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Sulphonation of TMP Fibers

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ABSTRACT

Paper made from TMP fibers offers good opacity and stiffness, but its use is limited because of its low strength. Chemical post-treatment of TMP offers possibilities of improving strength. Sulphonation of lignin appears to be the most economically feasible treatment. This thesis was oriented toward finding out if sulphonation of TMP fibers would improve the strength properties of TMP handsheets. Southern pine TMP fibers were treated with sodium sulfite (Na_2SO_3). The chemical concentration to be used was between 3-27% in alkali solution between pH 7-9. The temperature was between 90^{o}-150^{o}C. Pulp consistency was 10%. Handsheets were made using the Noble and Wood mold. The target grammage was 60 gr/m^2. Sheets were tested for density, tensile, brightness and opacity. The control variable was the nontreated pulp. This information helps to identify the relationship between, pH, temperature, yield and chemical concentration and the strength properties of modified TMP. The best strength properties were obtained at a temperature of 150^{o}C. Increasing the cooking time has some impairment on the optical properties but the opposite is seen on the strength properties. The optimum pH range for strength development was 7-8. The concentration of Na_2SO_3 should be high for the sulphonation to take place fast. It should be around 3%. Also, it could be proved that different treatment of pulp with Na_2SO_3 may be performed to obtain fiber with wanted properties by controlling temperature, time, and liquor concentration.

Keywords: Thermomechanical Pulp, Sodium Sulphite, Strength Properties, Optical Properties, Cooking

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LITERATURE SEARCH

Mechanical pulps are in many ways an outstanding raw material for paper production. They have a relatively low price and their opacity is excellent. It is known that by preserving the important advantages of mechanical pulps, such as high yield, lower capital investment and lower environmental impact, and removing the undesirable disadvantages such as low strength, poor bleachability and brightness stability the usefulness of these pulps would be greatly extended. This could lead to their use in a wider variety of end products. Because a very large portion of the chemical and chemomechanical pulps made today are used in products that have exacting requirements for physical strength and brightness, such as newsprint and magazine furnishes, a particular potential is the modification of mechanical pulps by chemical treatment. This improves bonding strength significantly without a large yield loss.[1,7]

Because of the high capital cost for new chemical pulp mill, little growth in Kraft as well as low yield sulphite is expected.[16] This will increase the price of the low yield pulp considerably. As a result, an encouraging development of paper grades with mechanical pulps and chemically modified mechanical pulp as part of several furnishes will have to arrive. For this reason, mechanical pulps will be used in tissue, multilayer board, linerboard, nonwoven and alike in a near future. Many of them have been proven by actual technology.[7,16]

Current trends in chemical mechanical pulping involve the application of the older high yield sulphite pulping technology to the development of RMP and TMP. Placing emphasis on improving the physical strength of the pulp and retaining as much as possible the mechanical pulp advantages of the pulp, a

high yield chemimechanical pulp (CMT) is available. Sulphonation of lignin appears to be the most economically feasible treatment.[7,18] It helps to increase pulp strength by chemical modification in contrast to the purely physical changes brought about by alkaline swelling agents. Sulphonation of lignin offers improved fiber flexibility and bonding potential with minimum yield loss[1,4,6,7,8,15]

Many studies have been published covering the entire pH range from acid sulphite and bisulphite through neutral and alkaline sulphite. The methods employed have included several approaches of wood pretreatment, interstage cooking and post-treatment.[1,2,13,14] Pretreatment cooking is done after chipping or press impregnation. The interstage treatment is usually done after the chips have been refined. Post-treatment is done after refining the chips.[7] The latter approach has been applied to whole pulps, but an alternative of treating just certain coarse pulp fractions as screen rejects is also possible.[4,8]

Post-treatment is going to be the base for this study. A project based on sulphonation of high yield southern pine TMP is proposed in this paper. The goal will be to find out if sulphonation improves the strength properties of this pulp and to determine the favorable conditions at which this treatment is optimum.

POST-TREATMENT

Chemical post-treatment is used to improve the fiber properties with as small yield losses as possible. Therefore, it is more beneficial to modify the property of lignin than to remove it.[15] The lignin content of mechanical pulp affects the paper properties of the fibers in two ways: 1) the fibers are stiff and uncompressible which give fibers with poor conformality, and 2) the fibers surfaces have low ability to form bonds between fibers which cause weak cohesiveness between them. Throughout the post-treatment methods those disadvantages can be removed (respectively) by 1) softening the lignin which makes fibers more comformable, and 2) improving the hydrophiliety of the fiber surfaces which increases the cohesiveness. Various chemicals have been proposed for this purpose such as ozone, chlorine dioxide, peroxide, hypochlorite and oxygen-alkaline and sodium sulphite as the most important. However, it is evident that different chemical treatments do not have the same effect on the properties of mechanical pulps. e.g. groundwood and TMP.[2,7,8,12,15,17,18,19]

Studies conducted by Gummerus have shown that TMP fibers treated with chlorine dioxide, ozone, and sodium sulphite improve the strength properties of those fibers. On the other hand, peroxide, hypochlorite and oxygen-alkaline do not. However, peroxide and hypochlorite tend to increase brightness effectively. (All observations were done at same yield).[15]

The strength properties of sulphonated TMP fibers are promoted by sulphonation of lignin, because then the lignin content has a smaller influence. After sulphonation, fibers are hydrophilic, softer and more swollen. Sulphonated fibers produce fibers with high conformability and relatively good cohesiveness.[8,15,18]

The strength properties of ozone treated TMP fibers are promoted by several factors. Next to chlorine dioxide, ozone is the most selective solvent of lignin. It forms hydrophilic groups which increase the chemical bonding ability of the fibers and so the cohesiveness between them. However, the conformability is not increased. It is because TMP fibers have a great amount of reactive lignin on the fiber surface.[12,15]

The weaker effect of the ozone compared with chlorine dioxide may be explained by the fact that most of the ozone, because of its great reactivity, dissolves lignin from the fiber surface, whereas chlorine dioxide dissolves lignin more evenly from the cell wall. This also explains the reason why ozone treatment gives higher cohesivess and lower conformability between the fibers than chlorine dioxide. However, chlorine dioxide still gives higher conformability with respect to other chemicals (but ozone) at the same yield and lignin content.[15]

The hypochlorite, peroxide and oxygen-alkaline treatments are performed under strongly alkali conditions. These conditions obviously have effect on lignin by improving conformability much more than in ozone and chlorine dioxide treatment at same lignin content. However, at the same yield they are almost the same with chlorine dioxide having the highest value. The cohesiveness at same yield is low for those three chemicals. In addition, the chemical charge in peroxide and hypochlorite treatment needed to develop high strength properties is too high to be used at reasonable cost.[15]

Sulphonation and ozone treatment reduce light scattering coefficient less than chloride dioxide as yield is decreased.[15,19] The brightness decrease is very small with sulphonation at high pH and ozone treatment. Sulfonation at high pH has some brightness effect. On the other hand, the peroxide and hypochlorite show an increasement in brightness as yield is decreased.

Also, it has been confirmed that at high yield sulphonation gives stronger fibers than ozone. This means that in order for ozone to get higher strength properties than sulphonation yield has to be sacrificed.[12,15]

Many of these results obtained for chemical treatment of TMP fibers are similar to those found in chemical treatment of groundwood fibers.[19] However, it has been found that low consistency ozone treatment on groundwood gave the highest strength value with the smallest effect on the apparent density.

In addition, it has been reported that at the same freeness level TMP has a larger coarse fiber fraction than groundwood pulps.[21] Furthermore, the long fibers of TMP have a more even structure, and are more intact than the long fibers of groundwood pulp. These intact fibers should lend themselves well to a delignifing chemical treatment and thus give a better result than conventional groundwood.

At it is visualized in this review, the best alternative for treatment of TMP fibers seems to be sulphonation. First, because it gives both cohesiveness and conformability of the fibers at reasonable high yield. Second, the brightness reduction is very small. Third, the strength properties are higher at high yield (approximately 95%) than other chemical due to the lignin modification. And last, the price.

SULPHONATION

In some investigations sulphonation of groundwood pulps have been performed at 90°C in order to get high yield. On the other hand, a treatment temperature of 100-150°C has resulted in a high degree of sulphonation when the yield is over 90%. Better strength properties can be achieved at higher temperature 160-240°C, but the strength improvement is always accompanied by loss in yield.(16)

Studies done by Gummers on sulphonation of TMP fibers has confirmed that the best strength properties were obtained by sulphonating these fibers at a temperature of 150°C.(18) A temperature below 90°C is not suitable at all. Also, he confirms that raising the cooking temperature from 90 - 150°C did not have any influence on the optical properties of the pulp. When using acid or neutral cooking liquor. Only minor negative effect on brightness is seen when using alkaline cooking liquor. However, the optimum brightness is higher at low pH and lower at high pH.(8,18)

He concluded from his work that the optimum pH range for retaining optical properties and improving strength was 7-8. Raising the ph from 8 to 10 seems not to cause any change in strength properties but brightness decreasement. He also stated that a pH range of 5-5.5 can be also acceptable.

The strength and optical properties achieved their maximum at pH 6; however, cooking time is too long to be feasible in the industry. Extending the cooking time over 70 minutes has only a minor effect on the yield in a pH range 8-10, whereas pH range 4-5 the effect is remarkable greater.

The treatment time also affects the degree of sulphonation. The sulphite reaction takes place in short time, if the pulp consistency is sufficiently high. In one study extension of the treatment time from 30 minutes did not

produce any change in the degree of sulphonation with a pulp consistency of 20%.[18]

The degree of sulphonation depends not only on the charge of Na_2SO_3 but on the concentration of it. When the charge of Na_2SO_3 is fixed at a given level and the pulp consistency is raised, the Na_2SO_3 concentration raises too, and thus the degree of sulphonation rises. Several author has advocated that a pulp consistency of 10% for sulphonation is very appropriate.[18,1]

Apparent density is increased with pH. This is caused by the increase in the degree of sulphonation and by swelling of fibers.[7] However, the cohesiveness of the fibers is decreased as pH is increased because more hemicellulose is dissolved than in the neutral range.

It can be concluded that the workable range to improve strength of the fibers at reasonable time, high yield (higher than 90%) and few loss in the brightness is in the alkaline range.

USE OF CMP

Sulfonated chemimechanical pulps have been suggested as being useful in several grades, ranging from linerboard to tissue. Newsprint, however, is the grade most commonly related with these pulps. The Eastern Canadian newsprint industry is commercially using these processes at increasing rate. Many industries are planning to adopt this method. Observers of the industry attribute this motivation to change, primarily to reduced legal limits of BOD discharge. The lingering Canadian depends on sulphite as chemical reinforcing pulp, combined with the high cost kraft. This makes CMP look attractive to these companies.[22] Sinkey says that by using high freeness CMP in newsprint in term of its chemical pulp, a replacement ratio less than 2:1 is obtained. For example, groundwood based newsprint usually requires 20% chemical reinforcement pulp. However, equivalent properties may be obtained with 40% CMP. This permits eliminating the low yield pulp, maintaining the utility of existing groundwood capacity and producing more newsprint per ton of wood.[1]

In other locations, where existing groundwood is not a factor the possibility of producing newsprint from mixture of CMP and TMP is receiving increasing attention. Along these lines, Gavelin has proposed a single furnish newsprint which he calls "monopulp" prepared by sulphonation of a coarse fraction of TMP.[4] In addition the Ontario paper "OPCO" process, involving sulphonation of high freeness TMP is scheduled to become a reality soon.

The concept of lignin modification by sulphonation applied to mechanical pulp is not a new concept. For example, many investigators have reported substantial bonding improvements as a result of post-sulfonation of groundwood and other high yield pulps.[1,8] Others have proposed sulphonation of high temperature TMP for including in linerboard furnish.[1]

The OPCO process involving interstage or post-treatment TMP with sodium sulphite, has been promoted primarily as a means of improving wet stretch and hence runability on paper machines with open draws.[2,3] The OPCO reaction is usually carried out at a temperature between 130-180^{o}C at a consistency over 10% using 7-10% sodium sulphite based on wood. The duration of reaction is usually between fifteen minutes and two hours. Comparing this pulp to conventional mechanical pulps, the treated pulps achieve a given level of strength development at higher freeness and with less energy consumption. Pulp yields are about 90% with effluent BOD around 100 lb./a.d.t. A 178 CSF "OPCO" pulp, prepared with about 1600 kwh/o.d.t., successfully replaced the chemical pulp in a seven-hour newsprint machine trial.[2]

As an alternative to chemical treatment of the whole pulp several workers have advocated sulphonation of TMP screen rejects prior to refining.[4,8] This approach has been suggested as a logical means of improving fiber flexibility of TMP long fiber fractions. Work in the C-E Bauer laboratory has confirmed that sulphonation of rejects affords properties similar to the whole pulp with some advantages in the efficiency of chemical utilization and with a minimal loss of scattering coefficient in the recombined furnish.[1]

A process proposed by Gavelin for producing a single furnish thermo-

mechanical pulp for newsprint by treating the coarse fraction separately from the final pulp would also produce similar properties.[4] This method has been suggested as a logical mean of improving the flexibility of TMP long fiber fractions. The major limitation is the amount of rejects which can be made available for the chemical treatment.

Gummerus in his recent work proved that sulfonation of screen rejects prior to refining was beneficial with respect to the properties of the final pulp.[8] This treatment improved the strength properties without seriously impairing the optical properties. The optical properties were slightly better when sulphonation was done at pH 5 than at pH 8. The strength properties were somewhat better at pH 8. He also proved that sulphonation of the refined rejects did not significantly influence the properties of the final pulp. Sulphonation of the whole pulp impaired the tearing resistance and the optical properties and increased consumption of chemicals compared with sulphonation of screen rejects only.

Sulphonation of lignin in high yield pulp is a well known technique for improving interfiber bonding. Chang has shown that the beneficial effects on sheet strength of cooking with sodium sulphite are improved if the alkaline conditions are high. He proved that when pulp is treated with sodium sulphite at high temperatures in an alkaline medium, the additive effects of both sulphonation and alkaline swelling from sodium hydroxide can be obtained after refining. The combined modification of carbohydrates and lignin is reported to have an additive effect on interfiber strength.[7,8]

Obviously, in many applications, TMP is good enough to be used alone, but sulphonation treatment of TMP fibers can add advantageous characteristics to the final combined pulp furnish. The papermaker can change the properties of this to meet the requirements of the papermachine or the demand on the paper.

TMP FIBER

The newsprint industry has long been looking for a 100 percent mechanical pulp with high safety margin of strength and printability. Thermomechanical pulp (TMP) offers definite advantages over stone groundwood (SGW) and refiner mechanical pulp because of its superior strength properties and low shive content. Pulp quality improvement for manufacturing of newsprint translates directly into improved processability and runnability. As it is known, the safety margin seldom permits the use of mechanical pulp only in the manufacture of newsprint. Some chemical reinforcement pulp has to be used to maintain the required strength level. Thus, there is still a need for improving the strength level of TMP.

The fibers of TMP restrict the development of the overall strength properties of the pulp. The bonding ability of the long fiber fraction of TMP has been reported to be marginally poorer than those of SGW and significantly poorer than those of the chemithermomechanical pulp and semibleached kraft.[8] In a sheet of TMP a comparatively small proportion of the surface area of the fiber is utilized for fiber to fiber bonding. On the other hand, large proportion of unbonded fiber surface and of fine material are available to give the sheet a high light scattering coefficient and opacity. This is the reason that mechanical pulp are quite stiff. This gives bad conformation between the fibers in the sheet. For better conformation between the fibers the flexibility should be increased.[1,5,6,7,,8,9,10]

Mottlin has confirmed that the large variation in properties observed between thermomechanical pulps is due to both variations in particle size distribution and variation in bonding ability of the particles.[10] He concluded that for both the coarse fraction and the middle fraction there

exists a large variation in their properties. The middle fraction variation is due to the differences in proportions of fibrillar, ribbon-like material to chunky material. The coarse fiber variation is due mainly to differences in fiber flexibility. The coarse pulp fraction and the middle fraction is the fiber retained between the 16-30 and 30-200 mesh (in the Bauer Mcnett) respectively.

The fibers and the ribbon-like and fibrillar material make different contributions to the pulp strength. The fibers are stiff and can not bond together in the same way as the fibers of a chemical pulp can. This is reflected in the low strength of the fiber fraction itself. The bonding between the fibers is provided by the conformable ribbon like and the fibrillar material found in the middle fraction and in the fine fraction.

It also has been stated that the long fraction and the fines are the two most important fractions in the TMP.[9] Further modifications of the long TMP fibers can be increased by giving them some kind of treatment either mechanical or chemical, in order to improve their papermaking quality.

For better conformation between the fibers, their flexibility must be improved. One way to increase the flexibility of the fibers in refiner mechanical pulp is to increase the beating. However, as the energy input in the refiner is increased the amount of fine material also increases. This makes this pulp difficult to dewater on the paper machine. This limits the possibilities of beating. In addition, it has been shown that refining of the coarse long fractions at high consistency in the TMP process improves the strength properties of this pulp. However, when comparing this pulp with the TMP made without selective screening and refining of long fibers no energy reduction or improvement in pulp drainage were observed.

Another way of improving the strength properties of TMP is through mild

chemical treatment to improve fibers cohesiveness and flexibility.[7,8,15] As before mentioned there are several methods of sulphonation treatments. Pre-treatment, interstage and post-treatment. Presulfonation of wood affects fiber separation. It gives a pulp with superior tear-tensile relationships, and insignificantly debris formation levels. The sulphonation of defibred pulps cause an increase in the specific surface of shorter fiber fractions, whic results in other advantages. These include improved wet web strength, reduce linting tendency and some advantages in specific energy bonding relationships. An option to the interstage treatment of coarse TMP, the cooking of screen rejects can also be very efficient.[1] Pretreatment approaches may afford the best replacement for low yield pulp if tear-tensile is critical. For printing grades, pretreatment may be beneficial if the furnish contains stone groundwood (light scattering is not critical), and specially if the paper machine is a twin wire, without open draws. On the other hand, if the chemimechanical component is required to contribute to light scattering or if linting and wet web strength are more important than tear, pulp treatment methods should be considered. In such a case, screen rejects might profitably be used as all or a portion of the pulp to be treated.

Several chemical treatments for upgrading mechanical pulp fiber have been published.[1,7,12,13,14] The most promising method for treatment of TMP fibers seemed to be sulphonation. Sulphonation of lignin appears to be the most economically feasible treatment. It helps to increase pulp strength by chemical modification in contrast to the purely physical changes brought about by alkaline swelling agents. Sulfonation of lignin offers improved fiber flexibility and bonding. This process avoids the discoloration of the pulp. Processes are available for treatment of pulp. These treatments are

mechanical or chemical in nature. They improve the strength characteristics without reducing the yield. Use of these pulps is advantageous in newsprint and magazine furnishes. They can replace the more expensive chemical pulps generally used on these grades.

OBJECTIVE

Based on this literature review, a question arise. What will be the effect of sulfonation on Southern Pine of TMP fibers? As we know from the literature, TMP offers many advantages in the production of paper products, such as high yield and opacity. Its main limitation is its relative low strength. However, if this drawback could be eliminated, while preserving the yield, TMP could be economically used in the newsprint and magazine industry.

The purpose of this thesis is to find out if sulphonation (with Na_2SO_3) of TMP fibers will improve the strenght properties of TMP handsheets. To answer this question considerations, such as percent chemical addition, pH range, temperature, pressure, time of cooking and consistency during the chemical treatment should be known.

In order to find out the optimum conditions at which sulphonation respond; treatment of the whole pulp at different conditions will be done.

The experimental approach for this study were based on obtaining a commercial high freeness-southern pine TMP. This pulp was provided by Augusta Newsprint S.A.. The reason for using southern pine TMP is that many of the researches done on this field have been oriented to the Canadian and European market. This study would probably extend the use of the Southern Pines in United States. The high freeness will give the pulp a considerable margin of strength development by mechanical action after chemical treatment.(7)

The ranges to find the optimum conditions are the following: pH 7-9, temperature between 90-150°C, time 30-90 minutes, consistency 10%, percent chemical addition 3-27%.

The pH range was chosen as to be the most appropriate for the sodium sulphite. It eliminates the discoloration at high alkalinity and avoids the

possibility of increasing the acidity at the end of the cook which may increase rapidly the dissolution of lignin from fiber (and so the yield). However, in this experiment the pH will be corrected by using NaOH to avoid acidification at the end of the treatment range seems to be the most appropriate. The consistency value is going to be set at 10%. In mill situation it can be actually the case. OPCO process also uses this value for the sulfonation of the pulp. The time range and the percent sodium sulphite addition are thought to be the most appropriate according to several references.[2,8,13]

EXPERIMENTATION

In order to do the sulphonation of the fibers an AMICO oil bath digester will be used. The temperature at this chamber can go as high to 150°C.

