4-1971

The Effectiveness of Some Enzyme-Containing Detergents of the Deinking of Newsprint

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THE EFFECTIVENESS OF SOME ENZYME-CONTAINING DETERGENTS OF THE DEINKING OF NEWSPRINT

by

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A Thesis Submitted to the
Faculty of the Department of Paper Science
and Engineering in partial fulfillment
of the
Degree of Bachelor of Science

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Kalamazoo, Michigan

April, 1971

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ABSTRACT

With an ever increasing use of wood by the paper industry and pollution of our waterways, it is only natural that we turn to recycling of our products.

The purpose of this paper was to investigate the possible use of enzymes detergents as a means of deinking newsprint. It was decided to deink several issues of newspaper by varying the concentration of enzyme detergent over a wide interval of temperature. The pH of the systems was monitored so as not to denature the enzyme. This method yielded pulp with a brightness three or four points over that of the untreated newsprint, with a slight increase in physical strength. An optimum temperature range of one hundred and twenty to one hundred and forty degrees fahrenheit was obtained, but beyond this point the effect of the enzyme was greatly decreased. It was concluded that the use of enzymes in the deinking process may have a future use if the same general results can be obtained with a bio-degradable enzyme.

INTRODUCTION

In the near future the paper industry may be faced with a shortage of the basic raw material required for papermaking, that is, wood. To help alleivate this shortage, the industry will have to use more and more secondary fiber. This is where the process of deinking becomes an important factor. The secondary fibers will have to meet certain specifications of brightness and strength for their use in liner board and make up furnish.

The conventional means of removal of ink involves cooking the wastepaper at elevated temperatures in excess of 120°F in the presence of harsh chemicals for an extended period of time. When fibrous materials are subjected to such conditions the loss of strength, reduction in yield and discoloration is inevitable.

It was the purpose of this paper to investigate the use of enzymes in the deinking process, and their effect on the optical and physical properties of the secondary fiber.

BACKGROUND

Several articles under the titles of deinking and enzymes were obtained but revealed little or no pertinent information on this subject. In 1961 the effects of some enzymes on coated magazine stock was studied by Edgar E. Moore, (10) but yielded negative results. It was therefore, concluded that this is a relatively new area of research and that the work done in 1961 on coated paper should be expanded to included uncoated paper, especially newsprint.

The work on coated paper envolved the use of a commercial detergent but without enzymes. Both amylolytic and proteolytic enzymes were added to the pulp slurries to aid in the digestion of the natural adhesives contained in the coated paper, but yielded no results.

Since the literature survey revealed that no work had been done on the effects of enzyme containing detergents on the deinkability of uncoated papers it was decided to experiment in this area.

DEFINITIONS

Enzymes

Enzymes are defined as a proteinaceous substance produced by living cells that bring about accelerated reactions without themselves being markedly altered during the process. They are thought to be protein in nature because enzymes react similarly to proteins towards acids, alkali, heat and in general stability. (1)

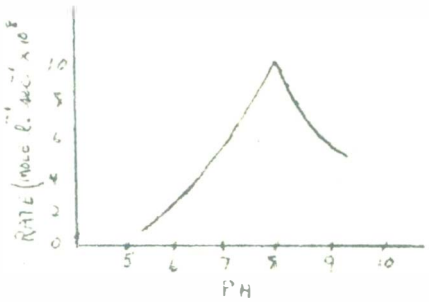
Each molecule of an enzyme is composed of several hundred simpler molecules called amino acids joined together in a long chain. The amino acids in the chain of an enzyme molecule are arranged in a specific order and the chain itself is tangled and twisted in space into a special shape. It is this special shape that permits the enzyme molecule to exert its catalytic properties. The rate at which a catalyzed reaction occurs is directly proportional to the concentrations of the catalyst which is also true of enzymes.

Enzymes are characterized by their catalytic effects and a very high order of specificity. By specificity it is meant that enzymes are highly selective in their reaction, that is, enzymes will cause only one particular type of reaction to occur and will cause only a few chemical compounds to undergo the reaction. Specificity is subdivided into several types. They are; absolute specificity, in which the enzyme brings about reaction in only one substrate; group specificity, where the enzyme reacts with a group of substractes but has a specific requirement with respect to the grouping that must be

present in the molecule; reaction or linkage, in which the enzyme acts upon a certain type of linkage, and stereochemical specificity, where the enzyme reacts with one particular sterochemical form. (2)

The kinetics of an enzyme reactions and the factors that influence its rate are extremely important in any study of enzymes. A rate may be expressed in terms of the concentrations of one of the reacting substances. The rate of reaction is influenced by several important factors; the pH of the solution, the substrate concentration, the temperature of the system, and the concentration of any inhibitors. (3)

The effect of pH on the rate of enzyme reaction has been found to pass through a maximum in the range 7.0-8.2. (2)



(From "Introduction To The Chemistry of Enzymes", Laidler)

An extremely important thing to remember when working with enzymes is that if the pH varies too far to the acid or alkaline side, the enzyme may be denatured, thus irreversibly losing its activity. There is an optimum range of pH in which a reversible behavior is noted, but this range may vary slightly depending on the specific enzyme.

As the substrate concentration of an enzyme-catalyzed reaction

is increased it is noted that the rate will increase up to a certain level, where it becomes independent of the substrate concentration. (2) One of the theories on enzyme reaction explains the above by the fact that at high substrate concentrations the enzyme becomes saturated and is complexed. According to this theory (1) the enzyme and substrate react to form a complex;

$$E + S \longrightarrow X \qquad \text{Equation (1)}$$

The complex then decomposes into the product and the enzyme is regenerated:

$$X \rightleftharpoons P + E \qquad \text{Equation (2)}$$

Temperature also has a very important effect on enzymes. At a certain optimum temperature the rate of reaction reaches a maximum but if it is exceeded greatly the enzyme will be denatured and thus becomes inactive. For most enzyme this temperature should not exceed 50-50°C.

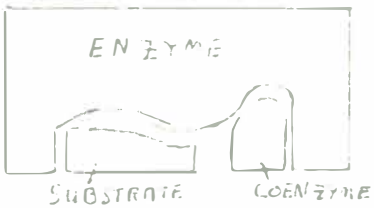
Some substances in a system may depress the rate of reaction, these substances being known as inhibitors. Examples of such inhibitors are; heat, high pressure, strong acids, and alkali. The presents of these inhibitors may destroy the enzyme thus making it ineffective. Certain ions may be toxic to enzyme action such as nickle, zinc, copper and mercuric, causing them to lose their effectiveness. (4) Various other ions may prove to be extremely beneficial to enzyme activity. Calcium, sodium and other alkaline metals tend to stabilize their activity resulting in a wider functional temperature and pH range.

