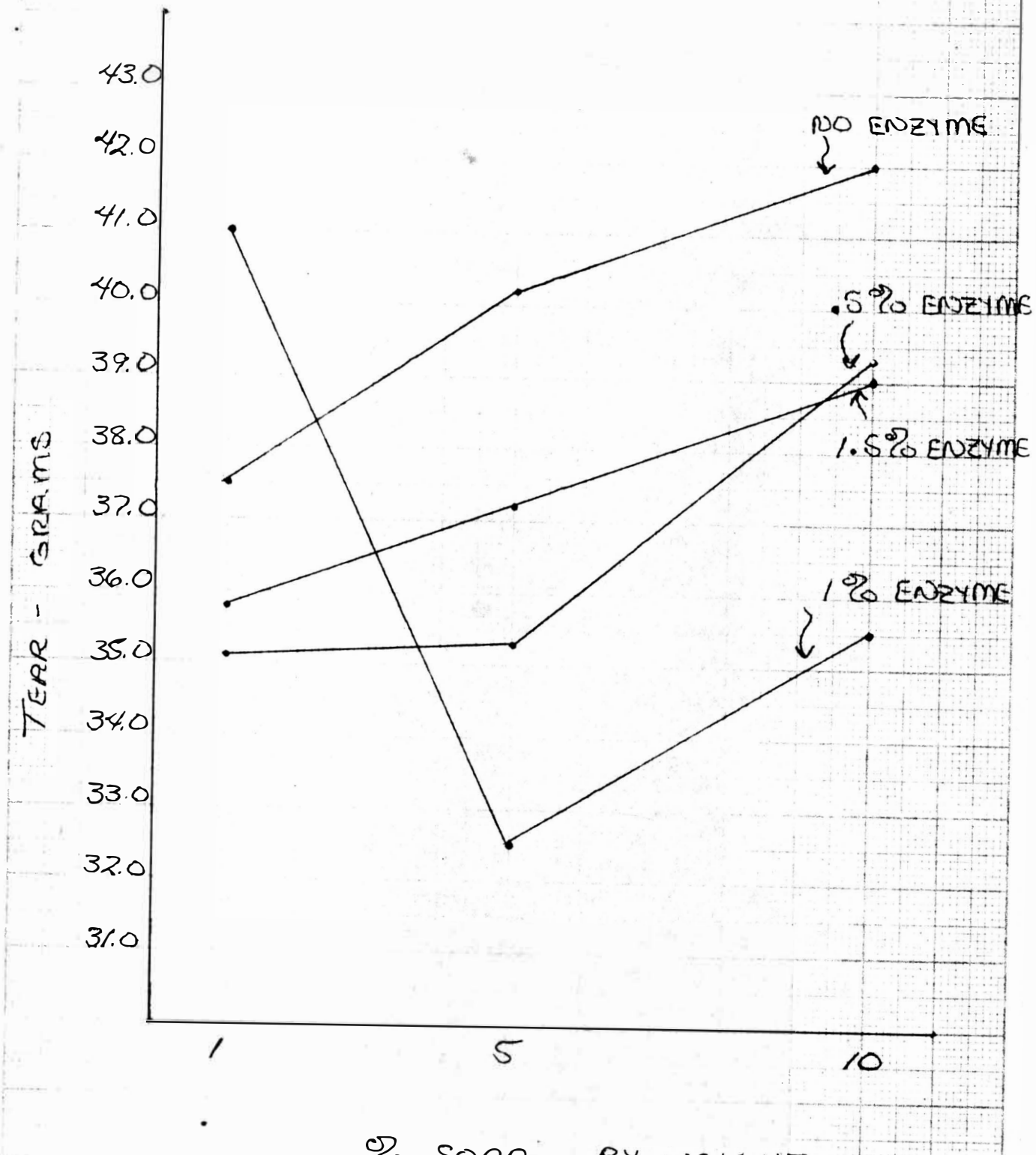


FIGURE 7

TENSILE VS. % SORP