In this experiment the pulp at 10% consistency is going to be treated with sodium sulphite at the different concentrations (3, 11, 19, 27%), pH's (7, 8, 9) and intervals of time (30, 60, 90 minutes). After the chemical treatment pulp will be washed thoroughly. Liquor will be tested for residual SO_2 concentration to determine chemical concentration according to Tappi procedure T604. The pulp will be diluted and handsheets will be made on the Noble and Wood handsheet mold. The target grammage will be 60 gr/m^2 (about seven handsheets for each condition will be made). After that handsheets will be conditioned at room temperature (25°C) and at a relative humidity of 40%. Physical and optical tests are also going to be performed in this conditions. Sheets will be tested for tensile, stretch, density, brightness. All those tests will be run according to Tappi Standard procedures. Pulp yield will also be determined.

With this information, the optimum conditions for sulphonation of Southern Pine TMP will be determined.

$Note_1$: Also, latency of the pulp to be received is going to be tested according to the procedure explained by Jame Clark's book, "Pulp Technology and Treatment for Paper", page 597. It has been reported that if latency is retained, the strength properties of the treated pulp are lower than they would otherwise be. This may lead to erroneous conclusion that chemical treatment fails to improve strength. For this reason, if pulps are compared at equal state of latency, a large improvement in strength effected by chemical treatment can become more evident.[2,3]

Note$_2$: Untreated pulp changes somewhat during storage. For that reason the properties of an untreated sample will be measured in all trial runs.

EXPERIMENTAL PROCEDURE

When pulp was received, the pulp slurry was diluted in the hydropulper to 2% consistency. Then, slurry was heated to 85^{o}C with agitation to remove latency for at least one half hour. Next, a 100ppm dose of Biocide was given to the pulp based on total material.

When treatment was completed the pulp was passed through a screw press to increase the consistency to 8%. This consistency was still too low for storage, so the pulp was dewatered further in a centrifuge increasing the pulp consistency to 18-25%.

Then, the stock was stored in plastic bags. The content of pulp in each bag was about 4kg. Pulp bags were stored in the student lab refrigerator. The temperature was about 4^{o}C.

Before each run, one or two pulp bags were allowed to stand at run temperature for at least 24 hours. Then samples from respective bags were taken to make consistency determination to know oven dry content in each plastic bag.

The oil bath was set to the desired temperature two to four hours in advance.

The pulp required to obtain 100g oven dry fiber for each condition was weighed and kept in plastic bags of known weight.

Then, the water required to make a 10% slurry was measured and poured in a 800ml beaker. The amount of Anhydrous Sodium Sulfite was weighed and added to the respective beaker to give the right percentage of addition. The water and the Sodium Sulfite were mixed. Next, the pH was corrected by using concentrated H_2SO_4 and NaOH. Finally, the pulp and the liquor were mixed and put inside the bomb.

Note: Straight labeling of the plastic bags, Sodium Sulfite samples and bombs position were performed during all runs.

Next, all six bombs were put in the oil bath rack. They were carefully sealed with their respective caps. The rack was then submerged in the oil bath digester for the determined temperature and time.

When the cook was completed, the rack was taken out of the oil bath digester and submerged in a water tank for at least ten minutes. When the rack was taken off from the water tank, bombs were opened and some liquor was saved for black liquor analysis. Then, the pulp was dewatered and washed in a Buchner funnel. At least 2000ml of tap water was used to rinse the pulp.

The pulp as saved in its respective plastic bag and stored in the refrigerator for at least two days.

Then the percentage of moisture of each bag for each condition was determined. This helps in obtaining the percentage yield and pulp needed for the handsheet making stage.

In the handsheet making stage 40 grams of pulp and its respective amount of water was weighed to make a slurry of .62% consistency. The slurry was mixed until fibers were well dispersed.

The handsheets were made on a Noble and Wood mold using around 400ml of the slurry to get handsheets of about $60g/m^2$.

Handsheets were conditioned at 40% relative humidity and $77^{o}F$ for two days. Handsheets were tested for brightness, opacity, basis weight, caliper, tensile, and stretch.

Tensile values were corrected by basis weight by determining the tensile factor.

A summary of these procedures is specified in Figure 1.

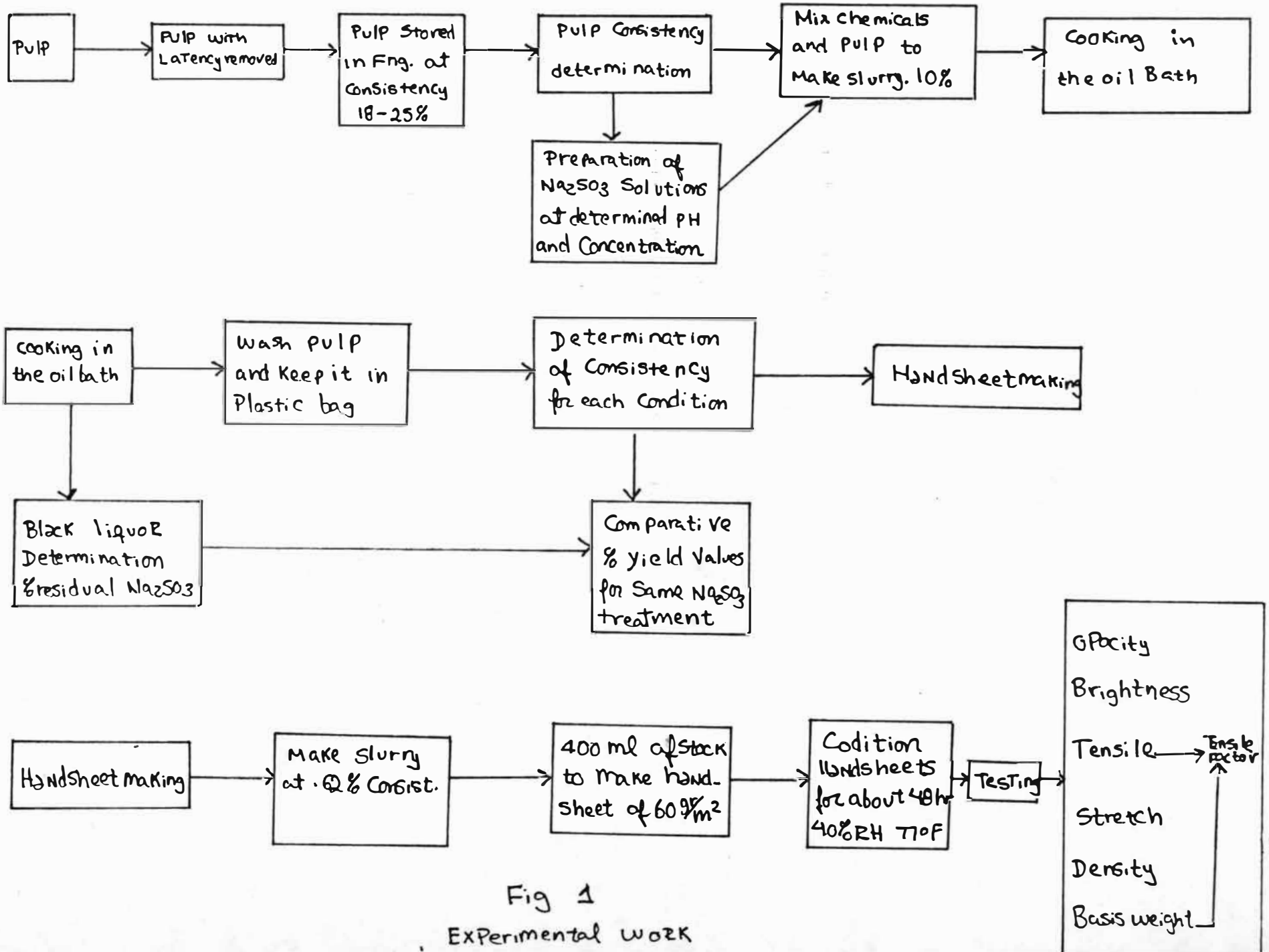


Fig 1

Experimental work

EQUIPMENT

1. Oil Bath Digester
2. Buchner Funnel and Filter Paper
3. Plastic Bags
4. Analytical Balance
5. 50ml Buret
6. Mixer and Mixing Capsule
7. 250ml Beakers
8. 800ml Plastic Beakers
9. Aluminum Tray
10. 2ml Pipets
11. Eye Dropers
12. 1000, 100, and 10ml Graduated Cylinders
13. Oven with Constant Temperature at 103^{o}C
14. pH Meter
15. Buckets
16. Noble and Wood Sheet Mold

CHEMICALS

1. Anhydrous Sodium Sulfite, Na_2SO_3
2. Iodine Solution of Known Normality Preferable .1 N
3. Sodium Thio Sulfate, $Na_2S_2O_3$, of Known Normality
4. Starch Indicator
5. Deionized Water
6. Sodium Hydroxide, Concentrated
7. Sulfuric Acid, Concentrated

DESIGN

The sequence of the cooks are specified in Figure 2. A code list for each condition is specified in Table I.

The different conditions are:

pH: 7, 8, and 9
Level of Percentage Na_2SO_3: 3, 11, 19, and 25% based on O.D.
Temperature: 90, 20 and 150°C
Consistency: 10%
Cooking Time: 30, 60, 90 minutes

The main purpose is to see the interaction between these variables with the tensile and brightness properties of the TMP handsheets.

Fig 2

TEMPERATURE

COOKING TIME	90°C	120°C	150°C
30 MIN.	1 2 5 6 9 10 3 4 7 8 11 12	9 11 1 3 5 7 10 12 2 4 6 8	5 8 9 12 1 4 6 7 10 11 2 3
60 MIN.	1 2 5 6 9 10 3 4 7 8 11 12	9 11 1 3 5 7 10 12 2 4 6 8	5 8 9 12 1 4 6 7 10 11 2 3
90 MIN.	1 2 5 6 9 10 3 4 7 8 11 12	9 11 1 3 5 7 10 12 2 4 6 8	5 8 9 12 1 4 6 7 10 11 2 3

EACH NUMBER IN THE BLOCKS ABOVE REPRESENTS A PARTICULAR pH & Na_2SO_3 LEVEL.

NUMBER	1	2	3	4	5	6	7	8	9	10	11	12
pH	7	7	7	7	8	8	8	8	9	9	9	9
Na_2SO_3 %	3	11	19	27	3	11	19	27	3	11	19	27

TABLE I

CONDITIONS TO BE TESTED

Code	Min. Time	°C Temperature	% Na_2SO_3	pH	Code	Min. Time	°C Temperature	% Na_2SO_3	pH
1	30	90	3	7	22	30	120	19	7
2	60	90	3	7	23	60	120	19	7
3	90	90	3	7	24	90	120	19	7
4	30	120	3	7	25	30	150	19	7
5	60	120	3	7	26	60	150	19	7
6	90	120	3	7	27	90	150	19	7
7	30	150	3	7	28	30	90	27	7
8	60	150	3	7	29	60	90	27	7
9	90	150	3	7	30	90	90	27	7
10	30	90	11	7	31	30	120	27	7
11	60	90	11	7	32	60	120	27	7
12	90	90	11	7	33	90	120	27	7
13	30	120	11	7	34	30	150	27	7
14	60	120	11	7	35	60	150	27	7
15	90	120	11	7	36	90	150	27	7
16	30	150	11	7	37	30	90	3	8
17	60	150	11	7	38	60	90	3	8
18	90	150	11	7	39	90	90	3	8
19	90	90	19	7	40	30	120	3	8
20	60	90	19	7	41	60	120	3	8
21	90	90	19	7	42	90	120	3	8

TABLE I

(Cont.)

Code	Min. Time	°C Temperature	% Na_2SO_3	pH	Code	Min. Time	°C Temperature	% Na_2SO_3	pH
43	60	150	3	8	64	30	90	27	8
44	60	150	3	8	65	60	90	27	8
45	90	150	3	8	66	90	90	27	8
46	30	90	11	8	67	30	120	27	8
47	60	90	11	8	68	60	120	27	8
48	90	90	11	8	69	90	120	27	8
49	30	120	11	8	70	30	150	27	8
50	60	120	11	8	71	60	150	27	8
51	90	120	11	8	72	90	150	27	8
52	30	150	11	8	73	30	90	3	9
53	60	150	11	8	74	60	90	3	9
54	90	150	11	8	75	90	90	3	9
55	30	90	19	8	76	30	120	3	9
56	60	90	19	8	77	60	120	3	9
57	90	90	19	8	78	90	120	3	9
58	30	120	19	8	79	30	150	3	9
59	60	120	19	8	80	60	150	3	9
60	90	120	19	8	81	90	150	3	9
61	30	150	19	8	82	30	90	11	9
62	60	150	19	8	83	60	90	11	9
63	90	150	19	8	84	90	90	11	9

TABLE I

(Cont.)

Code	Min. Time	°C Temperature	% Na_2SO_3	pH	Code	Min. Time	°C Temperature	% Na_2SO_3	pH
85	30	120	11	9	97	30	150	19	9
86	60	120	11	9	98	60	150	19	9
87	90	120	11	9	99	90	150	19	9
88	30	150	11	9	100	30	90	27	9
89	60	150	11	9	101	60	90	27	9
90	90	150	11	9	102	90	90	27	9
91	30	90	19	9	103	30	120	27	9
92	60	90	19	9	104	60	120	27	9
93	90	90	19	9	105	90	120	27	9
94	30	120	19	9	106	30	150	27	9
95	60	120	19	9	107	60	150	27	9
96	90	120	19	9	108	90	150	27	9

DETERMINATION OF Na_2SO_3

In each case, the sulphite content was determined as follows. A suitable solution containing sodium sulfite was weighed and diluted in a suitable volume of deionized water. Next, the solution was titrated slowly with continuous stirring, with .1 N iodine solution. The end point is the discharge at the iondine color. Starch was used as an indicator.

Then, one milliliter .1 N iodine = .003203 gr SO_2. The normality of the iodine solution used was .10317N.

The reaction taking place is $Na_2SO_3 + I_2 + H_2O$ ----- $Na_2SO_4 + 2\ HI$

Then, for A = 1ml .1 N I_2 corresponds to .003203 gr SO_2

For A = 1ml of .13017N I_2 corresponds to .003305 gr SO_2

To determine the quantity of sulfur on sodium sulphite basis the following relation holds:

$$1ml\ I_2 = .003305gr\ SO_2 \times (126.04gr\ Na_2SO_3/64.06gr\ SO_2) = .006491gr\ Na_2SO_3$$

$$1ml\ I_2 = .006491gr\ Na_2SO_3$$

$$\%\ Na_2SO_3 = (gr\ Na_2SO_3/gr\ of\ solution\ weighed) \times 100$$

The following approximation was used in this thesis:

$$\%\ Na_2SO_3\ consumed = \%\ Na_2SO_3\ white\ liquor - \%\ Na_2SO_3\ Black\ Liquor$$

In this experiment four levels on sodium sulfite addition were used; 3%, 11%, 19% and 27% based on O.D. fiber. They corresponds to liquor concentrations of .333%, 1.222%, 2.111% and 3.000% respectively for a pulp consistency of 10%.

Handsheet Testing

Area of handsheet = 64 in^2 = .0413 m^2

Basis weight = weight in grams/.0413 M^2

Density = B.W./25.4T gr/cm^3
T is thickness in thousand of an inch

Tensile factor = 200000P/3r M
P = tensile kg/15mm
r = B.W. gr/m^2

Yield Determination

In this experiment yield could not be determined because an operational problem arrived. When the pulp was washed and stored sulfur was retained in the free and bound water. For this reason actual yield could not be determined by standard method. Comparative yield data for pulp treated at the same percentage of sodium sulfite addition was used.

The approximate procedure was as follows: for each condition, 100 ml of slurry at 10% consistency (100gr of pulp) was used. After cooking the pulp, the residual liquor was tested for percent Na_2SO_3. The pulp was washed and stored in plastic bags, and solids determined. The following assumption was made:

1000ml - weight in plastic A.D. = volume of black liquor removed

Oven Dry Na_2SO_3 on liquor =
Volume of black liquor x (% Na_2SO_3 of black liquor/100)

Starting O.D. Na_2SO_3 - O.D. Na_2SO_3 on liquor = O.D. Na_2SO_3 on fiber

The assumptions could be true if the pulp would not have been washed. However, the relation between pulps treated at the same percent Na_2SO_3 levels could be encountered since washing was the same throughout the experimental work.

O.D. pulp on plastic bag - gr of Na_2SO_3 on pulp = gr of dry fiber

It is assumed all the Na_2SO_3 is bounded to the fiber:

(gr of dry fiber/100gr pulp) x 100 = % yield

See Appendix I for yield results at 150°C.

TABLE II
RESULTS

code	Day	$g/m^2 \times 100$ Density	% Brightness	% Opacity	meter Tensile	% Stretch	% Na_2SO_3 Consumed
1111	82	24.59	44.4	88.8	2088	2.44	.268
2111	73	23.70	45.4	87.4	2083	2.50	.179
3111	71	23.88	44.2	87.0	2172	1.96	.240
1121	82	24.99	46.4	88.3	2238	2.58	.729
2121	73	23.84	47.3	88.6	2186	2.05	.808
3121	71	24.59	47.5	86.8	2306	2.32	.680
1131	83	24.48	47.2	87.2	2157	2.48	1.369
2131	81	24.77	47.5	87.8	2138	2.56	1.207
3131	72	24.46	48.0	87.3	2261	2.34	1.473
1141	83	24.76	47.4	87.5	2227	2.54	1.913
2141	81	24.38	48.0	87.5	2321	2.64	1.438
3141	72	24.83	48.7	87.8	2444	2.60	1.726
1112	82	23.78	44.1	88.2	2148	2.50	.205
2112	73	23.94	44.4	89.8	2131	2.64	.126
3112	71	25.31	44.7	90.2	2356	2.32	.178
1122	82	24.40	45.6	88.1	2162	2.46	.343
2122	73	23.80	46.7	87.4	2108	2.32	.698
3122	71	25.17	46.5	89.6	2424	2.36	.366
1132	83	24.44	45.8	86.8	2132	2.28	.575
2132	81	25.01	46.4	87.9	2167	2.60	.484
3132	72	24.77	47.0	88.2	2501	2.54	.551
1142	83	24.60	46.0	88.2	2246	2.42	.679
2142	81	24.51	46.7	87.1	2245	2.32	.465
3142	72	25.07	47.3	87.7	2400	2.50	.830
1113	82	24.39	43.9	89.8	2155	2.48	.172
2113	73	23.81	44.6	90.7	2012	2.40	.207
3113	71	24.31	45.0	89.7	2292	2.24	.176
1123	82	24.68	44.8	87.8	2271	2.56	.319
2123	73	24.27	46.1	88.5	2166	2.66	.497
3123	71	25.10	46.3	89.1	2378	2.50	.342
1133	83	24.46	45.8	88.0	2120	2.38	.343
2133	81	24.70	46.1	87.9	2175	2.34	.633
3133	72	24.93	46.8	87.1	2403	2.40	.554
1143	83	24.56	46.5	87.6	2114	2.42	.465
2143	81	25.49	46.3	89.2	2356	2.46	.340
3143	72	24.81	46.6	88.7	2260	2.18	.670
1211	22	19.95	44.5	90.5	1683	2.28	.208
2211	21	19.98	44.9	89.6	1776	2.36	.237
3211	63	21.71	45.5	87.7	1868	2.42	.211
1221	62	22.32	47.4	88.4	1962	2.32	.825
2221	41	20.85	48.8	83.1	1746	2.18	.711
3221	61	22.78	48.1	88.0	2078	2.52	.606
1231	22	19.13	48.2	85.3	1706	2.48	1.534
2231	21	21.76	48.8	93.2	2150	2.72	1.164
3231	63	22.24	50.4	83.4	2148	2.94	1.093
1241	62	21.62	49.2	85.6	1944	2.62	1.634
2241	41	22.32	50.6	85.4	1939	2.76	1.480
3241	61	22.51	49.7	84.9	2254	2.60	1.178
1212	22	19.96	43.8	89.9	1806	2.53	.174
2212	21	20.07	43.4	88.9	1696	2.16	.203
3212	63	21.84	45.2	88.6	1872	2.40	.211
1222	62	22.44	46.4	88.4	1988	2.66	.548
2222	41	21.80	45.4	88.4	1780	2.62	.962
3222	61	22.87	46.8	88.0	2101	2.46	1.100
1232	22	19.95	46.3	87.9	1757	2.44	.781
2232	21	19.55	45.9	85.9	1830	2.42	1.604
3232	63	22.56	48.5	84.5	1960	2.40	.521