The exact operation of an enzyme is not totally known but strong evidence has been produced that an enzyme operates as follows:

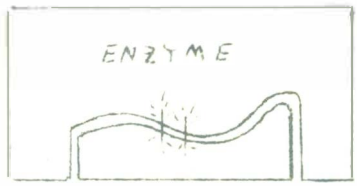
An enzyme comes together with its substrate or possibly a coenzyme in the form of a loose chemical association called a complex. The substrate becomes involved with a specific site, in the complex. With this site the substrate comes into contact with a specific portion of the side chain of an amino acid and is subject to some strain due to the close proximity to the enzyme. To relieve some of the strain the substrate may react with the amino acid side chain at the active site. This may alter the substrate and cause it to be released from the enzyme. (1)

The following figure illustrates the above theory:

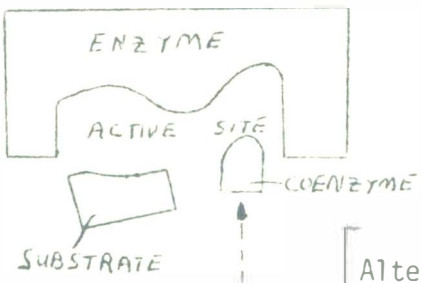
How Enzymes Operate



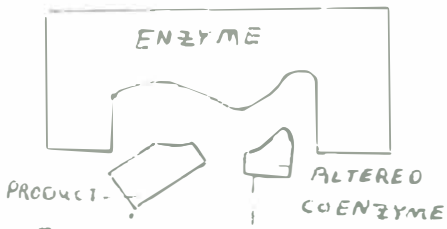
Complex formed-substrate and coenzyme fit into active side



Chemical groups on amino acid chain in enzyme reacts with substrate and coenzyme



Substrate and coenzyme encounter enzyme



Product and altered coenzyme released from enzyme

Altered coenzyme reconverted its original condition by participation in second enzyme reaction

(From - Enzymes-The Agent of Life, David M. Locke)

Ink:

Printing inks consists of a finely ground mixture of pigments, varnish and solvent. They may also contain certain additives such as wax, flow agents and plasticizers. (5)

The varnish is referred to as the ink vehicle or medium. It is required to bind the pigments to the paper, so that it will not smudge or rub away. The solvent used in inks is to dissolve resins, which are film-forming materials. When heat is applied the solvent evaporates leaving a non-volatile resin binder on the paper. Pigments suitable for printing inks must be permanent to light, heat, water and chemicals which may come into contact with the printed ink. (5) Examples of this would be soap, grease, alkalis, acids, and most solvents.

News ink consists of a carbon black pigment, varnish and solvent.

Newsprint:

Newsprint is highly absorbent, and the ink dries by the oil medium draining away into the paper. A stiff ink plug is left adhereing to and inbedded into the rough surface of the paper. During the moment of impression when printing pressure is a maximum, ink is forced into the open structure of the paper. Following the impression, varnish absorption from the ink film occurs becoming located on the walls of wide capillaries while the smaller ones become completely

filled due to the capillary action. (6)

F = INK
F_w = INK PENETRATED
K_1 = VARNISH ABSORBED

(Cross-Section of Sheet With Ink Penetration)

The carbon black pigment is distributed with decreasing concentration in the transverse direction of the sheet from the printed side. This is due to the interaction between ink and the fibrous network of the sheet.

EXPERIMENTAL DESIGN

The purpose of this paper was to investigate the effectiveness of some enzyme containing detergents on the deinking of newsprint so it was decided to use the enzymes contained in commercial detergents for the removal of ink.

Several issues of newspaper with high groundwood content were cut into small strips and soaked in water. Varying amounts of enzyme containing detergent were added to the mixture and then agitated at different temperatures while the pH was monitored within the desired limits. Control samples with both prue and no detergent were run at the different temperature levels to determine the effects of agitation and detergent on the removal of ink.

After each sample was fully treated it was washed throughly to remove any residual material. Handsheets were made, and optical and physical tests were run to determine the effect of the enzymes.

EXPERIMENTAL WORK

Materials

Detergents: (1) "Drive" - Enzyme containing detergent manufactured by Levers Brothers

(2) "Ivory Snow" - Pure detergent manufactured by Proctor and Gamble.

Newspaper: Kalamazoo Gazette

Equipment

Dispersion: "Cowles" drill press agitator running at 2900 R.P.M.

Washing: Buchner funnel

Sheet Making: Noble and Wood Sheet Machine

Method Used for Deinking

The newspaper was cut into small strips, four inches by two inches, and placed in a three to four liter metal beaker and enough water added to bring the consistency to three percent. Both prue and enzyme containing detergents were carefully weighted into separate piles to equal five, ten and fifteen percent of the dry fiber weight. They were then added to the separate systems and the temperature brought to one of the twenty degree intervals in the range sixty degrees fahrenheit. The temperature was maintained for twenty minutes on a steam plate and then the newspaper was disentigrated for fifteen minutes by the Cowles drill press at twenty-nine hundred R.P.M. The pulp slurry was then washed throughly on a buchner funnel and partically dewatered. The pulp was then redispersed and two and one-half gram

handsheets were formed on the Noble and Wood Sheet Machine. The handsheets were dried on a drum drier at two-hundred degrees fahrenheit and placed in the humidity room for three days before testing.

TABLE I

System: No. Det.