VANZYME 133 - PROTERSE

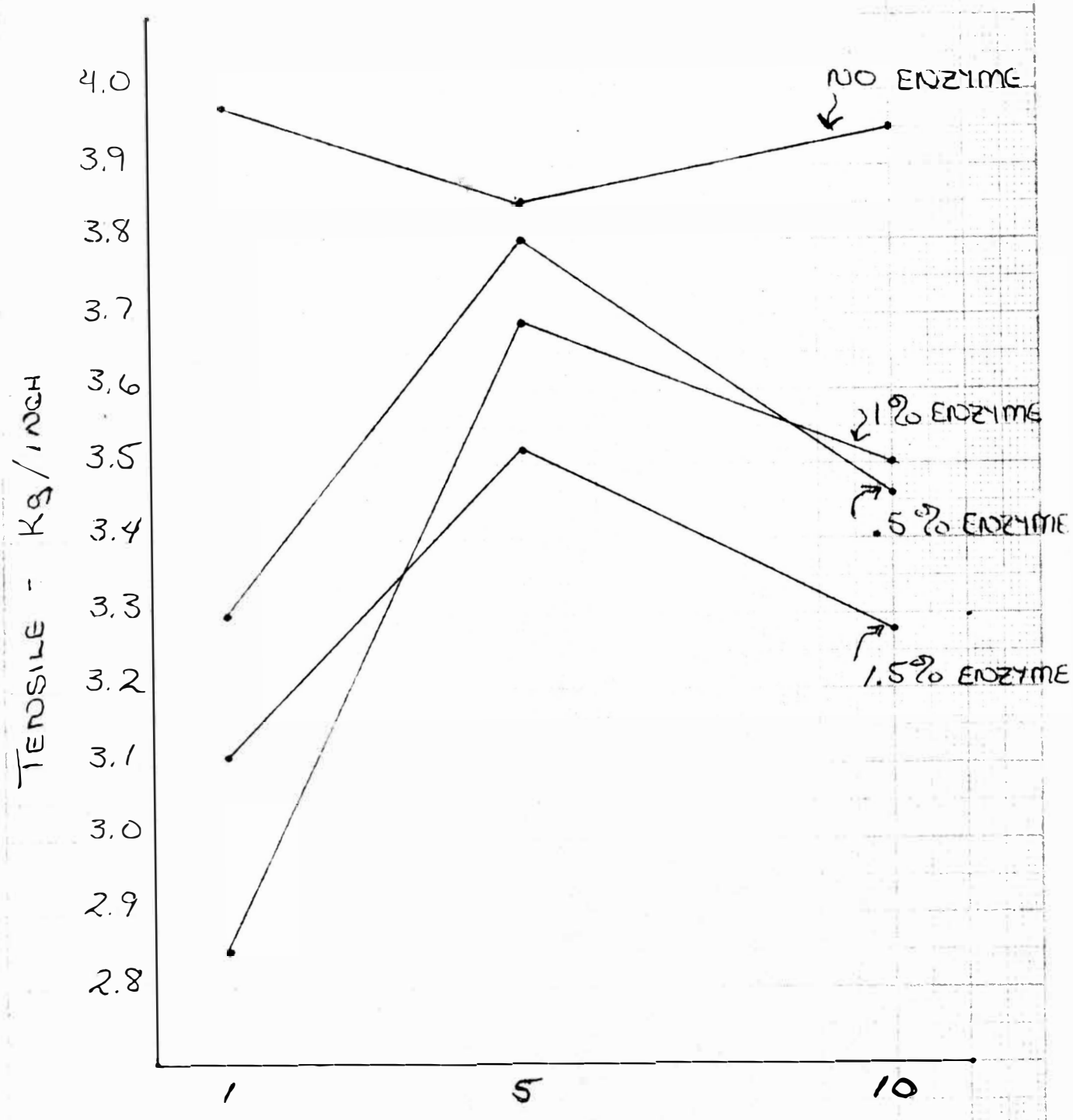