1242	62	22.82	47.5	85.6	2064	2.82	.861	33
2242	41	22.17	46.1	87.8	1971	2.84	1.980	
3242	61	23.51	46.9	86.6	2363	2.74	.989	
1213	22	19.76	44.1	90.5	1800	2.68	.203	
2213	21	20.20	43.4	90.1	1710	2.58	.205	
3213	63	21.18	44.9	86.8	1891	2.64	.270	
1223	62	22.90	46.1	87.4	1930	2.58	.643	
2223	41	22.16	46.4	87.6	1936	2.44	.518	
3223	61	22.99	47.0	85.2	2200	2.68	.577	
1233	22	18.64	46.7	83.7	1507	2.14	.658	
2233	21	20.10	45.4	89.6	1756	2.44	.876	
3233	63	22.78	47.7	84.7	2012	2.48	.640	
1243	62	23.18	47.0	86.3	1994	2.56	.767	
2243	41	22.22	45.5	87.8	1764	2.40	.970	
3243	61	23.81	46.6	85.9	2261	3.02	.966	
1311	11	19.21	40.4	89.7	1642	2.44	.205	
2311	12	19.94	43.1	86.8	1714	2.48	.206	
3311	51	24.00	40.5	91.2	2382	2.68	.268	
1321	52	23.74	44.9	90.0	2317	2.84	.653	
2321	32	21.37	46.2	80.1	2087	2.40	.633	
3321	31	21.73	45.9	86.0	2391	2.76	.580	
1331	52	23.61	47.9	88.0	2326	2.82	.974	
2331	32	21.42	46.8	86.2	2341	2.64	.737	
3331	31	20.13	47.4	82.9	2213	2.66	.659	
1341	11	19.90	48.2	85.7	1769	2.42	.421	
2341	12	21.13	47.0	84.9	2012	2.50	1.100	
3341	51	26.83	47.1	85.9	2858	2.88	.762	
1312	11	19.86	41.8	86.6	1738	2.62	.203	
2312	12	20.09	41.6	87.1	1607	2.40	.205	
3312	51	23.47	40.0	90.5	2145	2.68	.241	
1322	52	23.87	45.3	88.5	2338	2.86	.653	
2322	32	21.31	44.5	87.3	2103	2.66	.662	
3322	31	21.09	44.0	84.4	1962	2.40	.521	
1332	52	24.39	46.7	88.5	2140	2.66	.706	
2332	32	21.76	45.2	87.2	2448	2.62	.707	
3332	31	21.58	43.2	83.4	2178	2.46	.838	
1342	11	20.90	44.1	86.2	1826	2.66	.	
2342	12	21.02	44.0	87.8	2256	2.20	.330	
3342	51	26.45	45.2	83.7	2758	2.60	.884	
1313	11	19.87	41.5	88.8	1732	2.66	.142	
2313	12	20.17	41.3	90.5	1760	2.36	.269	
3313	51	22.99	40.2	89.5	2134	2.64	.274	
1323	52	23.56	45.9	88.0	2298	2.88	.555	
2323	32	21.76	44.1	88.9	2190	2.58	.590	
3323	31	21.35	42.4	87.4	2472	3.12	.447	
1333	52	24.02	46.4	87.6	2330	2.82	.550	
2333	32	21.64	44.5	87.9	2104	2.52	.852	
3333	31	22.33	43.4	85.7	2338	2.94	.656	
1343	11	20.96	45.5	83.6	1738	2.54	.600	
2343	12	20.60	45.3	85.1	1789	2.40	.620	
3343	51	25.96	44.5	84.3	2894	2.90	.847	

Code First N° - 1, 2, 3 Correspond to time 30, 60, and 90 min
second N° - 1, 2, 3 Correspond to temperature 90°C, 120°C and 150°C
third N° - 1, 2, 3, 4 Correspond to Percentage Na_2SO_3 3, 11, 19 and 27
fourth N° - 1, 2, 3 Correspond to PH 7, 8, 9 -

RESULTS

From the results obtained it could be observed that the values that give the highest tensile without impairing brightness were at 150°C, as seen in Table II. Tensile at 90°C tends to have higher tensile values than those of 150°C. The reason is due to the high density obtained when the 90°C handsheets were made. It was noted that the load applied during pressing the 90°C handsheets was very high (reported in handbook). As a good approximation, the average of all tensiles at their respective temperature were computed as well as their density. Table III shows them. Clearly, handsheets made at 90°C tend to have the highest tensile values. However, if the ratio of tensile to density is computed it could be observed that the handsheets at 150°C develop even higher strength when contrasted against the 90°C handsheets if the density is considered as a positive factor in inducing strength development. The 120°C and 150°C handsheets were made under the same conditions.

Based on this assumption, the discussion about the results will be oriented on the handsheets made at 150°C.

It is a good point to emphasize that the main purpose of this work was to improve the strength properties of the TMP fibers.

A brief discussion of each of the facts on each of the results is going to be mentioned.

TABLE III

Average Tensile and Density

°C Temperature	(M) Tensile	(x 100 [g/m^3]) Density	T/D
90	2221	24.54	90.50
120	1919	21.57	88.97
150	2148	22.05	97.42

DISCUSSION

Percentage Yield

From Graph 1A-1D it can be observed that yield decreases as cooking time progresses. This is due to the materials that are being dissolved at a very rapid rate. Fibers pulped at a pH of 7 and 9 tend to respond even faster. It could be predicted that yield decreases as the level of Sodium Sulfite increases, but as mentioned earlier this can not be assumed since the yields are comparative for pulps treated at the same level of Na_2SO_3. Howver, it could be assumed that the percentage yields are all above 90% since more than 50% of the initial Sodium Sulfite was considered to be attached to the fibers, something that tends to look unrealistic.

Density

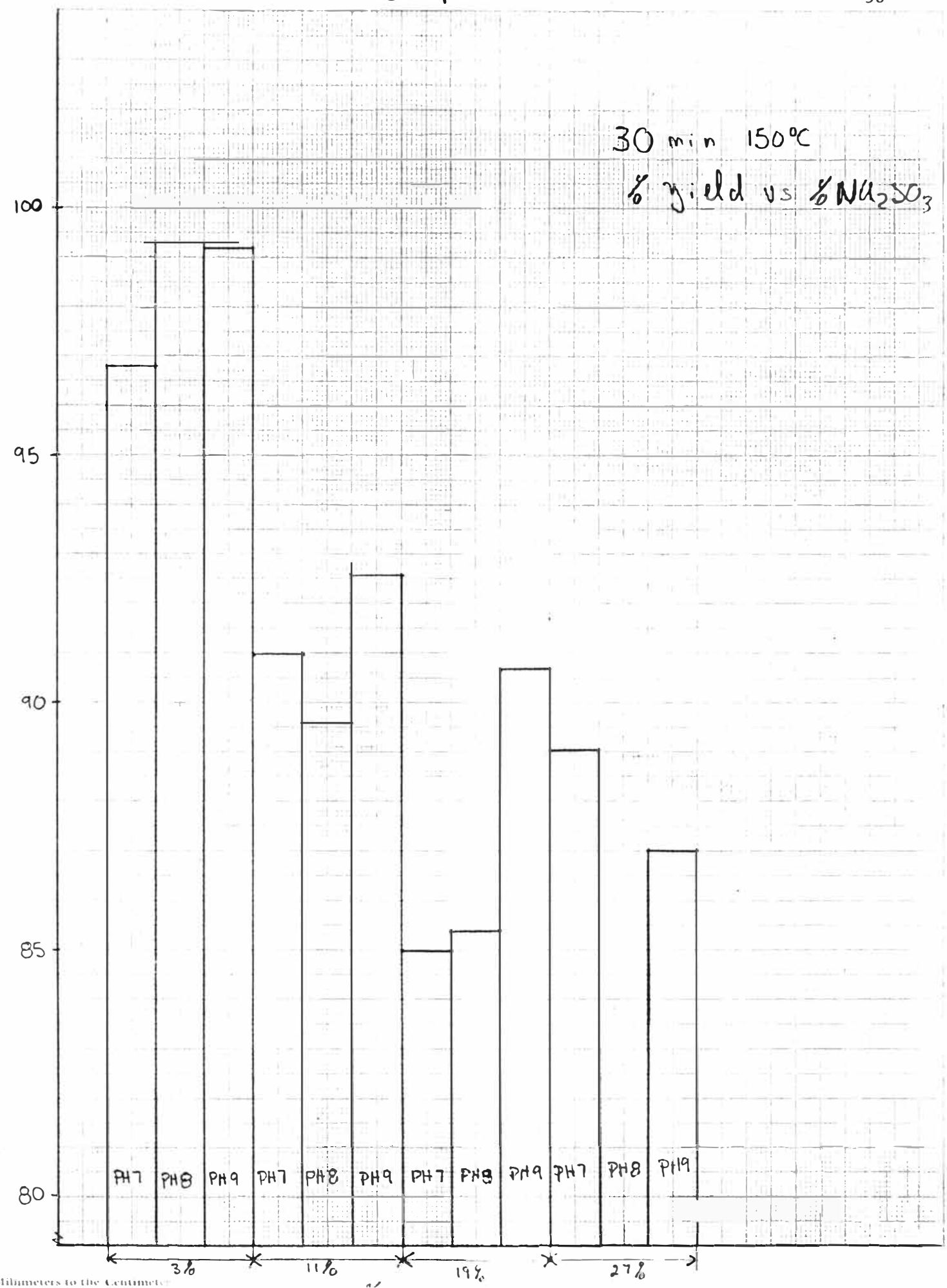
From Table IV it could be observed that density increases as cooking time, ph and percentage Na_2SO_3 increase. As it is known the comformability of fibers increases as cooking time is increased. It may be accompanied by an increase in the degree of sulphonation especially in pulps treated at high levels of Sodium Sulfite. At lower levels of Na_2SO_3 density changes were not observed. pH seems to influence the density to a smaller degree. However, at pH 9, high values of density were observed.

Tensile and Stretch

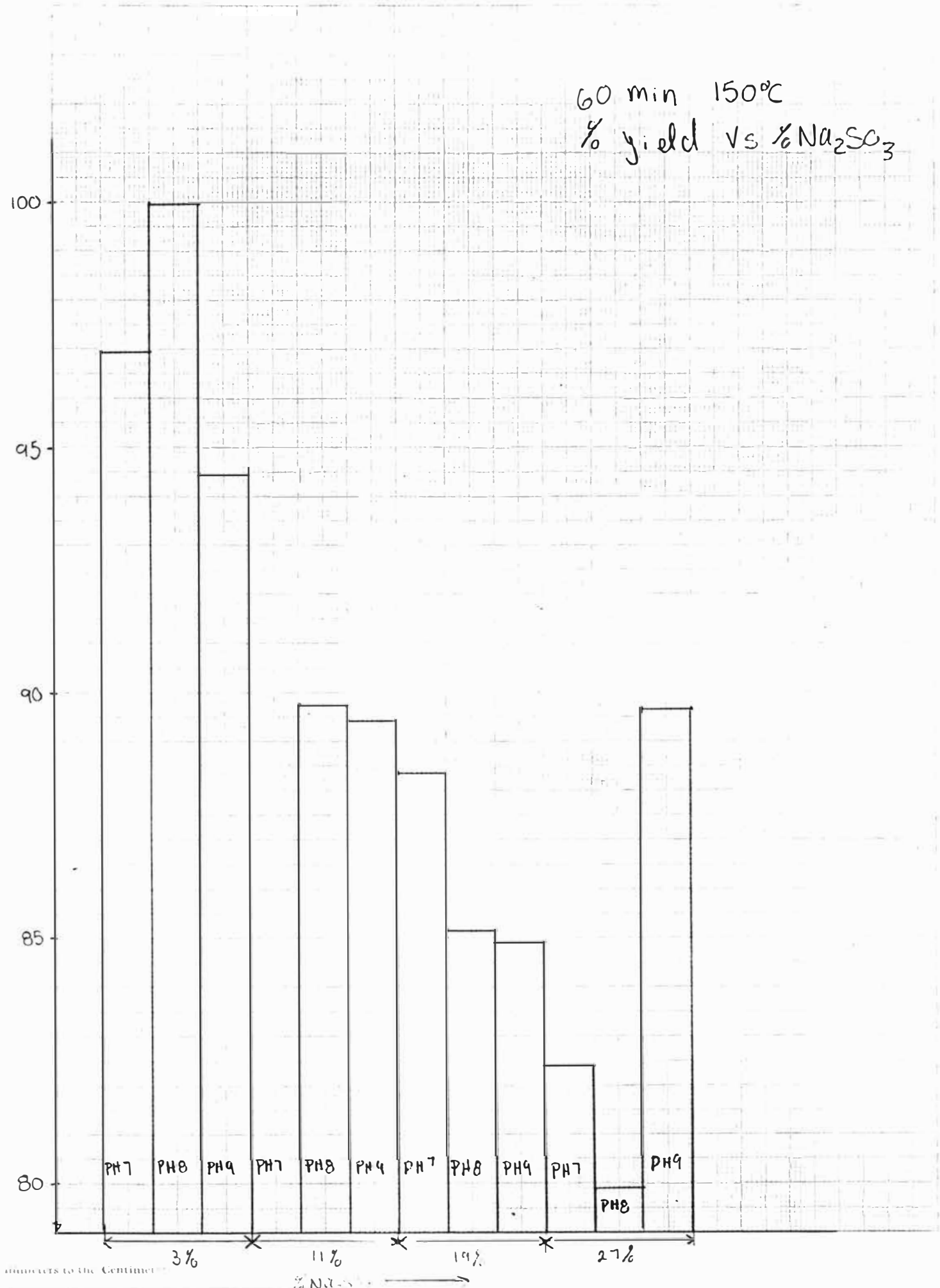
Stretch and tensile tend to increase in the same range as tensile. For this reason only tensile will be discussed.

It can be observed from graph 2.A-2C that the behavior of tensile with cooking at pH 7 and 8 is exactly the same, with the pH 7 having the highest values. At pH 9 the behavior is completely different especially for pulps

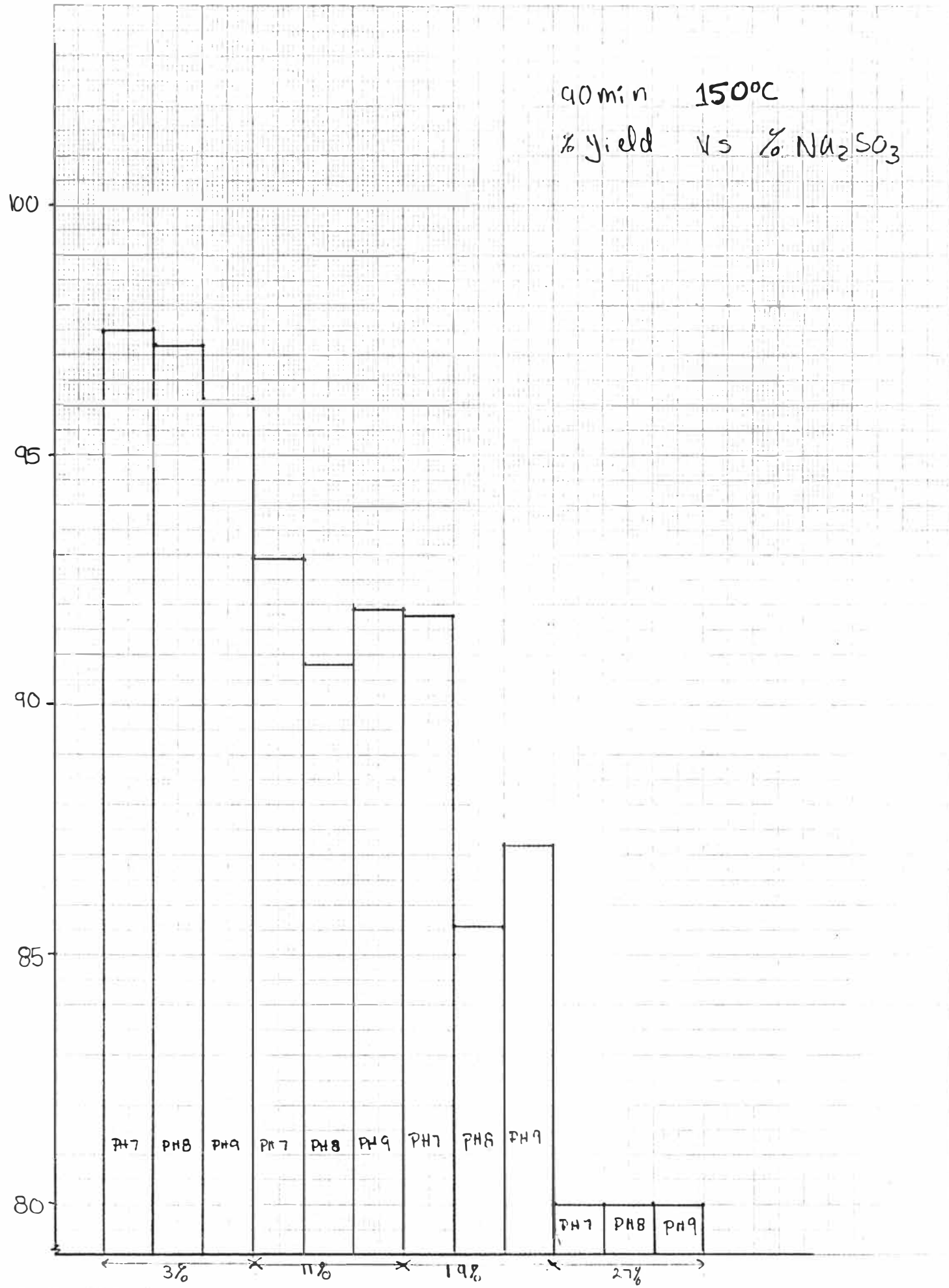
Graph 1a


30 min 150°C
% yield vs % Na_2SO_3
100
95
90
85
80
PH7
PH8
PH9
PH7
PH8
PH9
PH7
PH8
PH9
PH7
PH8
PH9
3%
11%
19%
27%

Graph 1 B


60 min 150°C
% yield vs % Na_2SO_3
100
95
90
85
80
PH7
PH8
PH9
PH7
PH8
PH4
PH7
PH8
PH9
PH7
PH8
PH9
3%
11%
19%
27%
% Na_2SO_3

GRaph 1C


90min 150°C
% yield Vs % Na_2SO_3
100
95
90
85
80
pH7
pH8
pH9
pH7
pH8
pH9
pH7
pH8
pH9
pH7
pH8
pH9
3%
11%
19%
27%