Temp. (°F)/Filter #	7	9	11	13	15	17	19	21
60°F	35.0	42.6	46.5	45.8	47.2	49.3	54.6	56.0
80°F	34.8	42.2	46.4	46.1	47.2	49.8	54.3	55.4
100°F	36.1	44.8	47.1	46.4	49.3	50.2	54.7	55.8
120°F	36.4	45.0	48.4	49.6	51.7	54.6	59.2	60.9
140°F	34.9	43.8	47.9	48.2	49.7	51.8	56.1	57.6
160°F	35.8	44.6	47.8	48.4	49.2	51.5	56.4	51.8

Filter #	Wavelength	Readings
7	419	% Reflectance
9	457	
11	497	
13	536	
15	575	
17	614	
19	652	
21	689	

TABLE 2

Type of Det./Filter #	7	9	11	13	15	17	19	21
5% P.D. @ 60°F	35.9	43.4	44.5	46.1	47.6	49.8	54.0	55.6
5% Enz. @ 60°F	37.9	46.4	47.4	50.1	52.3	53.6	56.3	58.0
10% P.D. @ 60°F	35.3	43.2	46.4	47.0	48.3	51.3	54.2	55.5
10% Enz. @ 60°F	39.7	49.3	52.9	54.3	56.1	57.8	62.0	63.7
15% P.D. @ 60°F	34.2	41.7	46.2	46.9	49.6	51.2	54.9	55.9
15% Enz. @ 60°F	37.3	46.4	50.0	52.3	54.8	57.1	62.5	64.4
5% P.D. @ 80°F	36.1	43.9	45.4	46.8	48.5	51.4	54.9	56.4
5% Enz. @ 80°F	38.3	47.0	48.5	50.9	53.1	55.2	57.8	59.9
10% P.D. @ 80°F	36.1	44.4	46.9	47.7	49.1	51.9	54.8	56.0
10% Enz. @ 80°F	39.9	49.6	53.3	54.9	56.4	58.2	62.0	64.1
15% P.D. @ 80°F	36.7	42.4	47.0	47.7	50.6	52.4	55.6	56.8
15% Enz. @ 80°F	40.4	50.5	52.9	55.3	57.2	58.9	63.6	64.9
5% P.D. @ 100°F	36.4	44.5	46.8	48.0	50.6	52.9	55.7	57.4
5% Enz. @ 100°F	38.6	47.8	51.7	53.2	54.6	57.0	61.5	62.7
10% P.D. @ 100°F	36.5	44.8	47.5	48.6	50.7	52.5	55.3	56.4
10% Enz. @ 100°F	40.1	50.2	53.4	55.6	56.8	58.8	63.1	64.6
15% P.D. @ 100°F	37.4	44.2	47.9	48.9	51.3	53.5	56.2	57.5
15% Enz. @ 100°F	41.6	51.3	54.2	57.2	58.6	60.1	64.3	65.7

TABLE 3

Type of Det/Filter #	7	9	11	13	15	17	19	21
5% P.D. @ 120°F	36.9	45.1	48.3	49.8	52.0	54.5	56.1	58.3
5% Enz. @ 120°F	41.6	51.8	55.7	57.5	58.9	60.8	65.7	67.5
10% P.D. @ 120°F	36.9	45.2	48.4	49.7	51.0	53.2	53.3	57.0
10% Enz. @ 120°F	42.0	52.5	55.9	58.2	60.1	61.3	66.0	68.2
15% P.D. @ 120°F	37.9	45.8	49.0	50.6	52.2	55.0	56.9	58.0
15% Enz. @ 120°F	43.3	53.4	56.4	60.0	61.3	62.0	67.3	69.2
5% P.D. @ 140°F	35.4	44.7	48.5	49.1	50.4	52.2	56.4	57.9
5% Enz. @ 140°F	41.8	51.1	55.5	58.1	58.9	60.2	65.7	67.8
10% P.D. @ 140°F	36.2	45.2	48.8	50.0	51.3	52.8	56.7	58.1
10% Enz. @ 140°F	42.3	51.8	55.9	58.3	60.3	61.5	66.2	68.0
15% P.D. @ 140°F	38.0	46.2	49.7	51.4	52.5	55.6	57.3	58.3
15% Enz. @ 140°F	43.4	54.4	57.3	60.2	62.4	62.6	67.9	69.4
5% P.D. @ 160°F	35.1	44.3	46.8	48.1	49.1	51.3	56.6	58.0
5% Enz. @ 160°F	36.3	45.2	49.0	48.8	50.2	54.0	57.0	58.8
10% P.D. @ 160°F	35.4	44.2	46.9	48.2	49.1	51.4	56.4	58.3
10% Enz. @ 160°F	36.9	45.4	49.3	48.9	50.4	54.4	56.9	59.0
15% P.D. @ 160°F	36.6	46.6	49.0	51.1	52.1	55.1	57.3	58.3
15% Enz. @ 160°F	36.9	47.1	49.9	53.0	53.2	56.7	59.2	60.2

TABLE 4

No. Det./Test	Tensile	Area	Elongation	TEA	Fold	Mullen	Tear X 4
60°F	3.30	89.6	1.60%	.014	4.3	8.39	10.2
80°F	3.40	119.9	1.85%	.019	4.1	8.81	11.7
100°F	3.51	137.8	2.36%	.022	3.8	9.30	11.1
120°F	3.58	146.6	2.89%	.023	2.1	9.65	11.2
140°F	3.97	156.6	2.24%	.025	3.1	9.82	10.3
160°F	4.44	166.0	2.19%	.027	3.6	9.48	9.6

Tensile . . . . . .Kg./in.

Area. . . . . .# of counts

Elongation. . . . . .%

TEA . . . . . .$Kg/cm.^2$

Fold. . . . . .# of folds

Mullen. . . . . .P.S.I.