FIGURE 8

TENSILE VS % SOAP

YRNZYME - AMYLASE

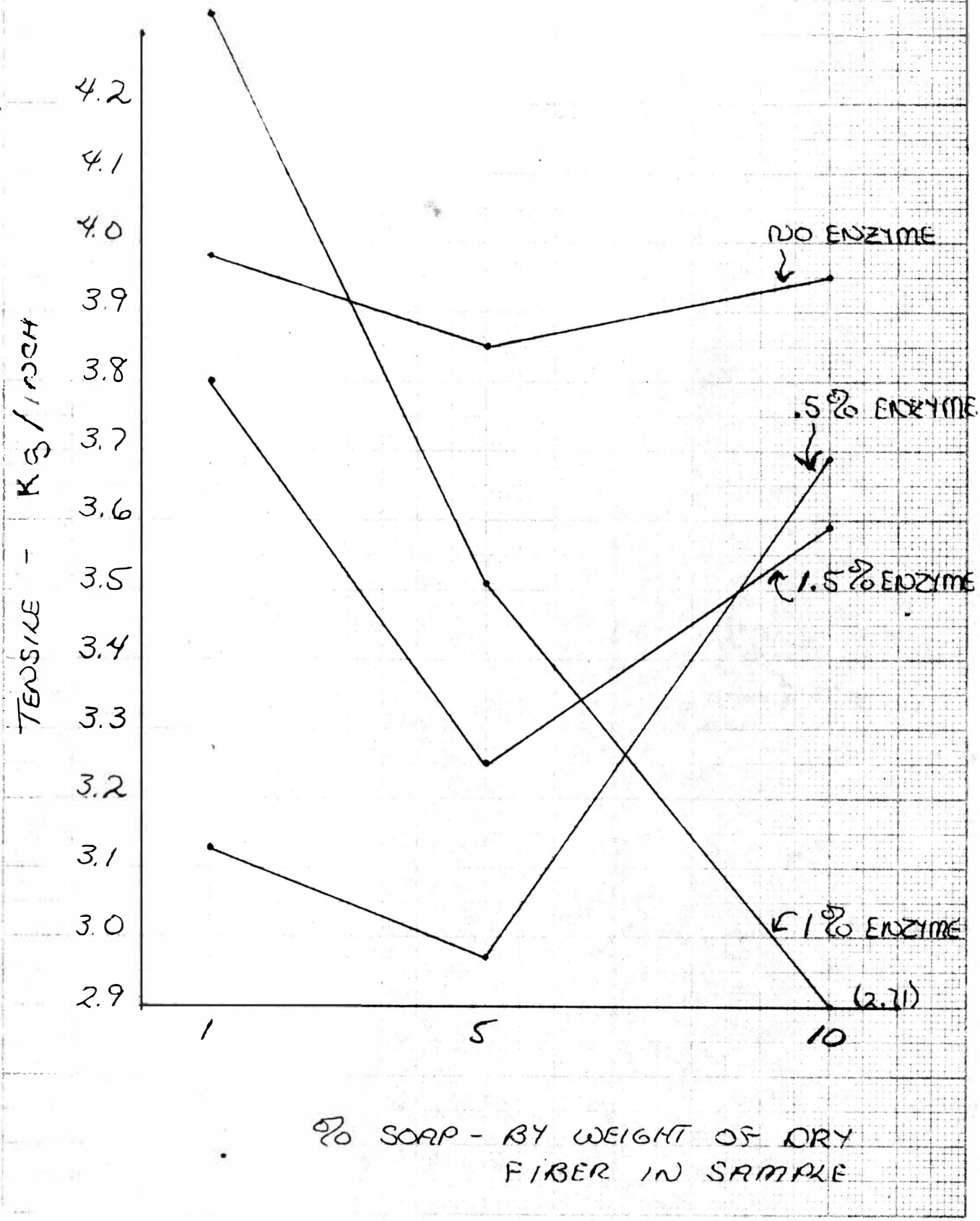
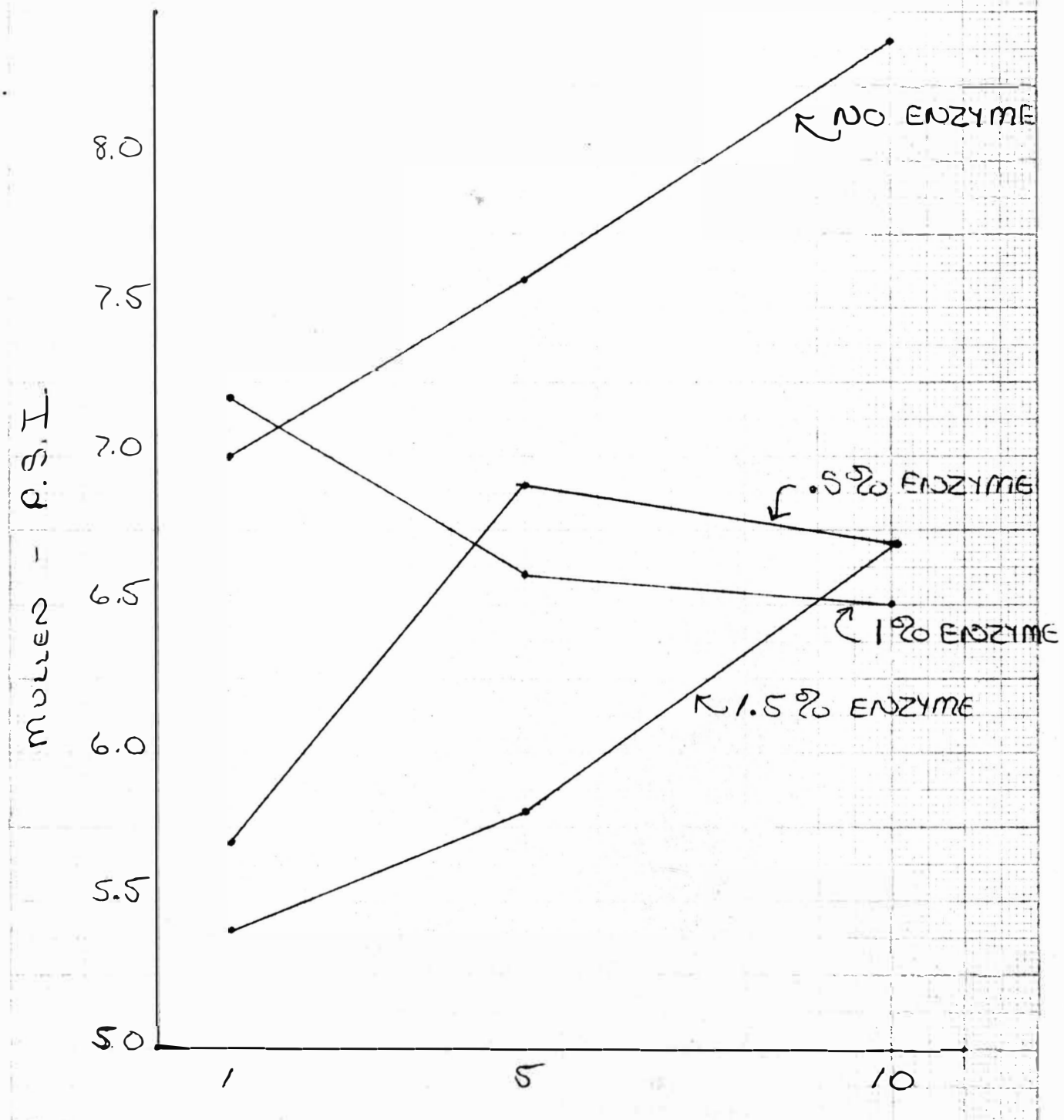