GRAPH 1D

Temp 150°C 2.7% Na_2SO_3

% yield VS Cooking time

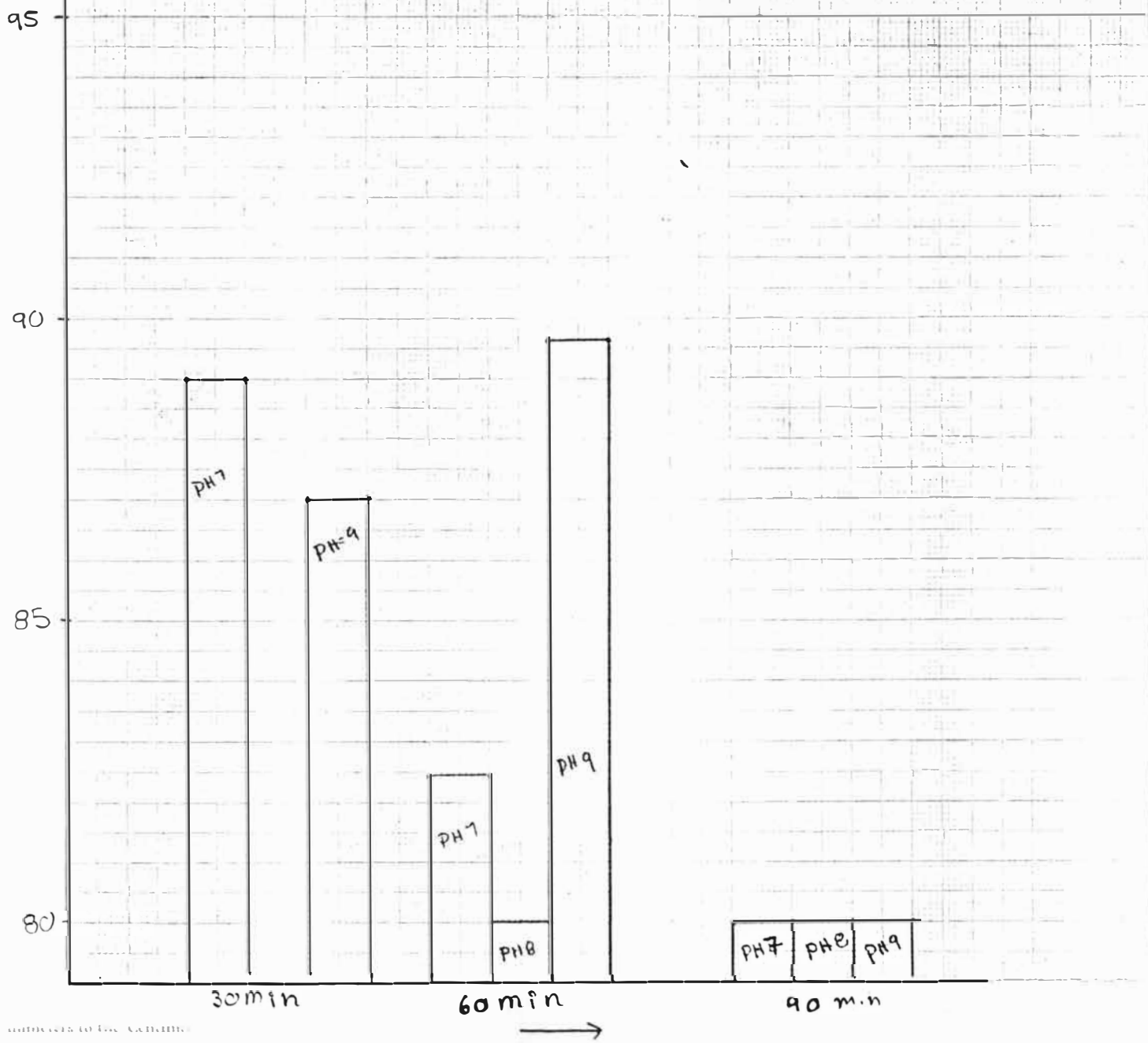
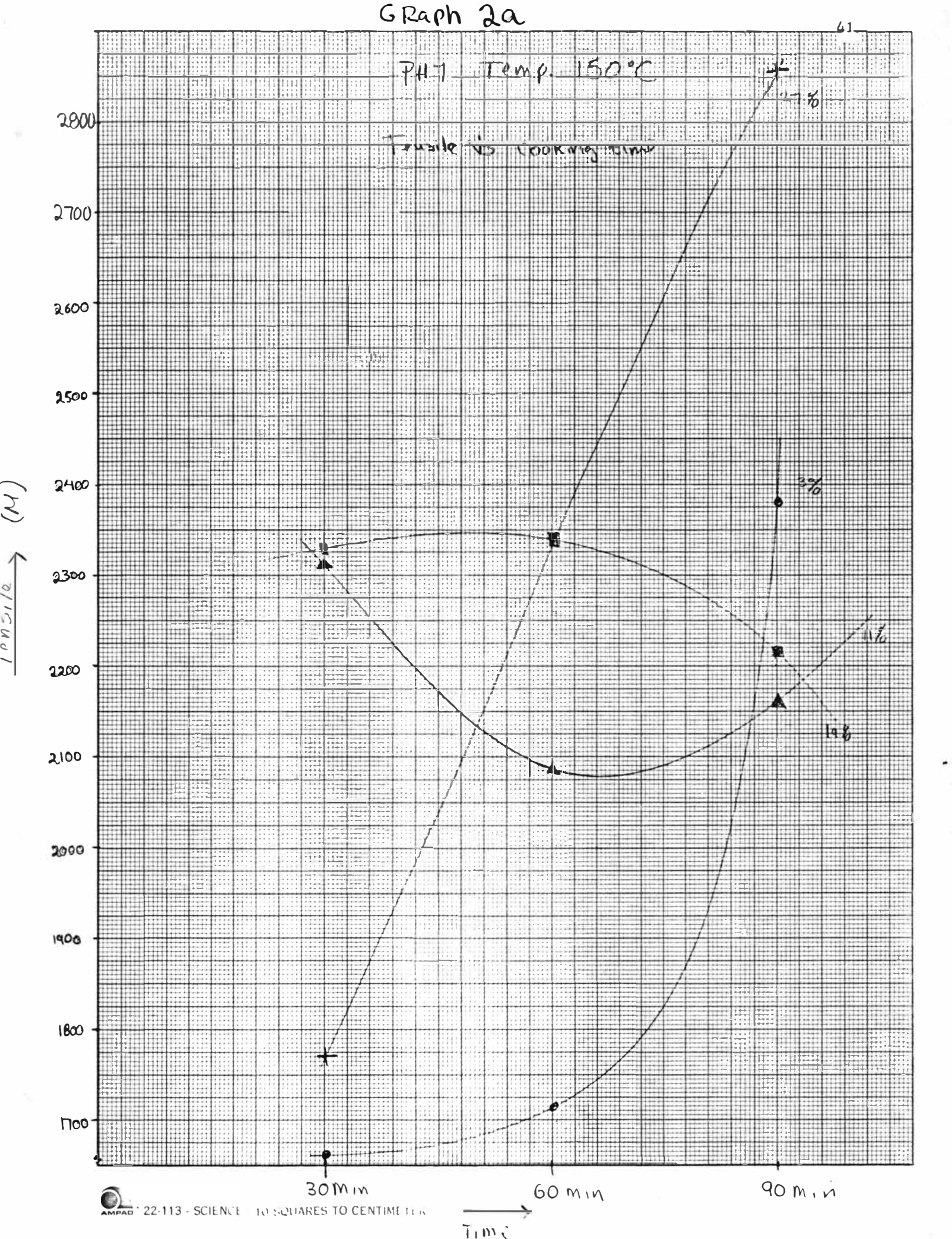


TABLE IV

RESULTS FOR 150°C CONDITIONS

Time	Temp.	pH	% Na_2SO_3	M Tensile	% Stretch	% Brightness	% Opacity	g/cm^3 x 100 Density
Control				1985	2.42	42-42.9	98.5	----
90	150	7	3	2382	2.68	41	91.2	24.6
		8		2145	2.68	40	90.5	23.5
		9		2134	2.64	40	88.8	22.9
90	150	7	11	2391	2.76	45.9	86.0	23.7
		8		----	2.40	44.0	84.4	21.1
		9		2472	3.12	42.4	88.0	21.3
90	150	7	19	2213	2.66	47.3	82.8	23.6
		8		2178	2.46	43.2	83.4	21.5
		9		2338	2.94	43.4	83.7	22.3
90	150	7	27	2858	2.42	47.1	85.9	19.9
		8		2854	2.66	45.2	83.7	26.5
		9		2758	2.90	44.5	86.3	25.9

Graph 2a



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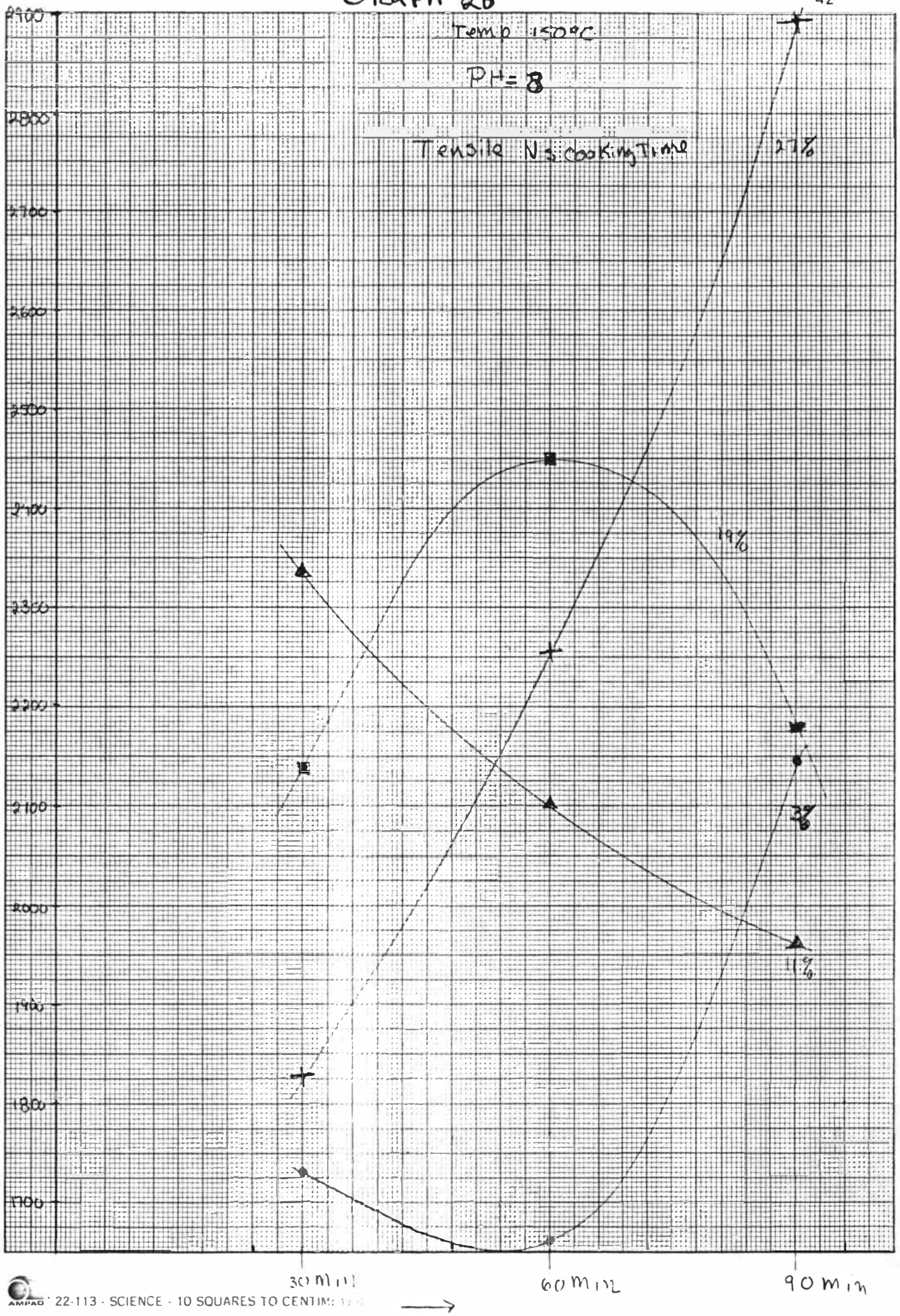
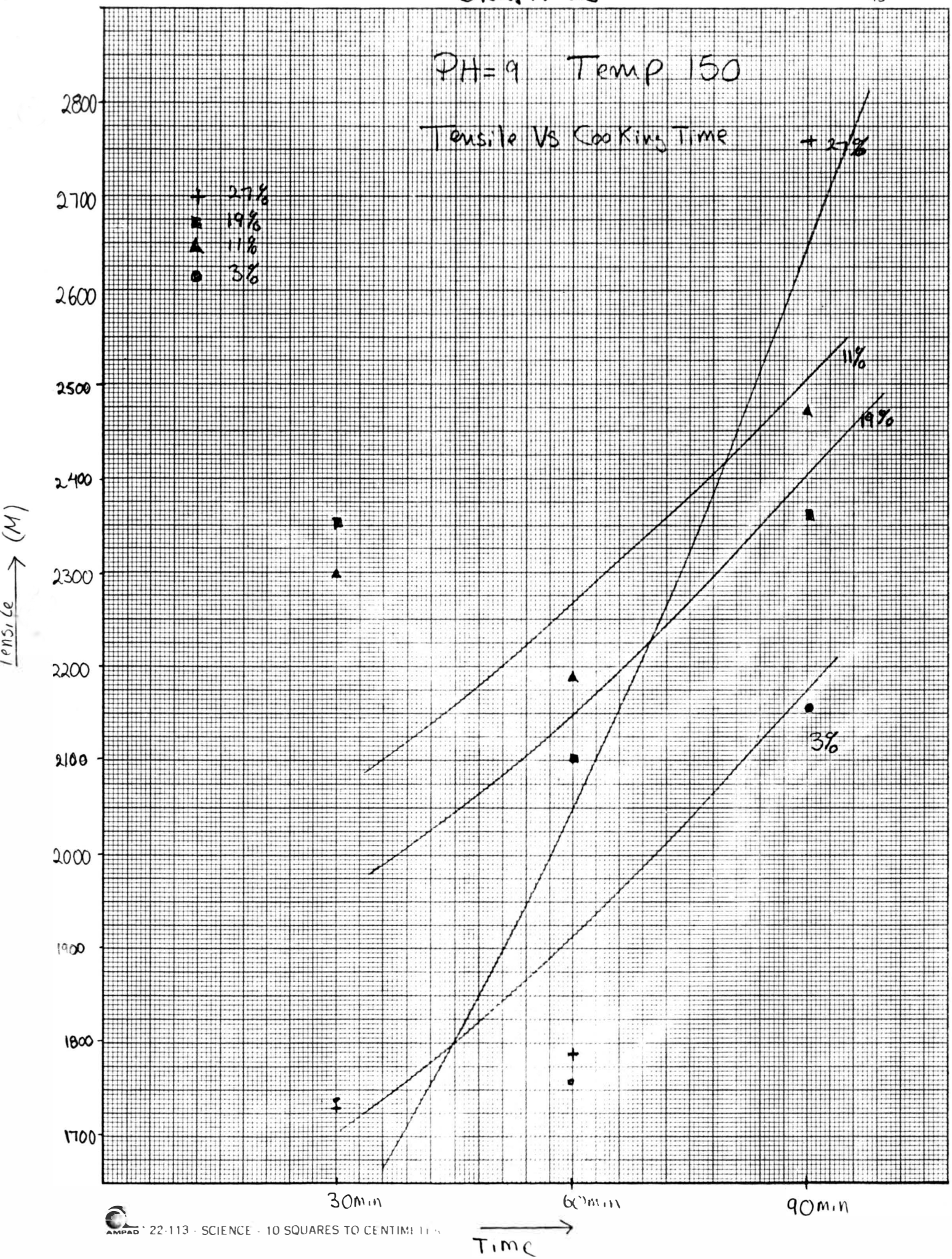
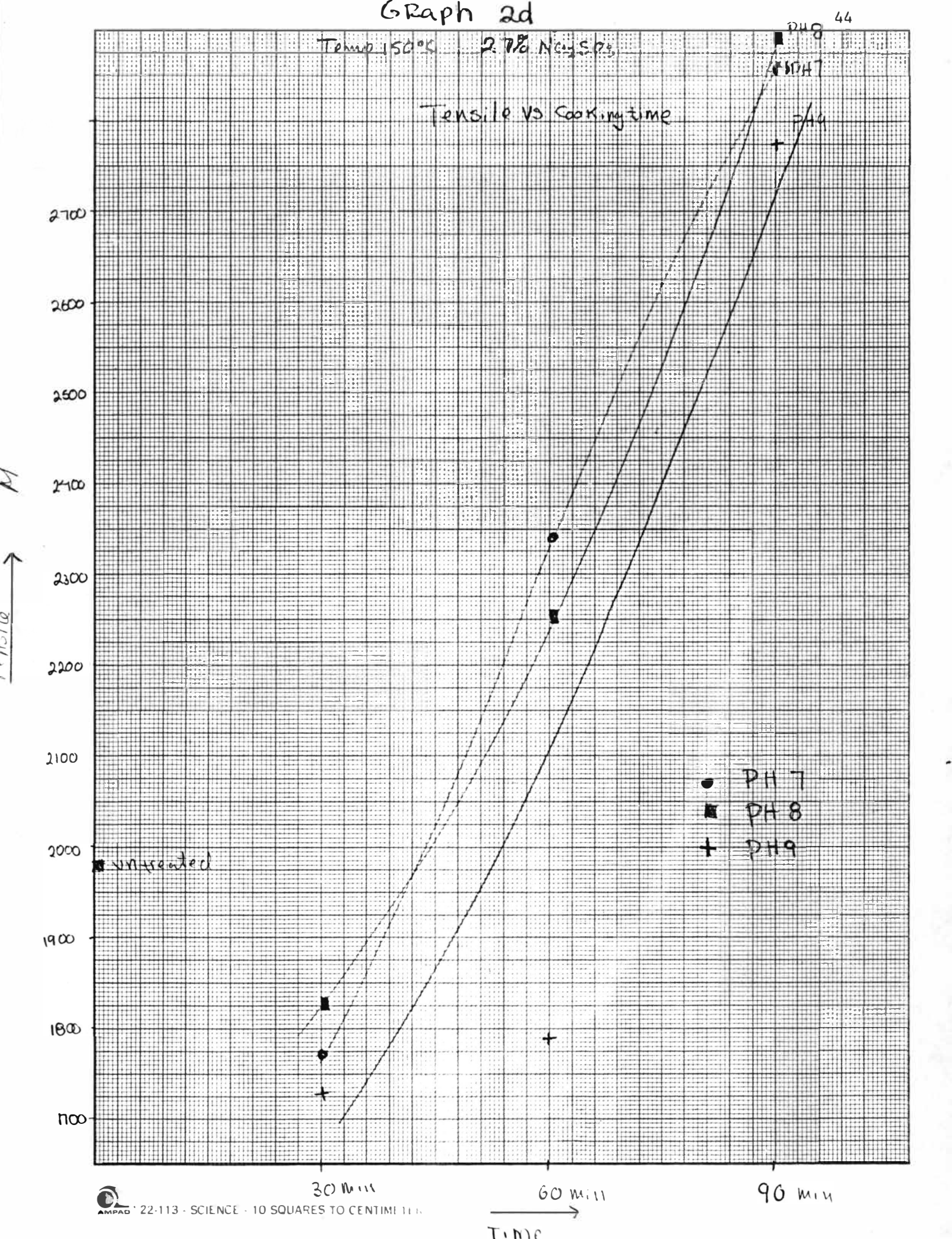
GRAPH 2b



Graph 2C



Graph 2d



treated at high levels of Sodium Sulfite (see Graph 2D).

From Graph 3A-3C, it can be affirmed that an increase in the level of Na_2SO_3 and temperatures have a positive effect on the comformability and flexibility of the fibers due to: 1) density is increased with tensile, 2) strength of the fibers is improved. The reason is due mainly to swelling of the fibers in the alkaline conditions and the modification of the fiber surface by the Na_2SO_3. This great increase in strength is obtained at the expense of yield and opacity. The important thing to note in this data is that strength properties did improve notably. Strength improvement were seen at every addition level of Na_2SO_3. Tensile increases of 45% from the original untreated pulp was seen.

Brightness

From Graph 4A-4C it can be seen how brightness is increased at every level of Na_2SO_3 addition (except 3%) at all the pH ranges. However, as it is expected, the highest pH gives the lowest brightness and vice versa. At pH 9 the values tend to be the same as the untreated pulp. Also, it is important to note that an increase in cooking time (Graph 5A) produces a decrease in brightness, especially at pH 9 which may be harmful for some kind of grades.