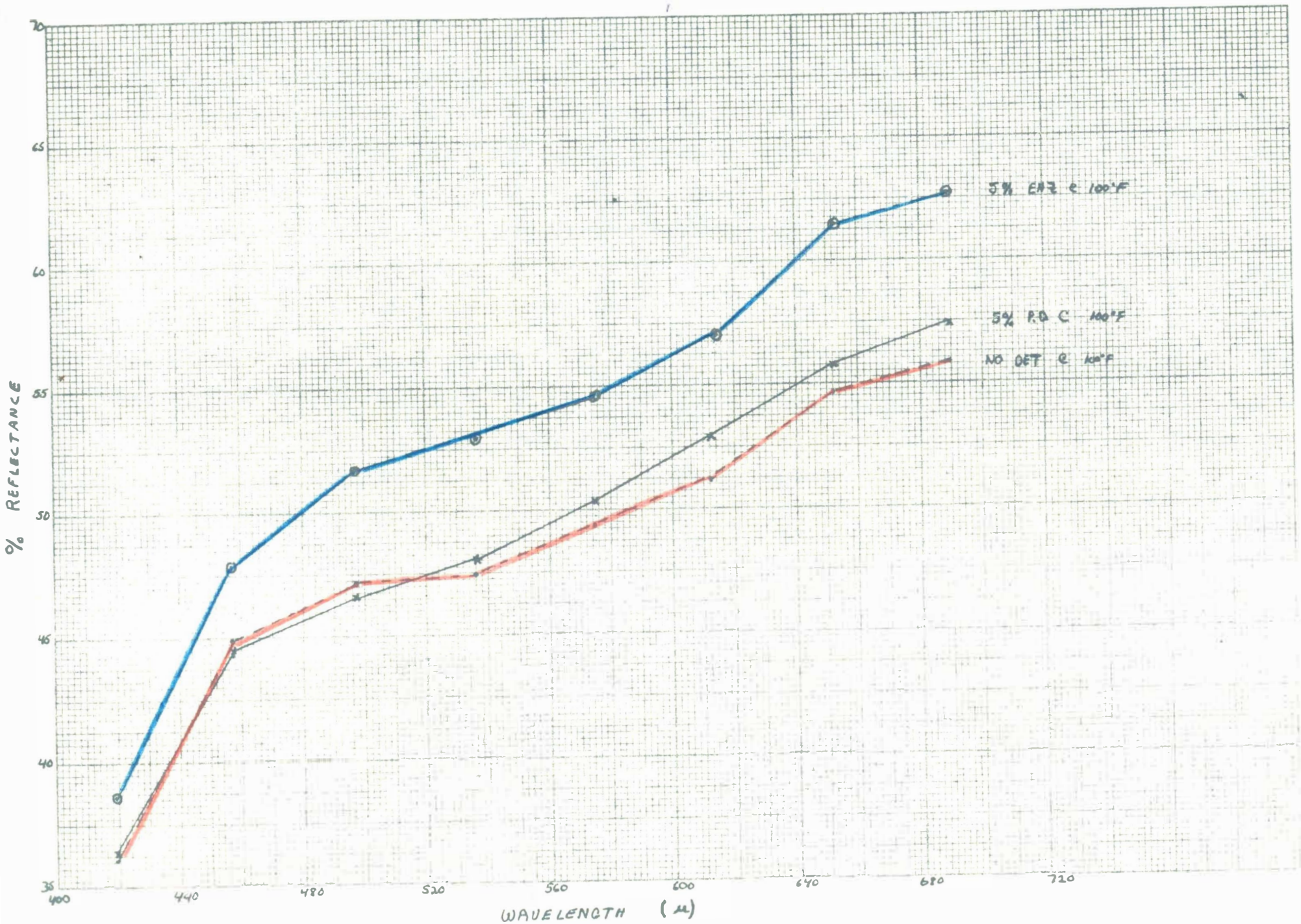
Tear . . . . . .Grams

TABLE 5

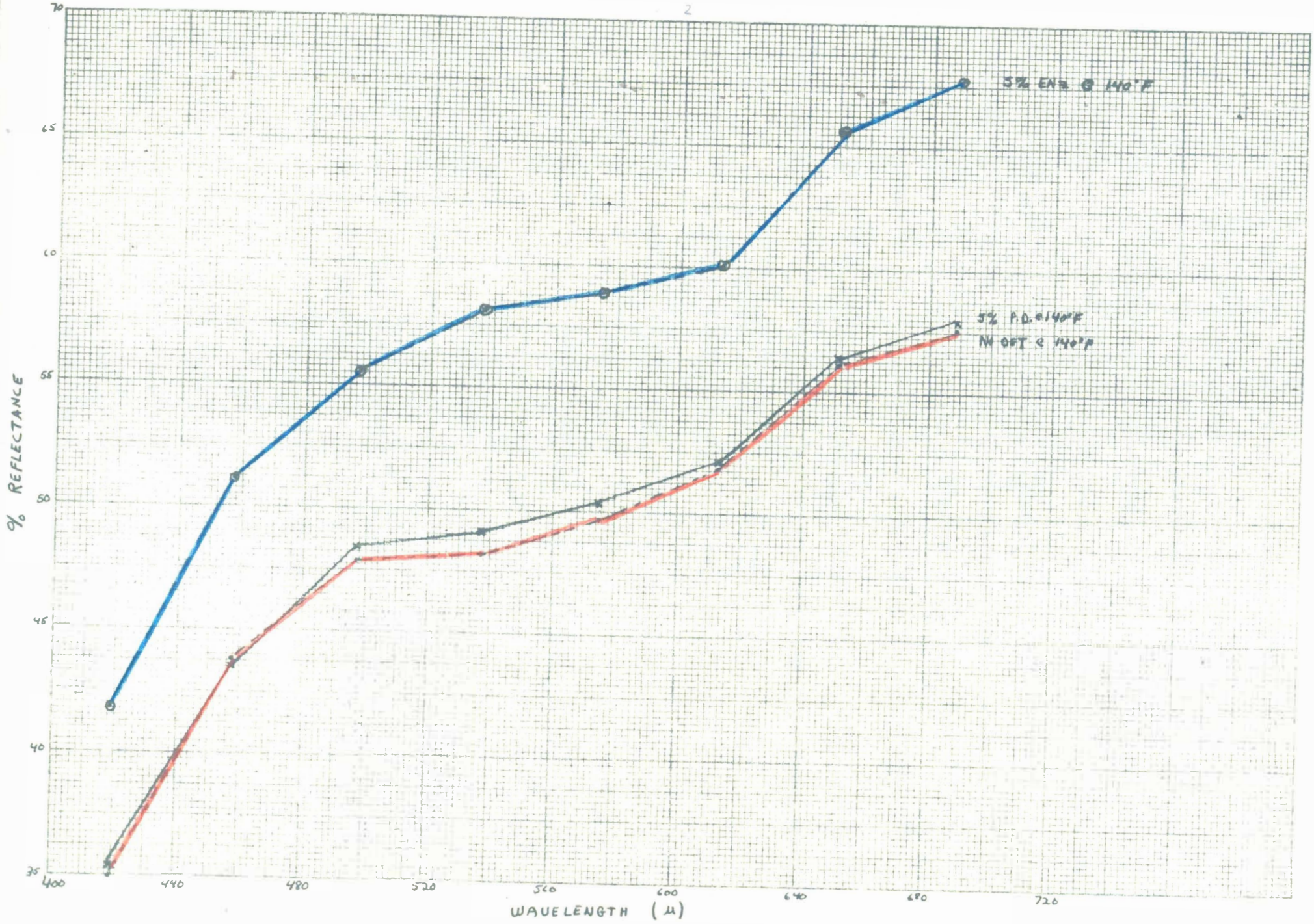
Type of Det./Test	Tensile	Area	Elongation	TEA	Fold	Mullen	Tear X 4
5% P.D. @ 60°F	3.36	114.8	1.95%	.018	3.4	8.64	10.2
5% Enz. @ 60°F	3.1	69.4	1.47%	.011	2.0	5.81	10.2
10% P.D. @ 60°F	3.49	120.3	2.01%	.019	3.1	8.35	10.4
10% Enz. @ 60°F	3.13	106.6	1.99%	.017	3.1	7.68	11.3
15% P.D. @ 60°F	3.52	128.5	2.08%	.021	3.2	8.64	10.1
15% Enz. @ 60°F	3.44	111.7	1.75%	.018	4.0	7.87	10.3
5% P.D. @ 80°F	3.48	124.6	1.88%	.019	3.0	11.5	10.8
5% Enz. @ 80°F	3.36	121.4	1.71%	.019	3.5	10.5	10.2
10% P.D. @ 80°F	3.49	139.6	1.87%	.022	3.6	10.5	10.9
10% Enz. @ 80°F	3.34	132.1	1.92%	.021	4.0	9.4	10.2
15% P.D. @ 80°F	3.70	149.6	2.11%	.024	4.4	10.9	10.5
15% Enz. @ 80°F	3.42	135.7	2.13%	.022	4.2	8.8	10.4
5% P.D. @ 100°F	3.57	136.4	1.81%	.022	3.8	13.3	10.7
5% Enz. @ 100°F	4.09	119.4	1.76%	.019	4.0	12.24	10.1
10% P. D. @ 100°F	3.81	148.9	1.91%	.024	3.7	12.4	10.7
10% Enz. @ 100°F	3.98	133.5	1.83%	.021	3.9	9.96	10.2
15% P.D. @ 100°F	3.88	144.9	1.89%	.023	3.6	11.5	10.9
15% Enz. @ 100°F	3.95	122.7	1.84%	.020	3.6	10.9	10.3