FIGURE 9

MULLEN VS % SOAP

VANZYME 133 - PROTEASE

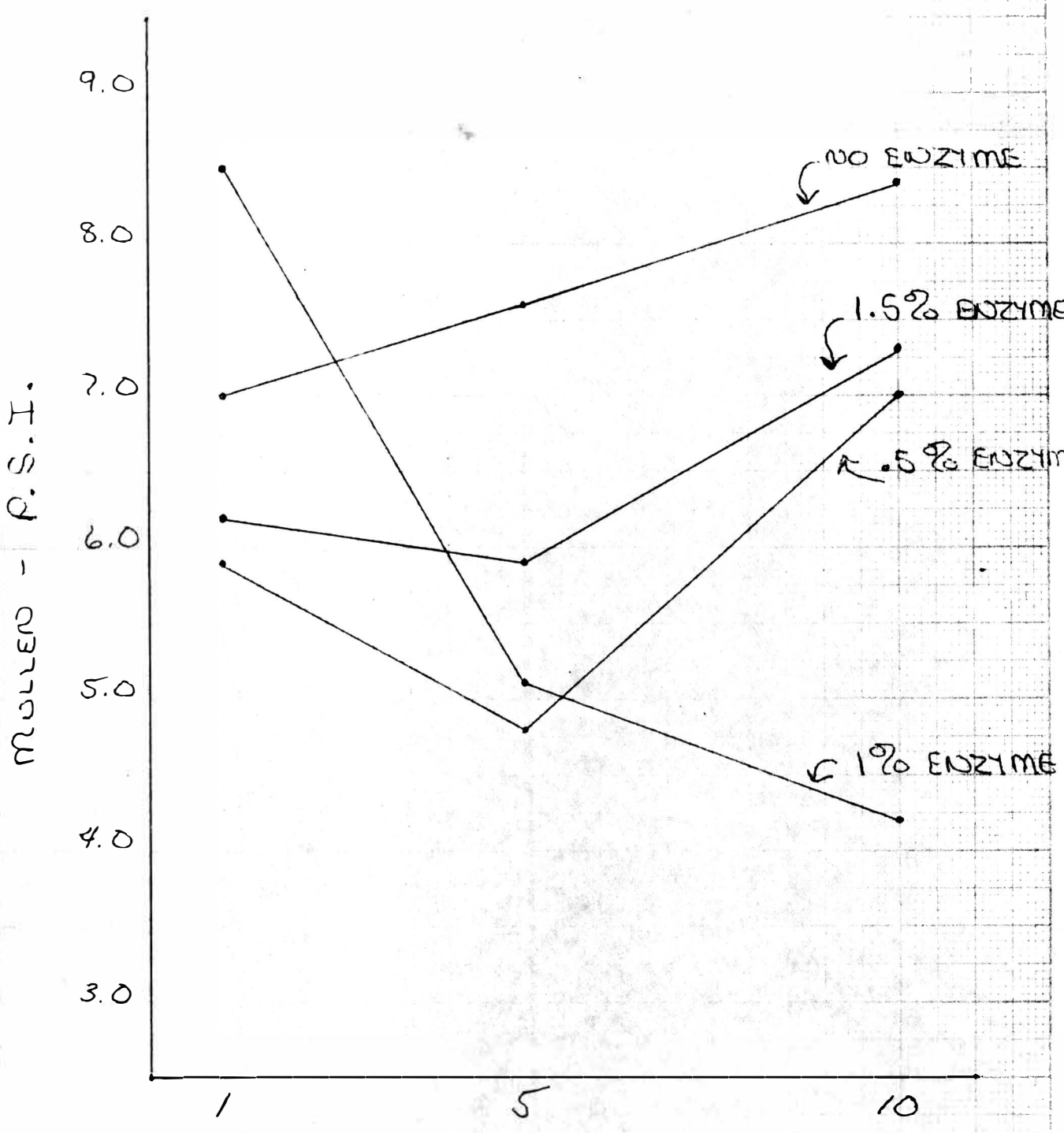


% SOAP - BY WEIGHT OF DRY FIBER IN SAMPLE

FIGURE 10

MULLEN VS. % SOAP

VANZYME - AMYLASE



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