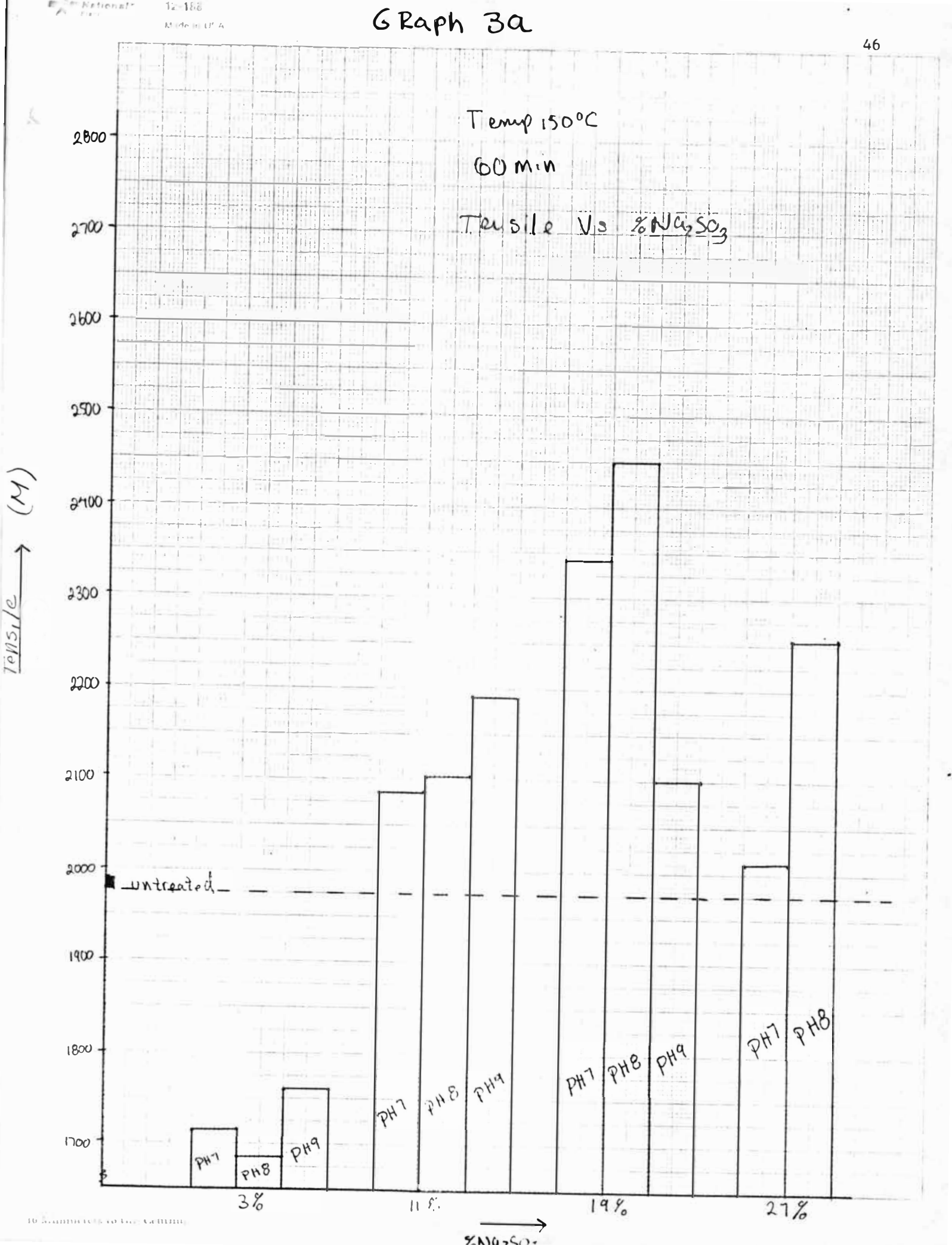
In Graph 6A it can be seen how at the same pH the brightness level off very slightly with cooking time at the same levels of Na_2SO_3.

pH 7 seems to give the most stable conditions.

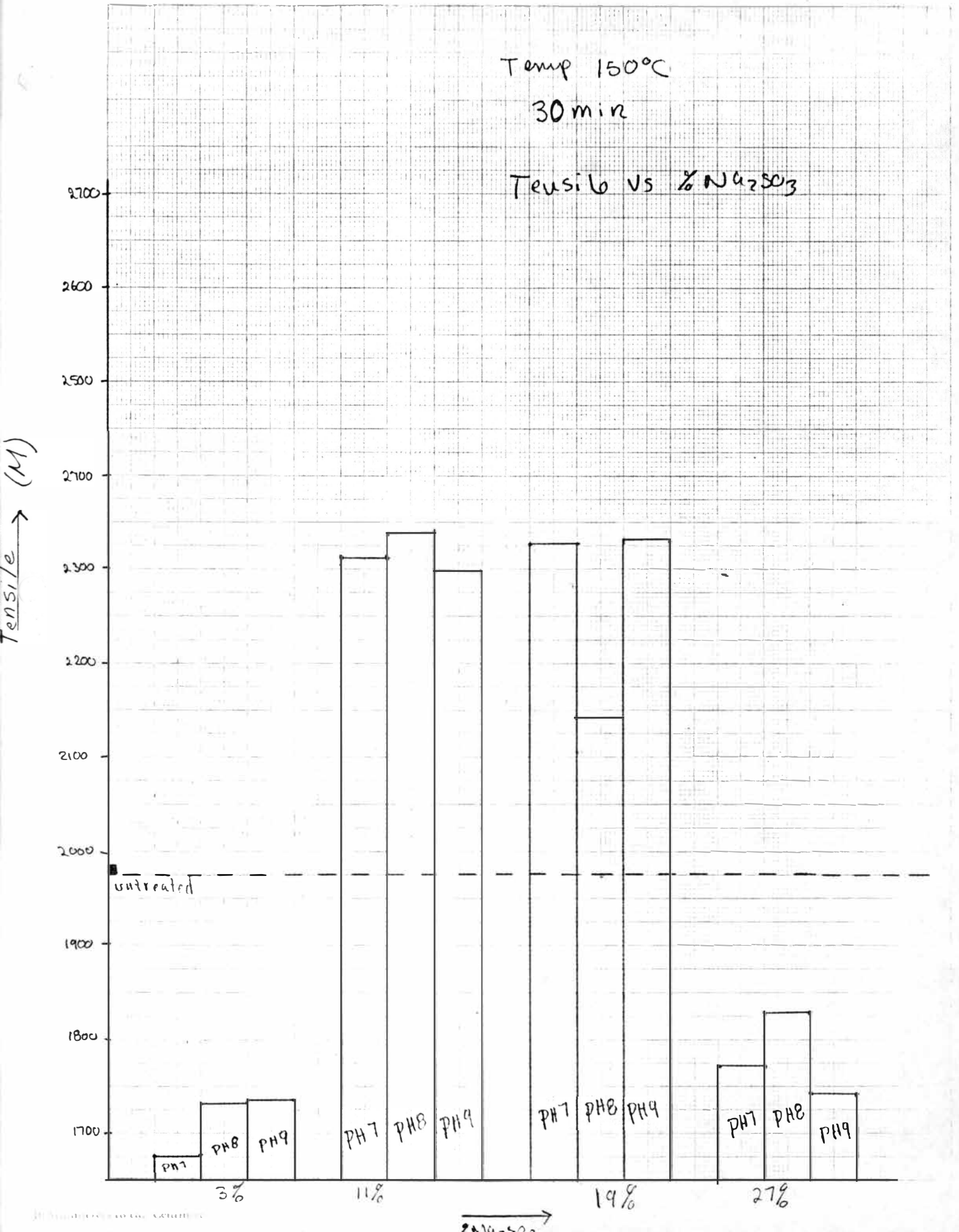
Opacity

Opacity tends to decrease as cooking time progresses and especially when the level of Na_2SO_3 is increased. This is due to the increase in density and relative bonding area due to the sulfonation of the fibers.

Graph 3a


Temp 150°C
60 min
Tensile Vs %Na2SO3
Tensile (M)
2800
2700
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
untreated
PH7
PH8
PH9
3%
11%
19%
27%
%Na2SO3

GRaph 3b

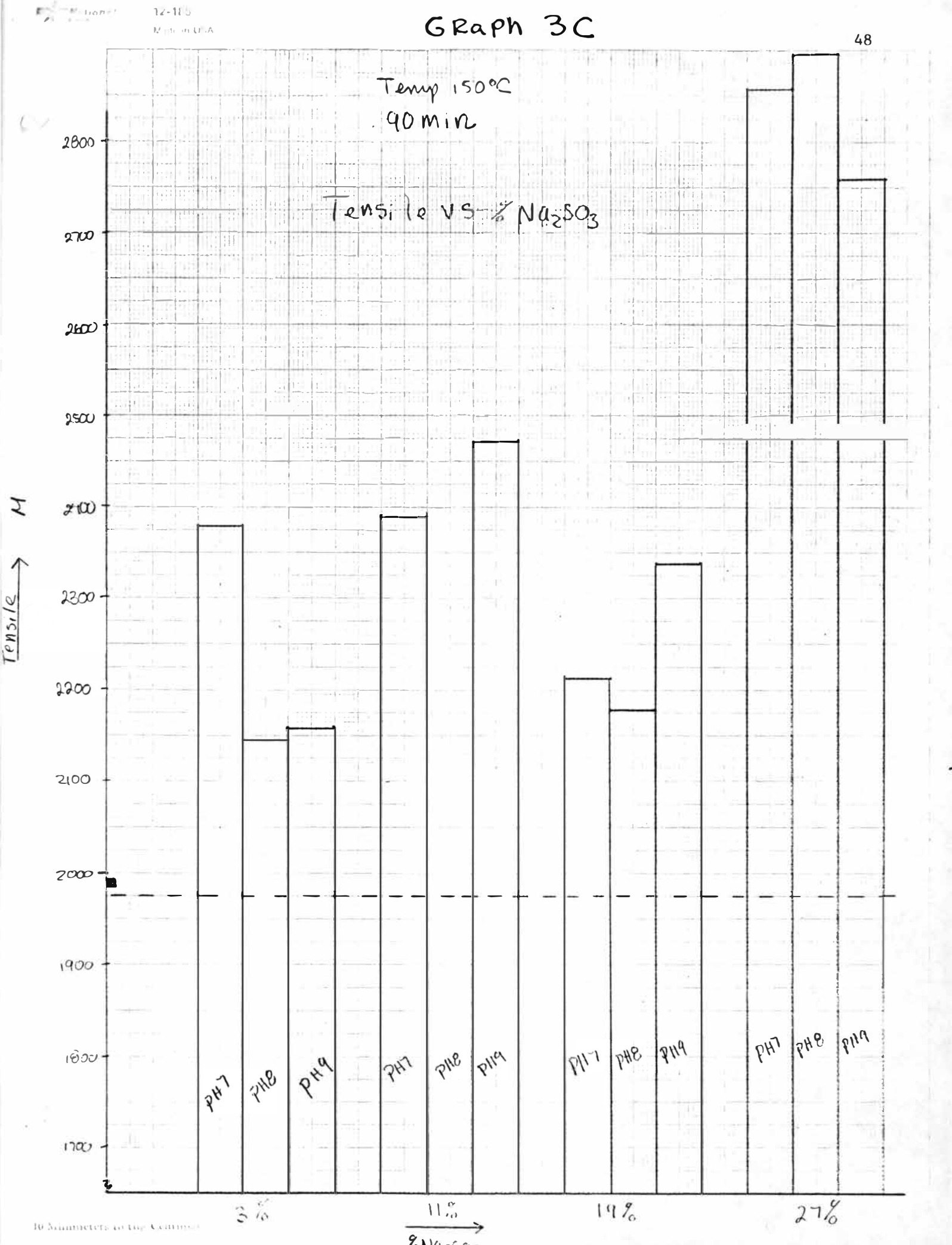

Temp 150°C
30 min
Tensile vs % Na_2SO_3
Tensile → (N)
2700
2600
2500
2700
2300
2200
2100
2000
1900
1800
1700
untreated
PH7
PH8
PH9
PH7
PH8
PH9
PH7
PH8
PH9
PH7
PH8
PH9
3%
11%
19%
27%