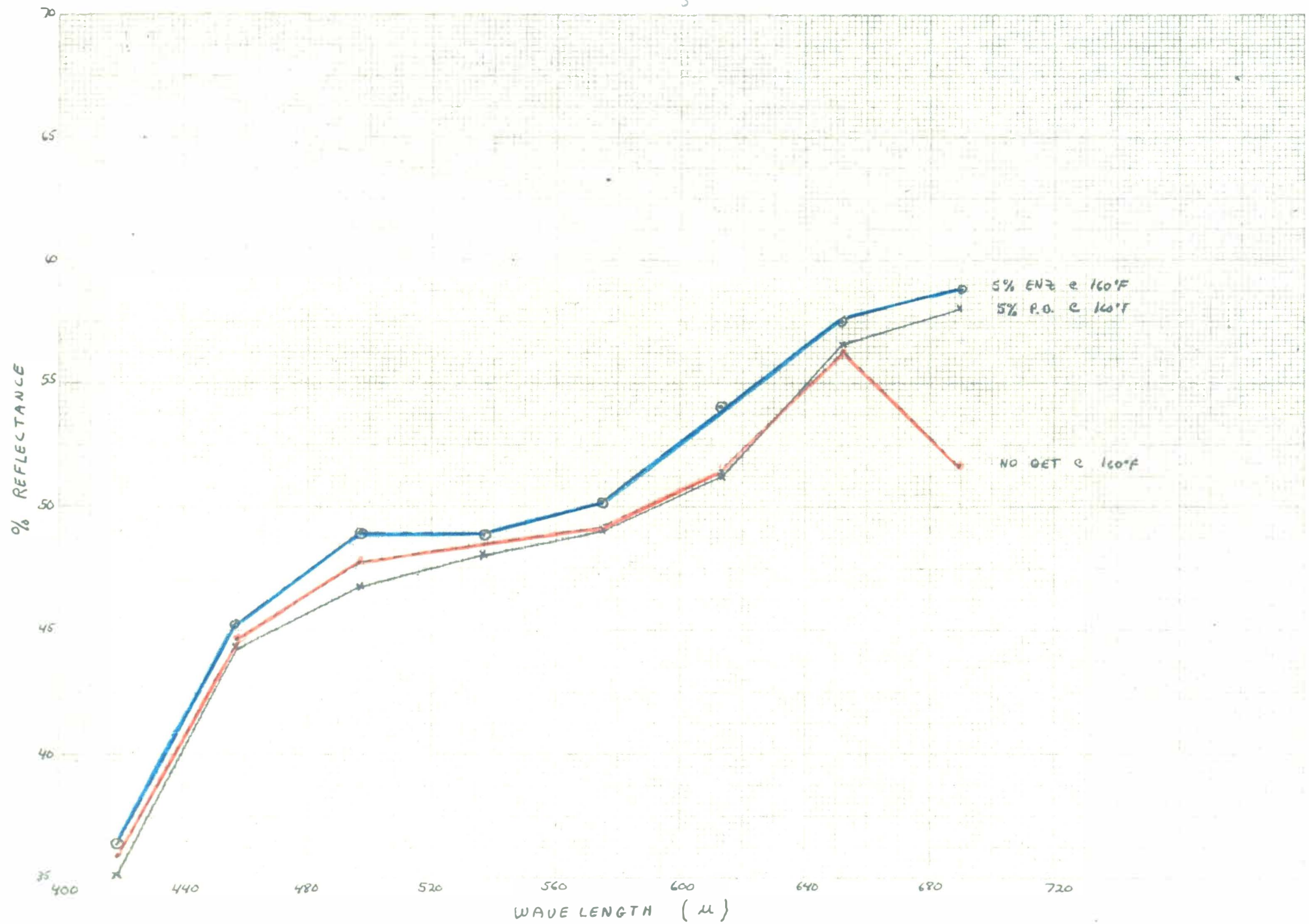
TABLE 6

Type of Det./Test	Tensile	Area	Elongation	TEA	Fold	Mullen	Tear X 4
5% P.D. @ 120°F	3.67	133.3	2.31%	.021	2.5	12.9	11.3
5% Enz. @ 120°F	3.43	134.2	2.26%	.021	3.5	9.6	9.4
10% P.D. @ 120°F	4.25	171.5	2.15%	.027	2.6	13.3	11.3
10% Enz. @ 120°F	3.93	117.4	1.71%	.019	3.3	10.6	9.1
15% P.D. @ 120°F	4.30	183.4	2.34%	.029	3.1	13.3	10.3
15% Enz. @ 120°F	3.98	124.7	1.82%	.020	3.1	9.7	7.3
5% P.D. @ 140°F	3.91	136.4	1.96%	.022	2.8	12.3	11.1
5% Enz. @ 140°F	3.73	147.1	1.99%	.023	2.8	11.3	10.6
10% P.D. @ 140°F	4.12	146.1	2.04%	.023	3.3	11.3	10.7
10% Enz. @ 140°F	4.10	173.4	2.59%	.027	3.6	10.4	9.1