GRAPH 3C

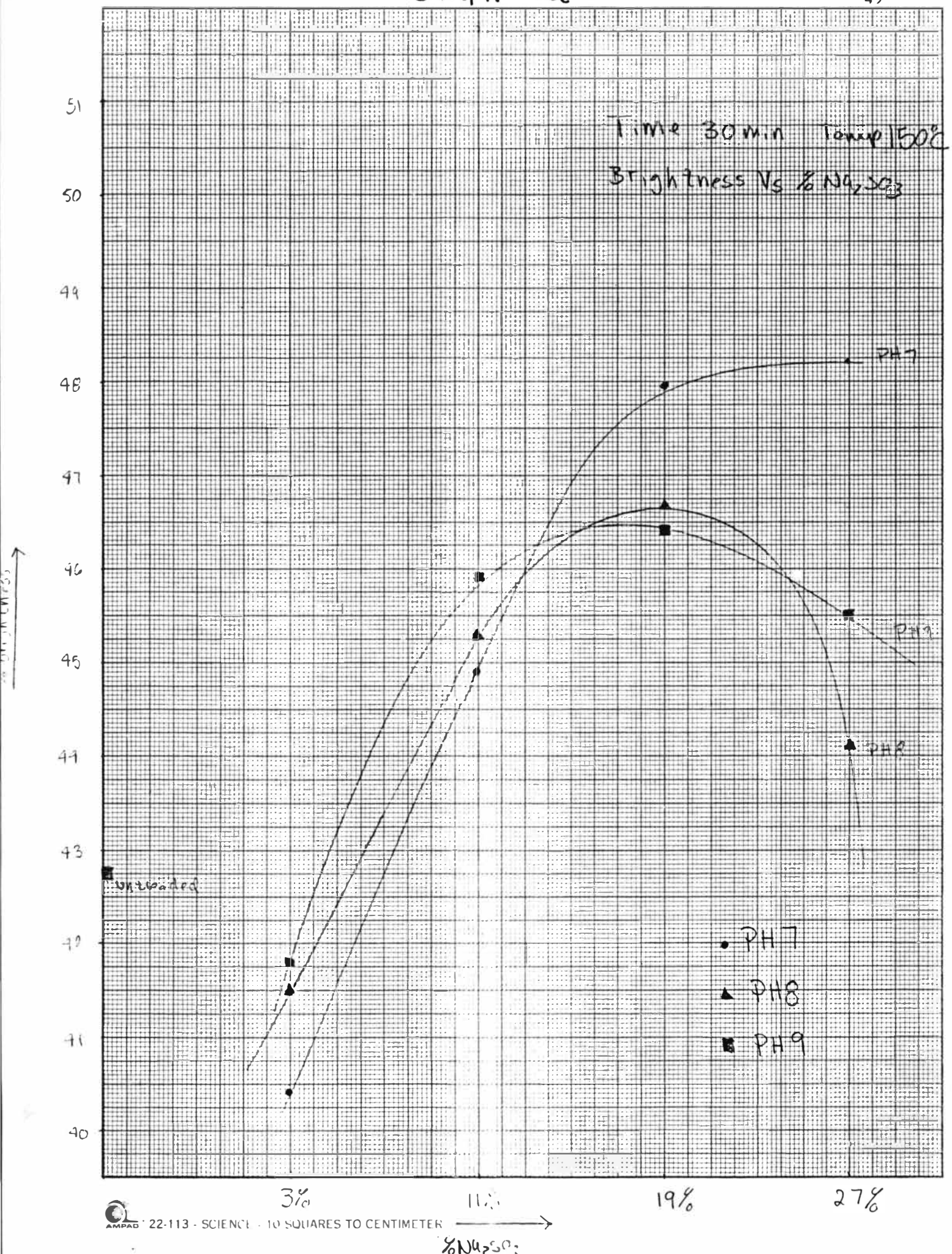
Temp 150°C

90 min

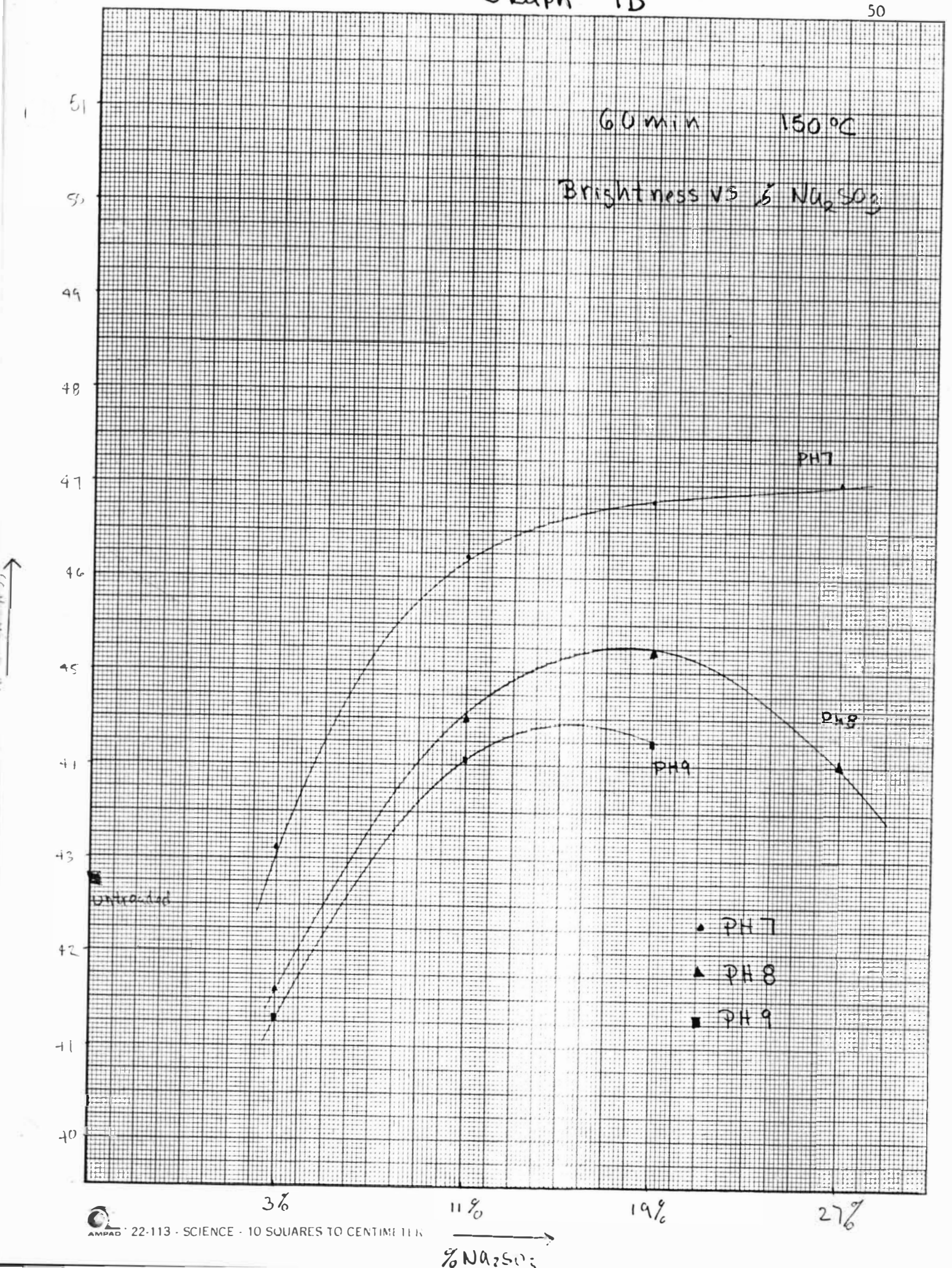
Tensile VS % Na_2SO_3



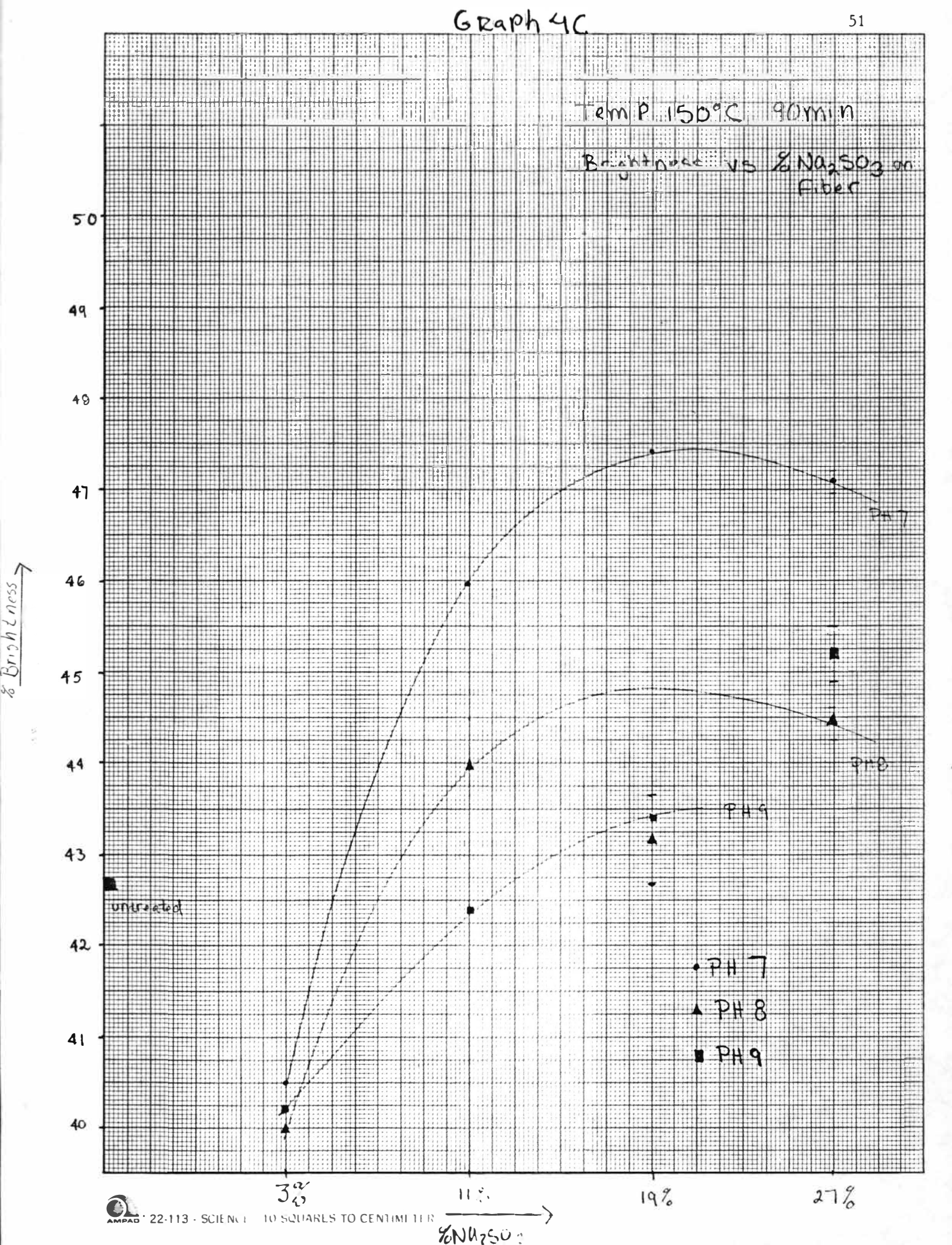
Graph 4a



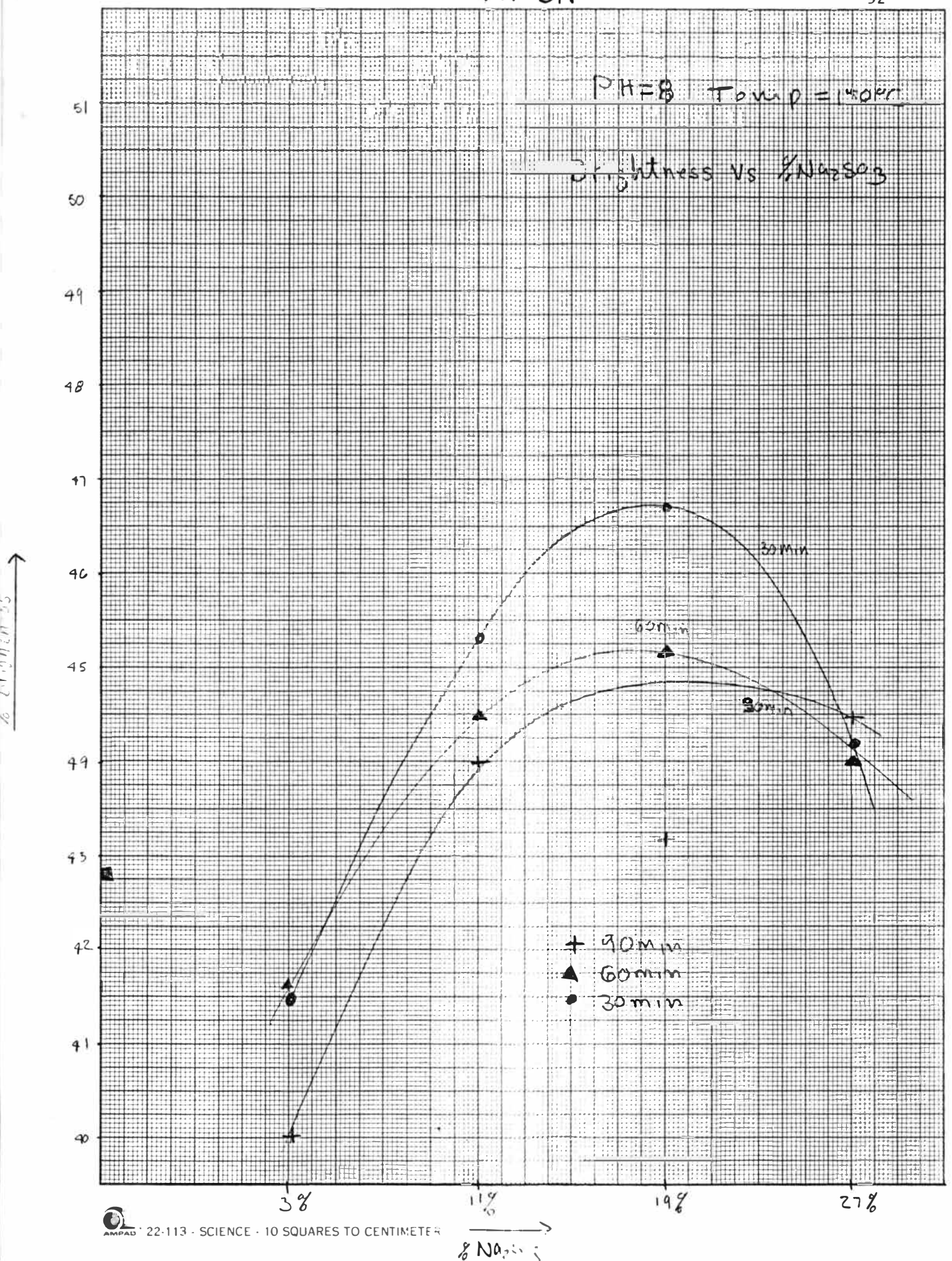
Graph 4B


60 min 150°C
Brightness vs % Na_2SO_3
PH7
PH8
PH9
Unbleached
51
50
49
48
47
46
45
44
43
42
41
40
3%
11%
19%
27%
% Na_2SO_3
AMPAD · 22-113 · SCIENCE · 10 SQUARES TO CENTIMETER

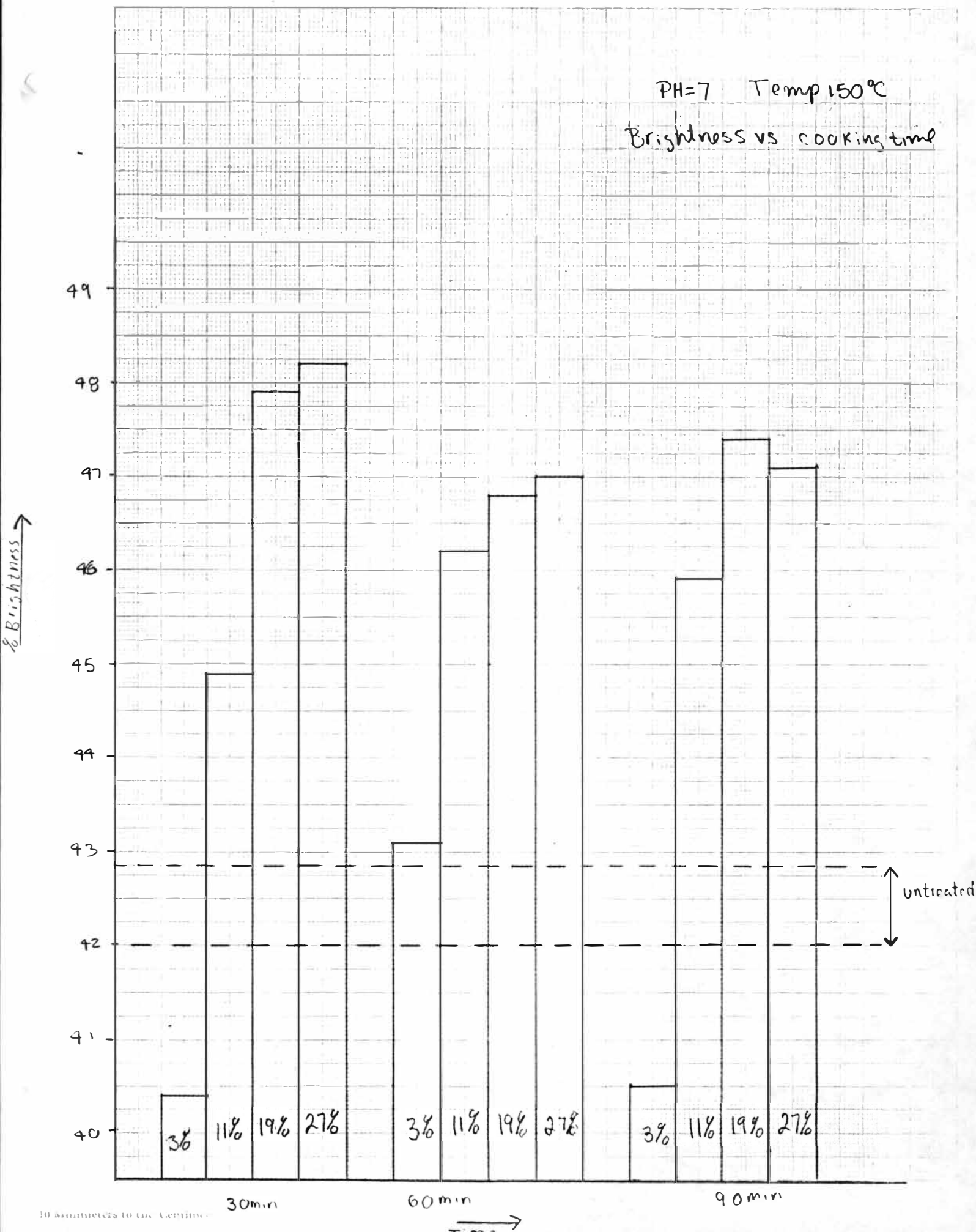
Graph 4C



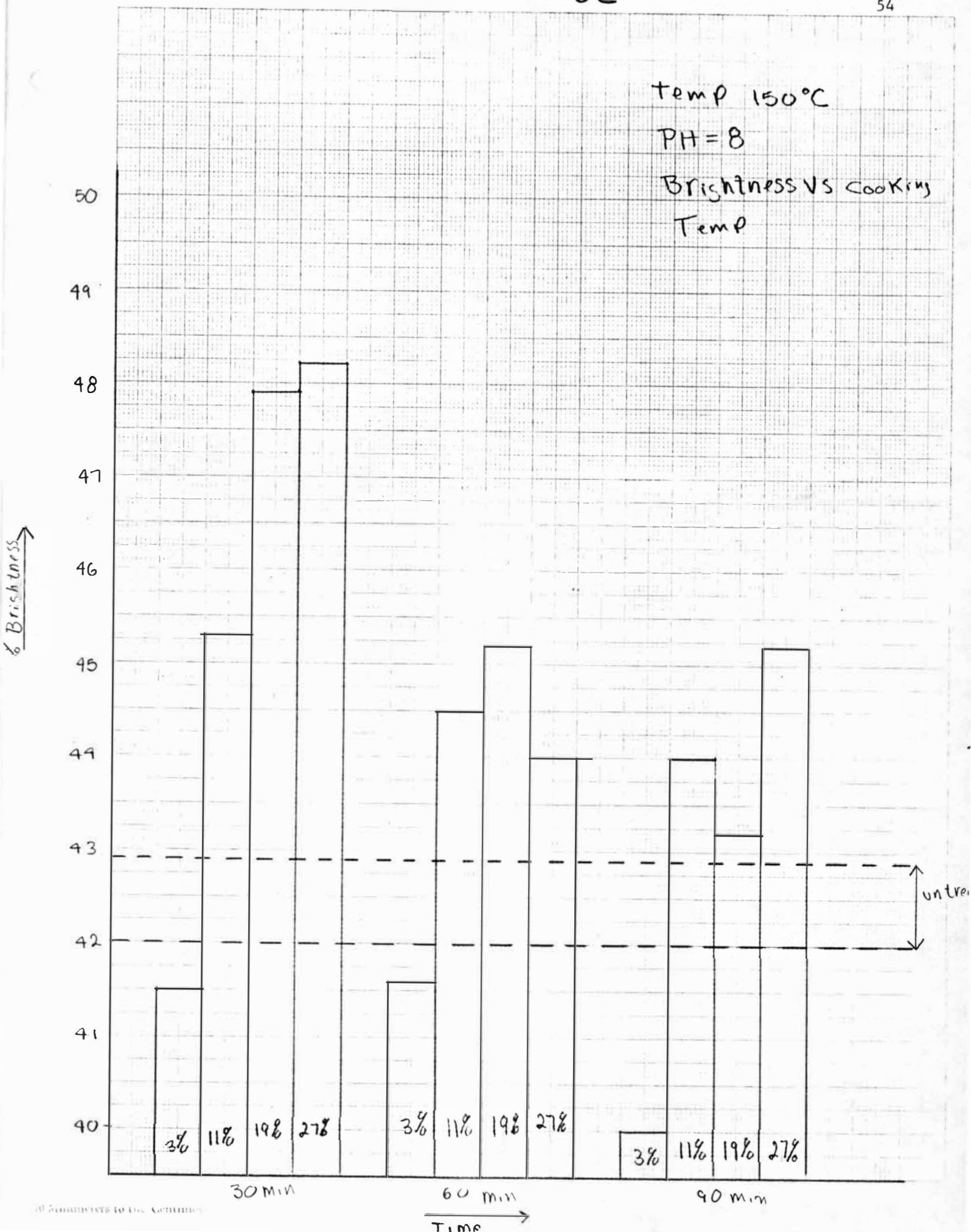
Graph 5A



GRaph 5B


PH=7 Temp 150°C
Brightness vs cooking time
% Brightness
49
48
47
46
45
44
43
42
41
40
untreated
3%
11%
19%
27%
3%
11%
19%
27%
3%
11%
19%
27%
30min
60min
90min

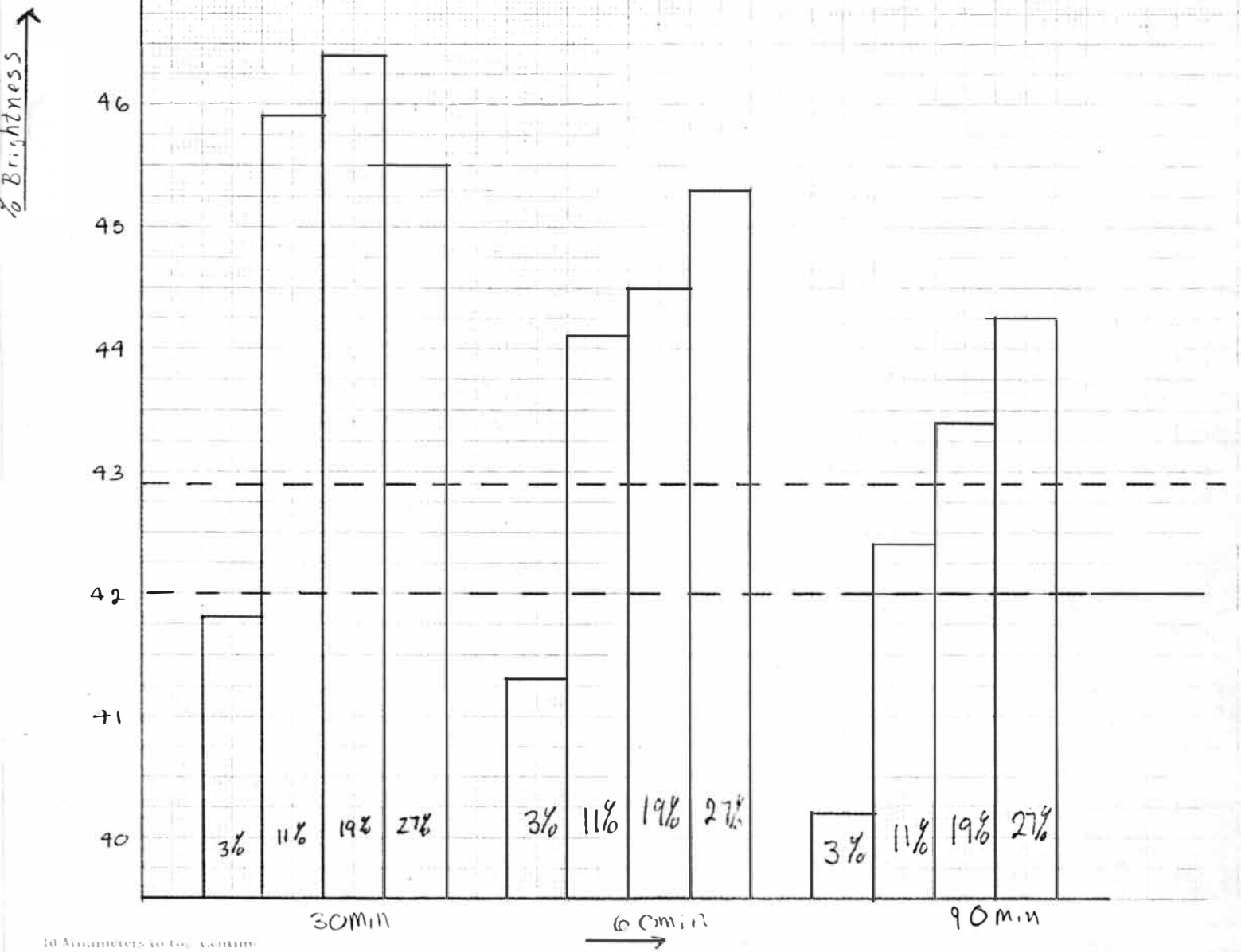
GRAPH 5C


temp 150°C
PH = 8
Brightness VS Cooking Temp
50
49
48
47
46
45
44
43
42
41
40
% Brightness
3%
11%
19%
27%
3%
11%
19%
27%
3%
11%
19%
27%
30 min
60 min
90 min
Time
untre

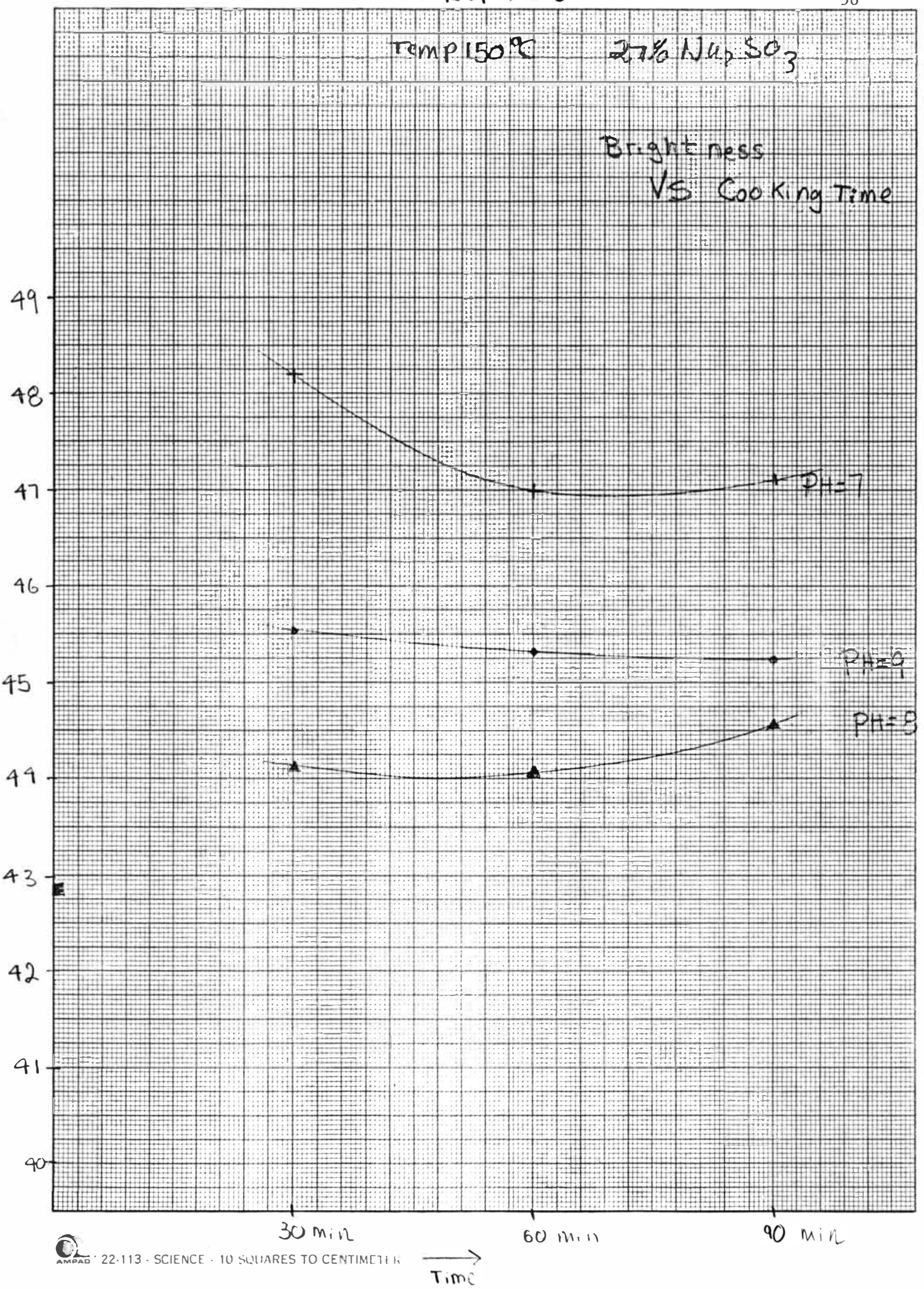
Graph 5D

Temp 150°C PH=9

Brightness vs time



Graph 6a



At different pH's this could not clearly be seen, but at pH 7 the opacity, in general, tends to have the highest values.