15% P.D. @ 140°F	4.23	159.3	2.22%	.025	3.3	13.1	10.8
15% Enz. @ 140°F	3.90	140.0	2.51%	.022	3.1	12.7	9.4
5% P.D. @ 160°F	4.45	133.4	1.82%	.021	3.3	12.6	10.1
5% Enz. @ 160°F	4.64	138.6	1.79%	.022	4.0	12.2	9.6
10% P.D. @ 160°F	4.40	166.0	2.19%	.026	4.5	11.8	8.1
10% Enz. @ 160°F	4.13	158.0	2.53%	.025	3.0	11.4	8.4
15% P.D. @ 160°F	4.36	173.1	2.40%	.027	3.6	11.4	8.7
15% Enz. @ 160°F	4.01	97.8	1.58%	.016	3.2	10.9	9.6



CROSS SECTION, 20 SQUARES TO INCH

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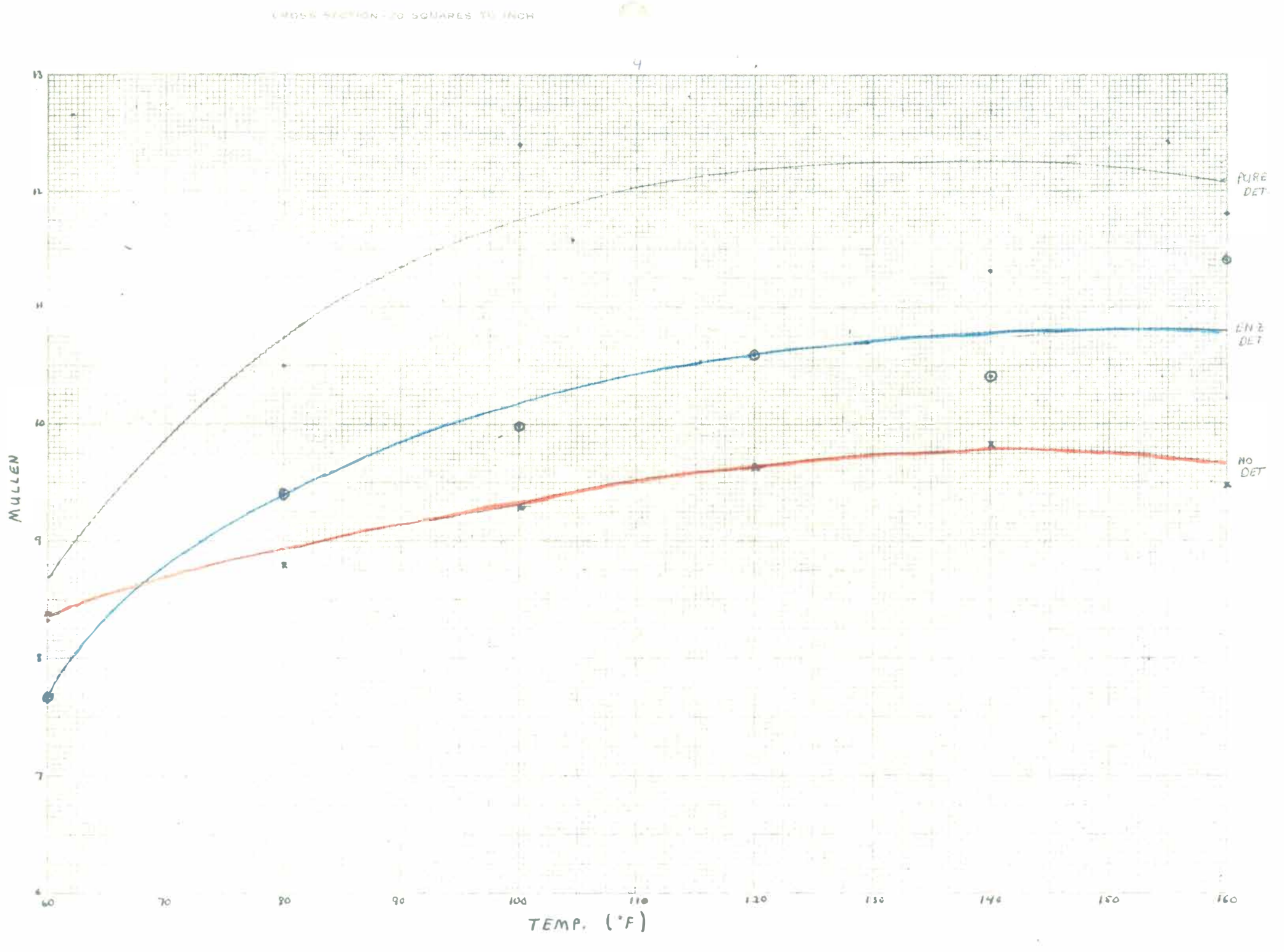
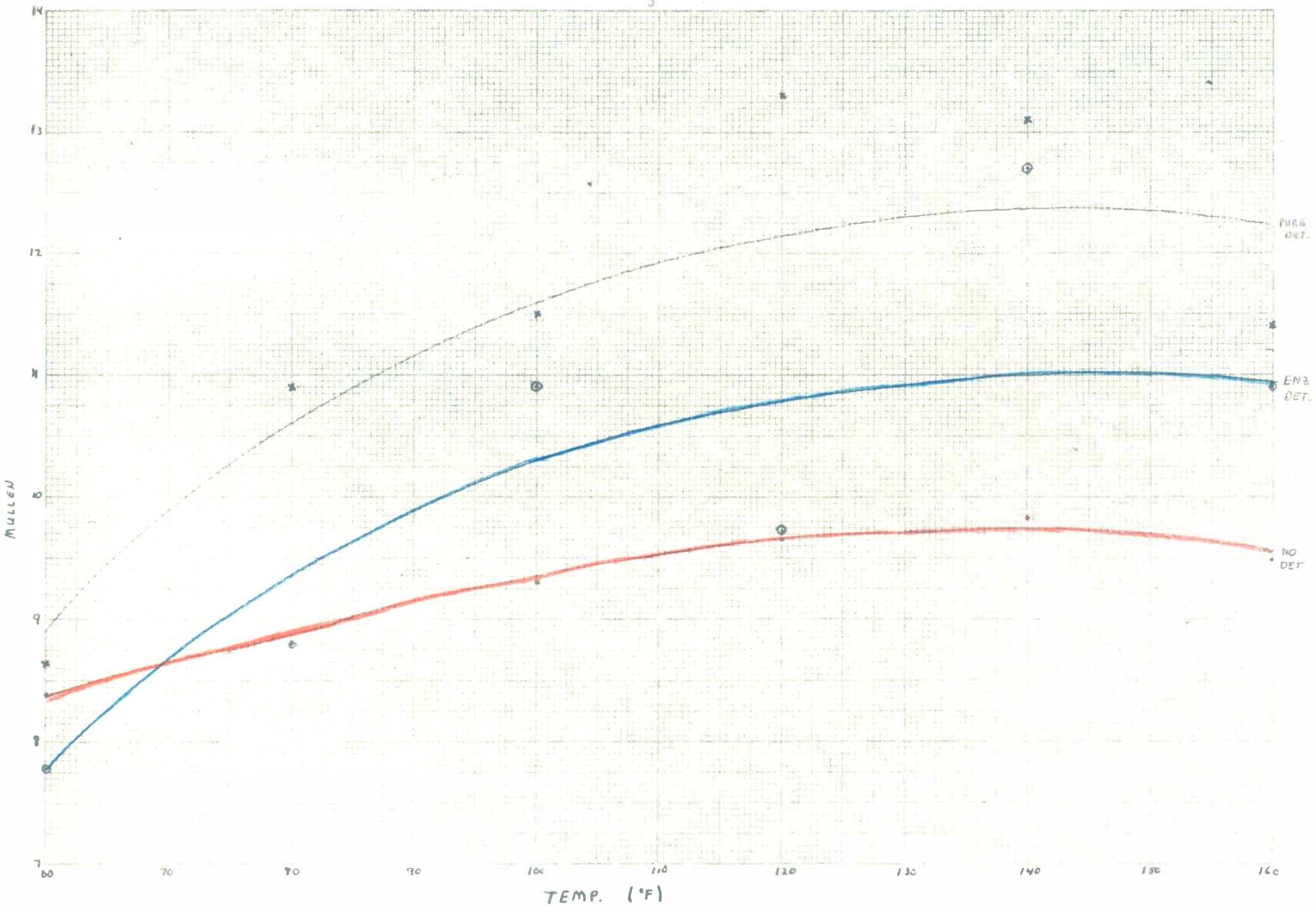
WAVE LENGTH (μ)
5% ENZ @ 160°F
5% P.O. @ 160°F
NO DET @ 160°F

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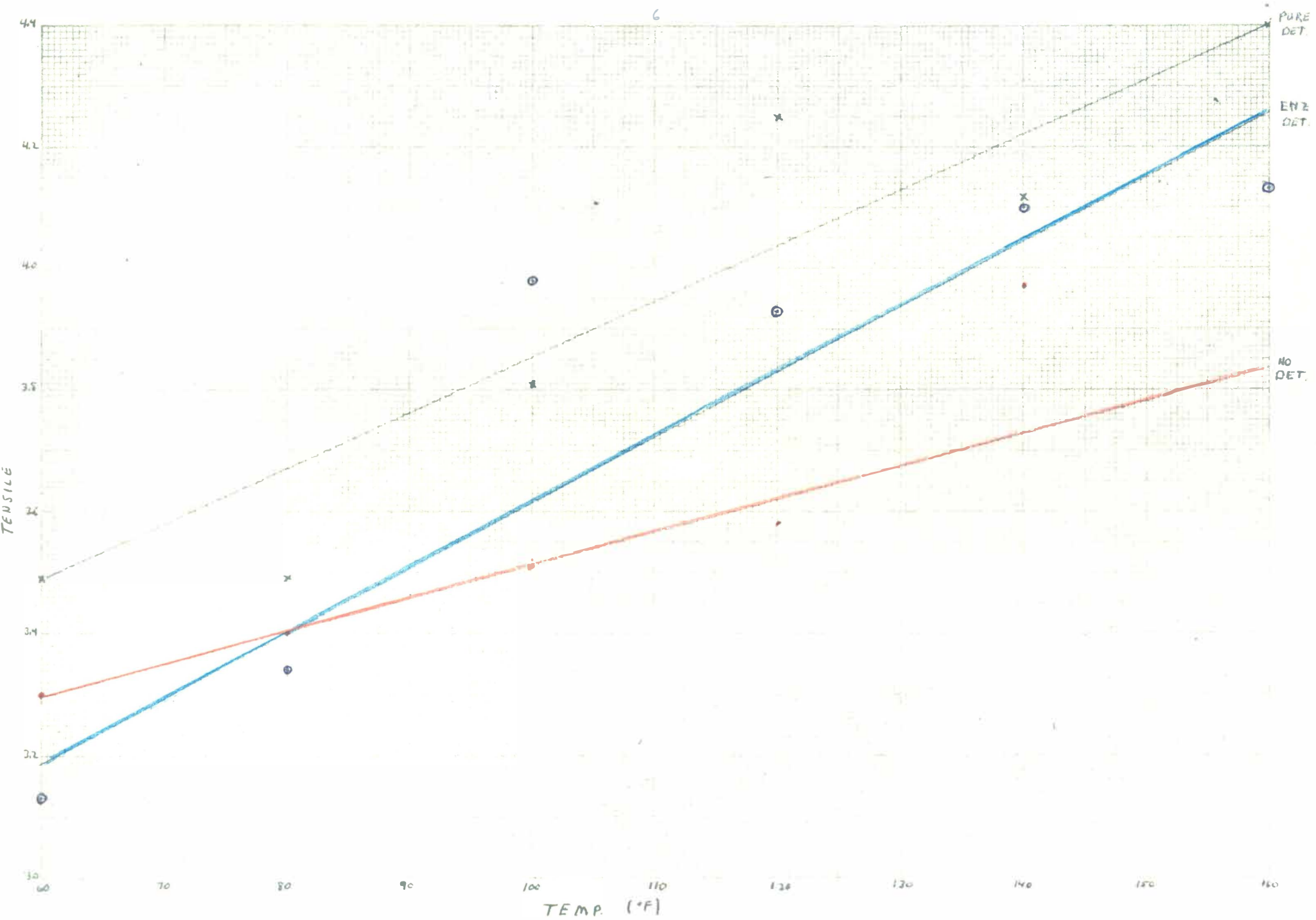
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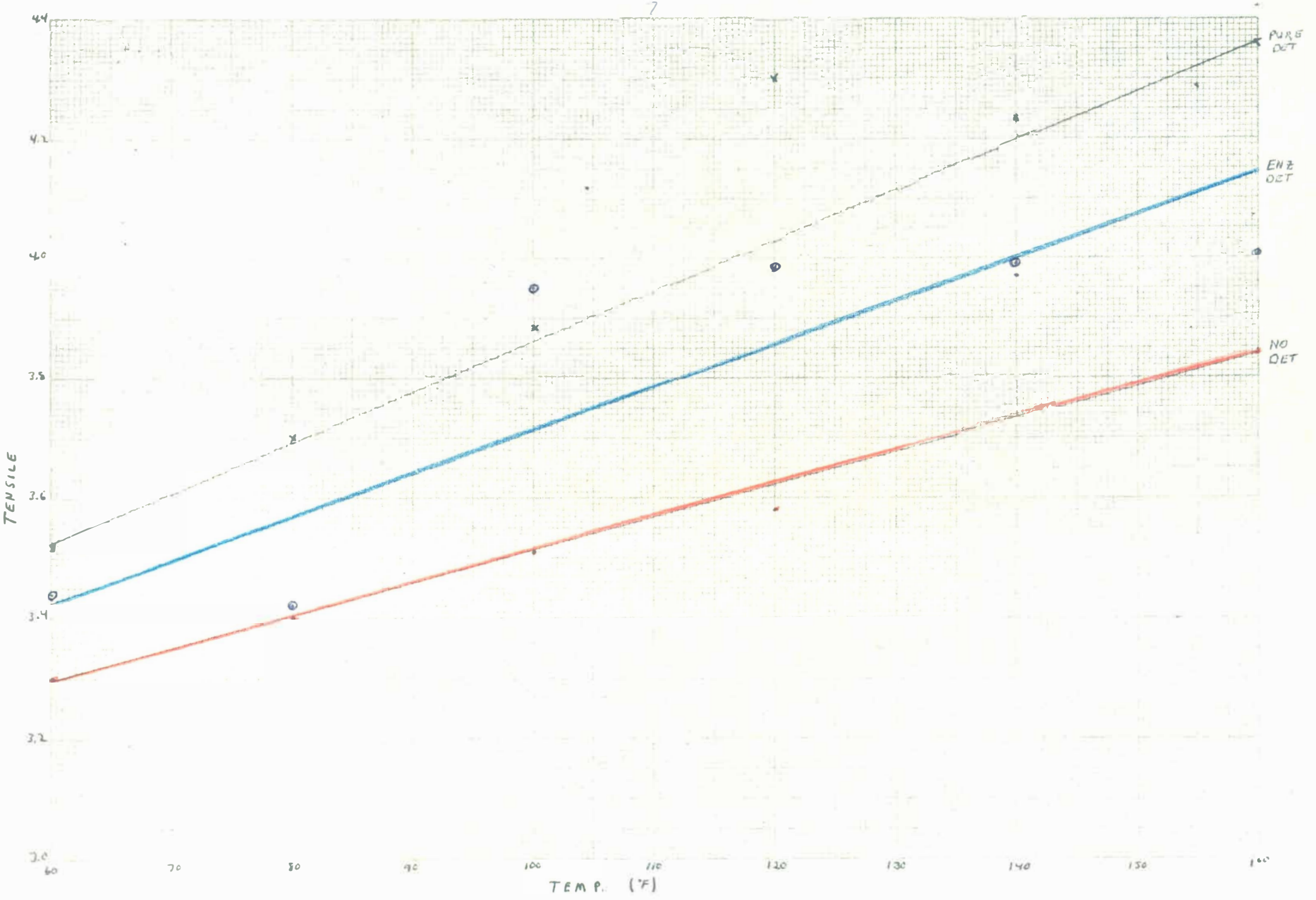
4.0
3.8
3.6
3.4
3.2
3.0
60
70
80
90
100
110
120
130
140
150
160
TEMP. (°F)