A clear picture could not be drawn but impairment is seen in all cooks. See Graphs 7A-7C.

From the results it be concluded that strength, density, and brightness are measured even at small addition rates of N_2SO_3 with respect to the untreated pulp. However opacity is impaired but not on a large scale. Some operational problems could arrive due to the last fact.

From this data and from the results analyzed the following conclusions could be drawn:

1. The best brightness is found to be at pH 7.
2. Tensile tends to be higher at pH 9, but brightness and opacity is impaired. At pH 7-8 values tend to be very close to pH 9 which tells us the optional should be in the neutral region.

The level of addition seems not to be as important as the concentration of the liquor, for this reason high concentration will be favorable. The 27% addition rate based on O.D. fiber which corresponds to a liquor concentration of 3% is advised.

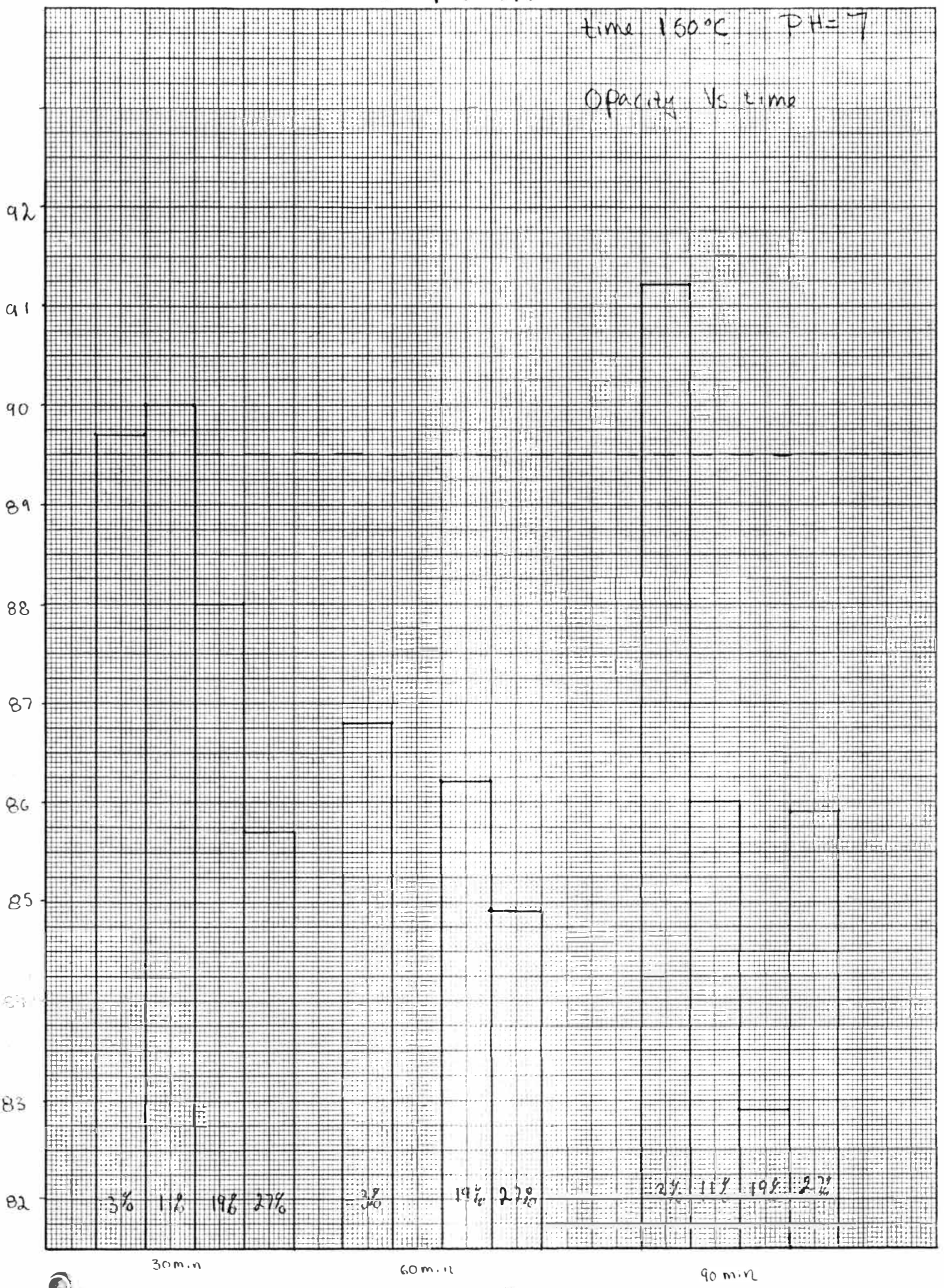
The temperature seems to be maximum at 150°C. The behavior tends to the same at 90°C and 120°C but as mentioned before that a strength increase is not notable. At low temperature ranges, brightness is by far much greater than those at 150°C. Brightness up to 50% was seen.

Opacity is impaired at small scale especially at high pH but at a neutral pH reduction is lower.

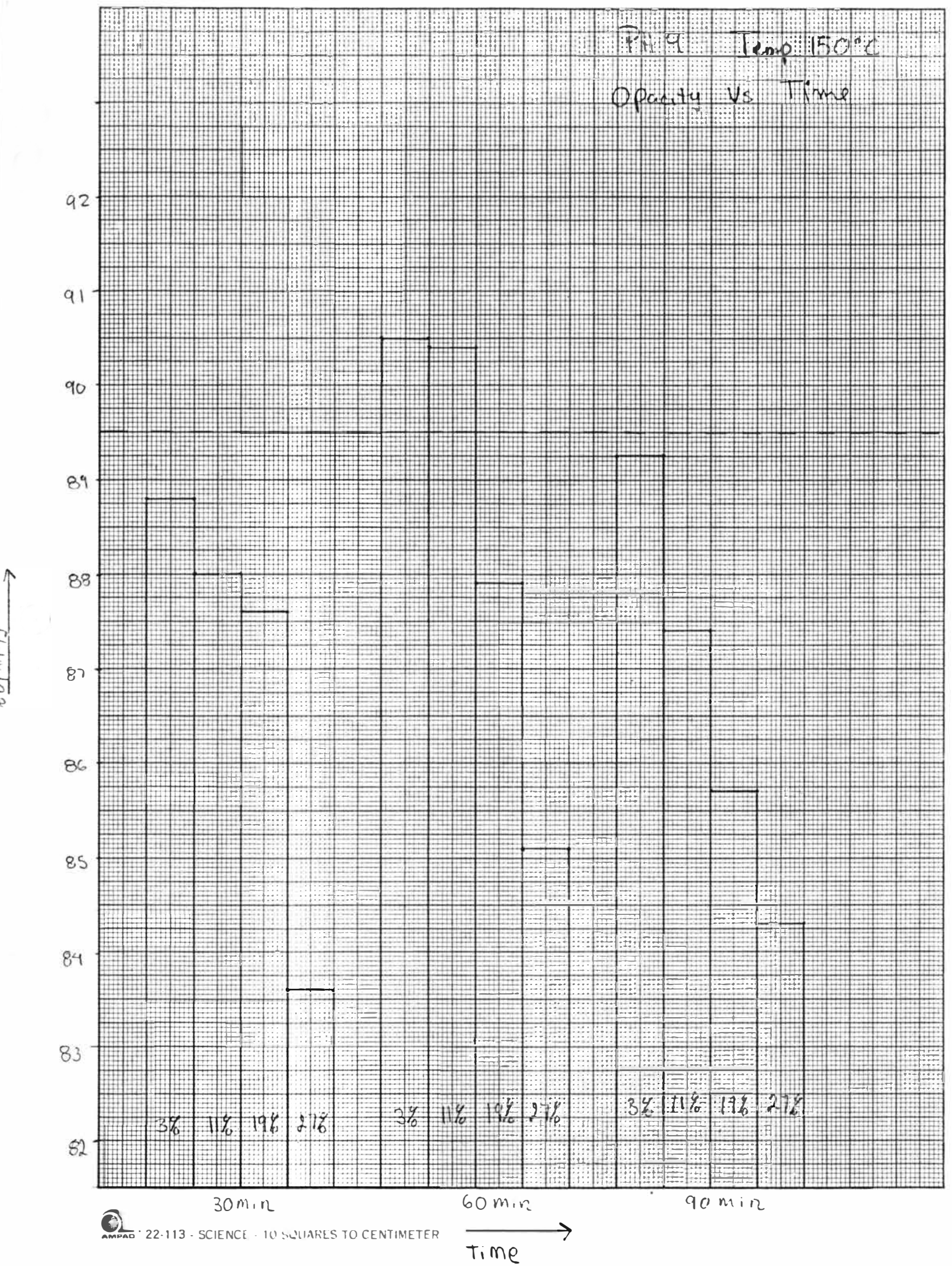
Yield tends to decrease but it could be affirmed that reduction is not below 90%. Higher cooking time yields better strength.

Note: See Appendix II for some regression models that help to confirm many of those results.

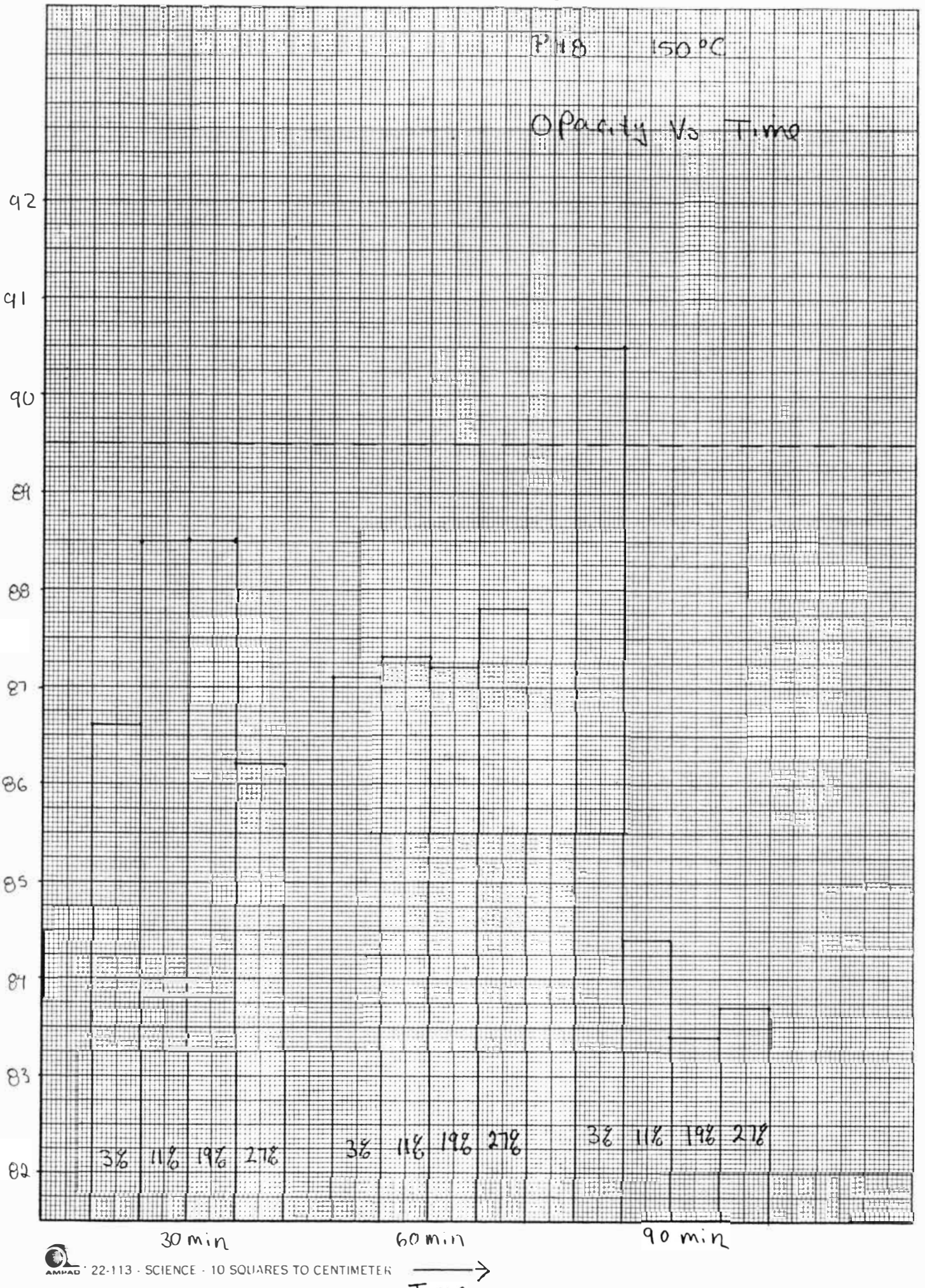
GRaph 7A


time 150°C PH=7
Opacity Vs time
92
91
90
89
88
87
86
85
83
82
3%
1%
19%
27%
19%
27%
2%
1%
19%
2%
30m.n
60m.n
90 m.n
Time

Graph 7B



Graph 7C



CONCLUSIONS

The best strength properties were obtained by sulphonating thermo-mechanical pulp at a temperature of 150°C, from the examined range of 90-150°C. Increasing the cooking time has some impairment on the optical properties. The optimum pH range was 7-8. Increasing pH to 9 did not cause any notable increase in strength but brightness decreased. Opacity is impaired but not at high degree. The degree of sulfonation seems to depend not only on the charge of Na_2SO_3, but also on the concentration. If the concentration is increased, sulfite reaction takes place very fast. For this reason the optimum advisable range is at liquor concentration between 2-3% which corresponds to the levels of 19%-27% Na_2SO_3 on O.D. fiber.

Throughout this experiment it was noted that an operational scale treatment of pulp with Na_2SO_3 could be done to obtain fibers with the wanted properties by experimenting with the pH, consistency, temperature, time and liquor concnetration. For this reason, further studies are highly recommended in this relatively new field.

POSSIBLE FUTURE WORKS

1. Study more carefully the yield along with the bound sulfur on fiber to have a better understanding of the process.
2. Work with the conditions obtained in this experiment and treat just the coarse fraction of the TMP fiber with sodium sulfite. Then mesure the strength propeties gained with the recombined pulp. This may help save some chemicals, and prevent the impairment of opacity at the same strength value, comparied to treating the entire pulp.
3. Run refining curves of the treated pulp and see how strength is increased.
4. Combination of numbers 2 and 3.

Many of these results could be starting points for future works in the new digester and TMP refiner. In this way runs could be done much faster and more precise.

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APPENdix 1

Appendix I

% yield Calculation (150°C)

Code	A.D. Fiber +Sulfur gr	O.D Fiber + Sulfur gr	Starting Na_2SO_3 gr	Black liquor Na_2SO_3 gr	% yield	Code	A.D. Fiber +Sulfur gr	O.D. Fiber + Sulfur gr	Starting Na_2SO_3 gr	Black liquor Na_2SO_3 gr	% yield
7	584.6	99.3	3	.128	96.8	26	575.4	101.5	19	1.374	88.3
43	731.9	101.9	3	.130	99.3	62	620.3	98.8	19	1.404	85.2
79	669.1	101.8	3	.128	99.2	98	543.9	98.2	19	1.259	84.9
16	584.3	99.6	11	.569	90.9	35	576.6	101.4	27	1.890	82.4
52	595.3	97.2	11	.569	89.6	71	657.0	96.8	27	2.670	78.9
88	603.4	99.6	11	.667	92.6	107	696.1	108.3	27	2.380	89.7
25	623.6	99.7	19	1.139	85.0	9	588.6	100.2	3	.0652	97.5
61	588.5	98.6	19	1.405	85.4	45	634.5	99.9	3	.0922	97.2
97	589.1	100.7	19	1.521	90.6	81	559.8	98.8	3	.0589	96.1
34	681.5	107.8	27	2.579	89.0	18	652.9	101.7	11	.6418	92.9
70	609.0	—	27	2.930	—	54	692.6	99.3	11	.7015	90.8
106	683.5	106.3	27	2.450	87.1	90	601.9	99.8	11	.7742	91.9
8	562.4	99.3	3	.127	96.9	27	760.6	101.3	19	1.452	91.8
44	599.3	101.8	3	.128	99.3	63	588.2	99.3	19	1.273	85.6
80	617.2	97.1	3	.097	94.5	99	566.6	99.9	19	1.455	87.2
17	—	—	11	.584	—	36	549.7	95.9	27	2.238	80
53	645.8	98.8	11	.560	89.8	72	516.0	97.0	27	2.116	80
89	521.7	97.4	11	.632	89.4	108	569.7	97.8	27	2.153	80

APPENDIX II

A multiple regration model on all the data and data at specific temperature was done.

With all the data, themodel was as follows:

$$\text{Property} = C_1\ \text{Time} + C_2\ \text{Temperature} + C_3\text{NA} + C_4\text{pH} + C_1C_1\ \text{Time}^2 + C_2C_2\ \text{Temperature}^2 + C_3C_3\ \text{NA}^2 + C_4C_4\ \text{pH}^2 + C_1C_2\ \text{Time Temperature} + C_1C_3\ \text{Time x NA} + C_1C_4\ \text{Time x pH} + C_2C_3\ \text{Temperature NA} + C_2C_4\ \text{Temperature pH} + C_3C_4\ \text{NA x pH}$$

For properties splitted on individual temperatures the model is:

$$\text{Property} = C_1\ \text{Time} + C_3\ \text{NA} + C_4\ \text{pH} + C_1C_1\ \text{Time}^2 + {}_3C_3\ \text{NA}^2 + C_4C_4\ \text{pH}^2 + C_1C_3\ \text{Time x NA} + C_1C_4\ \text{Time x pH} + C_3C_4\ \text{NA x pH}$$

The following tables give a summary of the major contributors to the different properties with their respective percent of confidence.

It could be seen from these results that tensile variations are due mainly to the time^2, NA^2, and temperature^2. pH seems to make a small contribution. Opacity determinations could not be predicted since percentage contribution was very small. Brightness depends strongly on the NA^2 pH^2 on the liquor. Stretch seems to follow the same pattern as tensile. The correlations values were not very high to support all these assumptions, but something is true that they all have the same trend. See Table VII to Table IX.

TABLE III

Regression of 90°C handsheet

Temperature	Property	contribution	% Contribution
90°C	Tensile (M)	$Time^2$ ↑ NA^2 ↑ PH^2 ↓ PH * NA ↓	70%
90°C	Brightness (%)	NA^2 ↑ PH^2 ↑	50%
90°C	Opacity (%)	NA^2 ↓ $Time^2$ ↓	25%
90°C	Stretch	NA ↑ PH * NA ↓	34%

TABLE VII

Regression 120°C handsheets

Temperature	Property	Contribution	% Contribution
120°C	Tensile (M)	$Time^2$ ↑ NA^2 ↑ $Time * NA^2$ ↑	70%
120°C	Brightness (%)	$Time^2$ ↑ NA^2 ↑ PH^2 ↑ $PH * NA$ ↓	50%
120°C	Opacity (%)	$Time^2$ ↓ NA^2 ↓	23%
120°C	Stretch (%)	$Time^2$ ↓ NA^2 ↓	34%

TABLE VIII

TABle REGression 150°C hANDsheets

Temperature	Property	Contribution	% Contribution
150°C	Tensile (M)	$Time^2$ ↑ NA^2 ↑ Time * NA ↑	60%
150°C	Brightness (%)	NA^2 ↑ PH^2 ↑ PH ↓	40%
150°C	Opacity (%)	NA^2 ↓ NA x PH ↓	33%
150°C	Stretch (%)	$Time^2$ ↑ PH^2 ↑ Time * NA	55%

Comment: Tensile and stretch seems to have the same correlation. All properties seems to be highly affected by the square of the controlled variables.

TABLE IX
Regression all Temp.

Property	Contribution	% Contribution
Tensile (M)	$Time^2$ ↑ $Temp^2$ ↑ NA^2 ↑ PH^2 ↑ Temp ↓ Time * Temp ↑ Time * NA ↑ Temp * PH ↑ NA * PH ↑	34 %

Comment: This Table proves many of the assumptions made during the discussion of the Results but with the difference that the properties depend strongly on the square on the input variable. The positive Contributions are Temperature, Time and Na_2SO_3 (in Tensile). PH (at The Studied range) Seems ~~not~~ to affect the Strength Values at very small Scale.

Regression model 90°C

Note :

C21 Time	C26 Brightness
C22 Temp	C27 opacity
C23 % Na_2SO_3	C28 Tensile
C24 PH	C29 Stretch

C31 = C21 * C21
C32 = C22 * C22
C33 = C23 * C23
C34 = C24 * C24
C35 = C21 * C22
C36 = C21 * C23
C37 = C21 * C24
C38 = C22 * C23
C39 = C22 * C24
C40 = C23 * C24

Tensile

REGRESS C28 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 445. - 12.4 X1 - 15.0 X2
+ 525. X3 + .0963 X4 + 1.18 X5
- 29.9 X6 + .0278 X7 + 0.417 X8
- 3.61 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	445	1835	0.24
X1	C21	-12.440	6.613	-1.88
X2	C23	-15.05	27.88	-0.54
X3	C24	525.1	445.0	1.18
X4	C31	0.09625	0.03054	3.15
X5	C33	1.1814	0.4049	2.92
X6	C34	-29.88	27.49	-1.09
X7	C36	0.02778	0.09352	0.30
X8	C37	0.4167	0.6479	0.64
X9	C40	-3.615	2.806	-1.29

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 77.75
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 67.8 PERCENT
R-SQUARED = 56.6 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	330375	36708
RESIDUAL	26	157168	6045
TOTAL	35	487543	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	330375
C21	1	190638
C23	1	7771
C24	1	273
C31	1	60031
C33	1	51453
C34	1	7140
C36	1	533
C37	1	2500
C40	1	10034

ROW	X1 C21	Y C28	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
19	90.0	2501.0	2331.9	31.7	169.1	2.38R
22	90.0	2260.0	2392.0	52.2	-132.0	-2.29R
30	60.0	2356.0	2197.1	43.0	158.9	2.45R

R DENOTES AN OBS. WITH A LARGE ST. RES.

brightness

EGRESS C86 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51

- THE FOLLOWING VARIABLES ARE HIGHLY
ELATED WITH OTHER PREDICTOR VARIABLES

REGRESSION EQUATION IS
75.2 + .0335 X1 - 0.521 X2
- 6.10 X3 - .0002 X4 + .0168 X5
+ 0.350 X6 - .0003 X7 + .0015 X8
- .0073 X 9

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
--	75.20	23.85	3.15
C21	0.03347	0.08598	0.39
C23	-0.5212	0.3625	-1.44
C24	-6.099	5.786	-1.05
C31	-0.0002083	0.0003971	-0.52
C33	0.016840	0.005265	3.20
C34	0.3500	0.3574	0.98
C36	-0.000278	0.001216	-0.23
C37	0.001458	0.008423	0.17
C40	-0.00729	0.03647	-0.20

ST. DEV. OF Y ABOUT REGRESSION LINE IS
1.011
(36-10) = 26 DEGREES OF FREEDOM

UARED = 49.5 PERCENT
UARED = 32.1 PERCENT, ADJUSTED FOR D.F.

YSIS OF VARIANCE

TO	DF	SS	MS=SS/DF
ESSION	9	26.076	2.897
IUAL	26	26.564	1.022
	35	52.640	

HER ANALYSIS OF VARIANCE
XPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

TO	DF	SS
ESSION	9	26.076
	1	4.770
	1	2.205
	1	7.260
	1	0.281
	1	10.454
	1	0.980
	1	0.053
	1	0.031
	1	0.041

X1 C21	Y C26	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
90.0	44.200	46.634	0.484	-2.434	-2.74R

OTES AN OBS. WITH A LARGE ST. RES.

```
NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y =    82.2 - .0422 X1 + .0467 X2
     + 1.30 X3 - .0002 X4 - .003 X5
     - .0958 X6 - .0001 X7 + .0090 X8
     + .0104 X 9
```

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	82.17	23.80	3.45
X1	C21	-0.04222	0.08578	-0.49
X2	C23	0.0467	0.3616	0.13
X3	C24	1.302	5.772	0.23
X4	C31	-0.0001898	0.0003961	-0.48
X5	C33	-0.003733	0.005252	-0.71
X6	C34	-0.0958	0.3565	-0.27
X7	C36	-0.000139	0.001213	-0.11
X8	C37	0.008958	0.008403	1.07
X9	C40	0.01042	0.03639	0.29

```
THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 1.008
WITH (  36-10) =  26 DEGREES OF FREEDOM

R-SQUARED = 25.4 PERCENT
R-SQUARED = -0.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE
```

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	8.991	0.999
RESIDUAL	26	26.439	1.017
TOTAL	35	35.430	

```
FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN
```

DUE TO	DF	SS
REGRESSION	9	8.991
C21	1	0.350
C23	1	0.467
C24	1	6.100
C31	1	0.233
C33	1	0.514
C34	1	0.073
C36	1	0.013
C37	1	1.156
C40	1	0.083

ROW	X1 C21	Y C27	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
20	90.0	87.100	89.127	0.483	-2.027	-2.29R

```
R DENOTES AN OBS. WITH A LARGE ST. RES.

DURBIN-WATSON STATISTIC = 1.60
```

REGRRESS C29 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = - 0.757 - .0023 X1 + 0.103 X2
+ 0.584 X3 - .0001 X4 + .0004 X5
- .0204 X6 + .0001 X7 + .0006 X8
- .0155 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	-0.757	3.477	-0.22
X1	C21	-0.00233	0.01253	-0.19
X2	C23	0.10321	0.05283	1.95
X3	C24	0.5845	0.8434	0.69
X4	C31	-0.00005463	0.00005788	-0.94
X5	C33	0.0004253	0.0007674	0.55
X6	C34	-0.02042	0.05209	-0.39
X7	C36	0.0001111	0.0001772	0.63
X8	C37	0.000625	0.001228	0.51
X9	C40	-0.015521	0.005317	-2.92

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.1473
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 34.8 PERCENT
R-SQUARED = 12.2 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	0.30083	0.03343
RESIDUAL	26	0.56447	0.02171
TOTAL	35	0.86530	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	0.30083
C21	1	0.06827
C23	1	0.00405
C24	1	0.00000
C31	1	0.01934
C33	1	0.00667
C34	1	0.00333
C36	1	0.00853
C37	1	0.00562
C40	1	0.18501

ROW	X1 C21	Y C29	FRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
15	60.0	2.0500	2.3247	0.0814	-0.2747	-2.24R
24	90.0	1.9600	2.3154	0.0705	-0.3554	-2.75R

R DENOTES AN OBS. WITH A LARGE ST. RES.

Regression Model 120°C

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 1777. - 16.7 X1 - 79.5 X2
+ 286. X3 + 0.140 X4 + 2.91 X5
- 14.9 X6 + 0.131 X7 + 0.167 X8
- 4.12 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
		1777	2962	0.60
X1	C21	-16.69	10.68	-1.56
X2	C23	-79.49	45.01	-1.77
X3	C24	285.7	718.4	0.40
X4	C31	0.14042	0.04931	2.85
X5	C33	2.9054	0.6537	4.44
X6	C34	-14.88	44.37	-0.34
X7	C36	0.1309	0.1510	0.87
X8	C37	0.167	1.046	0.16
X9	C40	-4.125	4.529	-0.91

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 125.5
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 67.7 PERCENT
R-SQUARED = 56.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	857169	95241
RESIDUAL	26	409578	15753
TOTAL	35	1266747	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	857169
C21	1	342487
C23	1	38364
C24	1	10292
C31	1	127765
C33	1	311178
C34	1	1770
C36	1	11844
C37	1	400
C40	1	13068

ROW	X1 C21	Y C28	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
25	60.0	2150.0	1760.9	51.2	389.1	3.40R

R DENOTES AN OBS. WITH A LARGE ST. RES.

DURBIN-WATSON STATISTIC = 2.22

Brightness

REGRESS C26 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 110. - .0195 X1 - 0.223 X2
- 14.7 X3 + .0007 X4 + .0207 X5
+ 0.938 X6 - .0009 X7 - .0044 X8
- .0583 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	109.72	35.30	3.11
X1	C21	-0.0195	0.1272	-0.15
X2	C23	-0.2231	0.5364	-0.42
X3	C24	-14.683	8.562	-1.72
X4	C31	0.0007083	0.0005876	1.21
X5	C33	0.020747	0.007791	2.66
X6	C34	0.9375	0.5288	1.77
X7	C36	-0.000868	0.001799	-0.48
X8	C37	-0.00437	0.01247	-0.35
X9	C40	-0.05833	0.05398	-1.08

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 1.496
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 52.0 PERCENT
R-SQUARED = 35.4 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	62.974	6.997
RESIDUAL	26	58.174	2.237
TOTAL	35	121.148	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	62.974
C21	1	4.250
C23	1	2.494
C24	1	26.670
C31	1	3.251
C33	1	15.867
C34	1	7.031
C36	1	0.521
C37	1	0.276
C40	1	2.613

DURBIN-WATSON STATISTIC = 1.42
--

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 59.2 + 0.124 X1 + 0.269 X2
+ 6.15 X3 - .0014 X4 - .0177 X5
- 0.429 X6 + .0010 X7 + .0010 X8
+ .0354 X9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	59.21	54.41	1.09
X1	C21	0.1236	0.1961	0.63
X2	C23	-0.2694	0.8267	-0.33
X3	C24	6.15	13.20	0.47
X4	C31	-0.0014352	0.0009057	-1.58
X5	C33	-0.01771	0.01201	-1.47
X6	C34	-0.4292	0.8151	-0.53
X7	C36	0.001007	0.002773	0.36
X8	C37	0.00104	0.01921	0.05
X9	C40	0.03542	0.08319	0.43

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 2.306
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 23.2 PERCENT
R-SQUARED = -3.4 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	41.806	4.645
RESIDUAL	26	138.202	5.315
TOTAL	35	180.009	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	41.806
C21	1	9.627
C23	1	4.109
C24	1	0.010
C31	1	13.347
C33	1	11.560
C34	1	1.473
C36	1	0.701
C37	1	0.016
C40	1	0.963

ROW	X1 C21	Y C27	FRED. Y VALUE	ST.DEV. FRED. Y	RESIDUAL	ST.RES.
11	30.0	83.700	87.872	1.104	-4.172	-2.06R
25	60.0	93.200	88.519	0.941	4.681	2.22R
32	60.0	83.100	88.147	1.274	-5.047	-2.63R

R DENOTES AN OBS. WITH A LARGE ST. RES.

Stretch

REGRESS C29 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 1.65 - .0101 X1 - .0118 X2
+ 0.236 X3 + .0001 X4 + .0020 X5
- .0058 X6 + .0001 X7 + .0002 X8
- .0071 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	1.655	4.586	0.36
X1	C21	-0.01012	0.01653	-0.61
X2	C23	-0.01175	0.06969	-0.17
X3	C24	0.236	1.112	0.21
X4	C31	0.00007269	0.00007635	0.95
X5	C33	0.002005	0.001012	1.98
X6	C34	-0.00583	0.06871	-0.08
X7	C36	0.0000903	0.0002338	0.39
X8	C37	0.000167	0.001620	0.10
X9	C40	-0.007083	0.007013	-1.01

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.1943
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 33.5 PERCENT
R-SQUARED = 10.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	0.49493	0.05499
RESIDUAL	26	0.98204	0.03777
TOTAL	35	1.47696	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	0.49493
C21	1	0.05900
C23	1	0.20056
C24	1	0.00807
C31	1	0.03423
C33	1	0.14823
C34	1	0.00027
C36	1	0.00563
C37	1	0.00040
C40	1	0.03853

ROW	X1 C21	Y C29	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
3	90.0	2.9400	2.5189	0.0930	0.4211	2.47R

R DENOTES AN OBS. WITH A LARGE ST. RES.

DURBIN-WATSON STATISTIC = 2.01

Regression Model 150 °C

Regression for 150°C

150

Tensile

REGRESS C28 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 6110. - 37.4 X1 - 131. X2
- 485. X3 + 0.190 X4 + 2.42 X5
+ 34.7 X6 + 1.15 X7 - 0.104 X8
- 3.99 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	6110	5810	1.05
X1	C21	-37.44	20.94	-1.79
X2	C23	-130.63	88.29	-1.48
X3	C24	-485	1409	-0.34
X4	C31	0.18968	0.09673	1.96
X5	C33	2.418	1.282	1.89
X6	C34	34.71	87.05	0.40
X7	C36	1.1476	0.2962	3.87
X8	C37	-0.104	2.052	-0.05
X9	C40	-3.990	8.885	-0.45

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 246.2
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 58.7 PERCENT
R-SQUARED = 44.4 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	2243224	249247
RESIDUAL	26	1576266	60626
TOTAL	35	3819489	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	2243224
C21	1	855415
C23	1	3698
C24	1	3105
C31	1	233131
C33	1	215605
C34	1	9637
C36	1	910252
C37	1	156
C40	1	12224

ROW	X1 C21	Y C28	FRED. Y VALUE	ST.DEV. FRED. Y	RESIDUAL	ST.RES.
3	60.0	2448.0	1933.7	100.5	514.3	2.29R

R DENOTES AN OBS. WITH A LARGE ST. RES.

Brightness

```
REGRESS C26 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51
```



```
NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y =    99.6 + 0.126 X1 - 0.867 X2
     -  12.1 X3 - .0002 X4 + .0280 X5
     + 0.800 X6 + .0010 X7 - .0173 X8
     - .0250 X9
```

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	99.55	50.01	1.99
X1	C21	0.1260	0.1803	0.70
X2	C23	-0.8670	0.7599	-1.14
X3	C24	-12.14	12.13	-1.00
X4	C31	-0.0002222	0.0008325	-0.27
X5	C33	0.02795	0.01104	2.53
X6	C34	0.8000	0.7493	1.07
X7	C36	0.000972	0.002549	0.38
X8	C37	-0.01729	0.01766	-0.98
X9	C40	-0.02500	0.07647	-0.33

```
THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 2.119
WITH (  36-10) =  26 DEGREES OF FREEDOM

R-SQUARED = 37.3 PERCENT
R-SQUARED = 15.6 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE
```

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	69.441	7.716
RESIDUAL	26	116.779	4.492
TOTAL	35	186.220	

```
FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN
```

DUE TO	DF	SS
REGRESSION	9	69.441
C21	1	9.127
C23	1	3.294
C24	1	17.340
C31	1	0.320
C33	1	28.801
C34	1	5.120
C36	1	0.653
C37	1	4.306
C40	1	0.480

ROW	X1 C21	Y C26	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
19	30.0	40.400	44.587	1.015	-4.187	-2.25R
25	90.0	40.500	44.391	1.015	-3.891	-2.09R

```
R DENOTES AN OBS. WITH A LARGE ST. RES.
```

THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y = 75.6 - 0.211 X1 + 1.73 X2
+ 0.407 X3 + .0003 X4 - .0263 X5
+ .0958 X6 + .0025 X7 + .0131 X8
- 0.122 X 9

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	75.56	54.50	1.39
X1	C21	-0.2106	0.1965	-1.07
X2	C23	1.7335	0.8282	2.09
X3	C24	0.41	13.22	0.03
X4	C31	0.0003009	0.0009073	0.33
X5	C33	-0.02630	0.01203	-2.19
X6	C34	0.0958	0.8166	0.12
X7	C36	0.002465	0.002778	0.89
X8	C37	0.01312	0.01925	0.68
X9	C40	-0.12187	0.08334	-1.46

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 2.310
WITH (36-10) = 26 DEGREES OF FREEDOM

R-SQUARED = 33.3 PERCENT
R-SQUARED = 10.3 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	69.381	7.709
RESIDUAL	26	138.695	5.334
TOTAL	35	208.076	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	9	69.381
C21	1	11.070
C23	1	9.976
C24	1	4.084
C31	1	0.587
C33	1	25.503
C34	1	0.073
C36	1	4.201
C37	1	2.481
C40	1	11.407

ROW	X1 C21	Y C27	FRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
8	60.0	80.100	85.197	1.277	-5.097	-2.65R
25	90.0	91.200	86.309	1.106	4.891	2.41R

R DENOTES AN OBS. WITH A LARGE ST. RES.

DURBIN-WATSON STATISTIC = 1.51

Stretch

```
REGRESS C29 9 C21,C23-C24 C31,C33-C34,C36-C37,C40 C50 C51
```



```
NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C34
C37
C40

THE REGRESSION EQUATION IS
Y =    9.10 - .0404 X1 - .0033 X2
     -  1.38 X3 + .0003 X4 + .0004 X5
     + .0933 X6 + .0004 X7 + .0005 X8
     - .0056 X 9
```

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	9.105	3.634	2.51
X1	C21	-0.04041	0.01310	-3.08
X2	C23	-0.00330	0.05523	-0.06
X3	C24	-1.3815	0.8815	-1.57
X4	C31	0.00025093	0.00006050	4.15
X5	C33	0.0004340	0.0008021	0.54
X6	C34	0.09333	0.05445	1.71
X7	C36	0.0003681	0.0001852	1.99
X8	C37	0.000500	0.001283	0.39
X9	C40	-0.005625	0.005557	-1.01

```
THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.1540
WITH (  36-10) =  26 DEGREES OF FREEDOM

R-SQUARED = 55.0 PERCENT
R-SQUARED = 39.5 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE
```

DUE TO	DF	SS	MS=SS/DF
REGRESSION	9	0.75488	0.08388
RESIDUAL	26	0.61671	0.02372
TOTAL	35	1.37159	

```
FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN
```

DUE TO	DF	SS
REGRESSION	9	0.75488
C21	1	0.01042
C23	1	0.10889
C24	1	0.02940
C31	1	0.40801
C33	1	0.00694
C34	1	0.06969
C36	1	0.09363
C37	1	0.00360
C40	1	0.02430

ROW	X1 C21	Y C29	FRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
29	90.0	3.1200	2.8561	0.1035	0.2639	2.31R
30	90.0	2.4000	2.6678	0.0851	-0.2678	-2.09R

```
R DENOTES AN OBS. WITH A LARGE ST. RES.
```

Regression model
all Temperature

REGRESS C9 TENSTLF 14 C1-C4 C11-C20 C50 C51

NOTE - THE FOLLOWING VARIABLES ARE HIGHLY
CORRELATED WITH OTHER PREDICTOR VARIABLES
C12
C14
C17
C19
C20

THE REGRESSION EQUATION IS
Y = 4549. - 27.2 X1 - 87.5 X2
- 41.5 X3 + 971. X4 + 0.175 X5
+ 0.225 X6 + 2.21 X7 - 68.2 X8
+ 0.111 X 9 + 0.435 X10 - 1.51 X11
+ 0.189 X12 + 3.00 X13 - 11.8 X14

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	4549	4957	0.92
X1	C1	-27.22	17.60	-1.55
X2	C2	-87.49	22.94	-3.81
X3	C3	-41.52	74.45	-0.56
X4	C4	971	1119	0.87
X5	C11	0.17502	0.07566	2.31
X6	C12	0.22517	0.07566	2.98
X7	C13	2.207	1.003	2.20
X8	C14	-68.18	68.10	-1.00
X9	C15	0.11095	0.05350	2.07
X10	C16	0.4354	0.2317	1.88
X11	C17	-1.508	1.605	-0.94
X12	C18	0.1892	0.2317	0.82
X13	C19	2.996	1.605	1.87
X14	C20	-11.781	6.950	-1.69

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 333.6
WITH (108-15) = 93 DEGREES OF FREEDOM

R-SQUARED = 33.3 PERCENT
R-SQUARED = 23.2 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	14	5159221	368516
RESIDUAL	93	10350562	111296
TOTAL	107	15509784	

FURTHER ANALYSIS OF VARIANCE

SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	14	5159221
C1	1	707257
C2	1	38033
C3	1	32257
C4	1	398546
C11	1	595518
C12	1	985664
C13	1	538792
C14	1	111559
C15	1	478601
C16	1	393129
C17	1	98193
C18	1	74238
C19	1	387683
C20	1	319753

ROW	X1 C1	Y C9	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
105	90.0	2.0	1851.0	123.3	-1849.0	-5.96R
107	60.0	89.2	1716.6	137.1	-1627.4	-5.35R

R DENOTES AN OBS. WITH A LARGE ST. RES.

DURBIN-WATSON STATISTIC = 2.21

-- PLOT C51 C50 RESID VS YHAT

```
          C51
       2900.+
            -
            -
            -
            -                                        *
       2650.+                                       *
            -
```

MTB > C18=C2**2