4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
TENSILE
60
70
80
90
100
110
120
130
140
150
160
TEMP. (°F)
PURE DET
ENZ DET
NO DET

DISCUSSION

Effects of Enzymes

Tables 2 and 3 give a comparison of the effect of enzymes on the color curve of the deinked newsprint. It is noted from graph 1-3 that the reflectance curve for the enzyme treated pulp is shifted upwards in all cases by at least two or three points over the others. Exceptions to this trend are the enzyme treated system at 160°F where the curve is shifted upwards by only one point over all wavelengthy. At the 140°F temperature interval the enzymes increased the color curve almost seven points over the curve of the pure.detergents. This trend is noted at the various concentration of enzymes and detergents (see graphs 2 and 3) indicating that the optimum temperature range is between 120°F and 140°F. It further indicates that above 140°F the enzymes are denatured resulting in lower readings. Looking at the 457 wavelength, which is used for brightness measurement, the readings increase both with temperature and concentration of enzymes up to the optimum temperature level and then falls off beyond that point.

Tables 4-6 and graphs 4-7 relate the effects of detergents and enzyme concentration with temperature on the physical properties of the papers. The data shows that as the detergent and enzyme containing detergent were added the physical properties of the paper increased in most cases over that of the untreated stock. An interesting point is noted in that the strength curve for the enzyme containing detergent is between those of the pure and no detergent curves indicating that the

enzymes had increased the fiber strength but not as much as the untreated stock.

Effect of Temperature

Table 4 indicates that as the temperature increased, the physical strengths also increased. Normally as the temperature of a pulp slurry is increased the physical strengths decrease. In this case where the strengths increase, it is thought that the increased temperature softened some of the lignin present in the groundwood allowing it to be partically removed. With less lignin present, the hemicellulose could partly hornify upon drying increasing the strength of the sheet.

CONCLUSIONS

The results have shown that a slight increase in the color curve of newsprint can be obtained by treatment with enzymes containing detergents. Above 140°F, the enzymes are severly denatured resulting in a decrease in the color curve from that of the optimum curve. It was further noted that the enzyme containing detergent increased the physical strengths of the groundwood over that of the untreated stock, but resulted in a slight decrease when compared to the pure detergent.

Since the enzymes appear to increase the color quality of the groundwood, while slightly increasing the strength properties, it would be concluded that this method of deinking may possibly have a future use.

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