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Western Michigan University

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THE EFFECTS OF TEMPERATURE ON RETENTION

by

Michael D. Holt

A Thesis submitted to
Faculty of the Department of Paper Science & Engineering
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan
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TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
HISTORICAL BACKGROUND	2
First Pass Retention	2
Britt's Dynamic Drainage Jar	4
Dynamic Retention	5
ELECTROKINETIC EFFECTS IN PAPERMAKING SYSTEMS	7
Electrokinetic Phenomena	7
Measurement Techniques	9
Streaming Current Detector (Hydrascan)	10
Pilot Machine at WMU	13
Parameters that Affect Zeta Potential	14
Bridging	16
Temperature	17
EXPERIMENTAL	19
Experimental Design	19
Preparation of Pulp	20
Calibration and Standardization of the SCD (Hydrascan)	20
Dynamic Drainage Jar	21
Retention Aids	22
Heating	22
pH	23
Paper Machine	23
Retention Aids	24
pH	24

TABLE OF CONTENTS (CONT.)

RESULTS AND DISCUSSION	25
CONCLUSIONS	30
LITERATURE CITED	31
TABLES AND FIGURES	32

ABSTRACT

The purpose of this thesis was to study the effects of temperature and concentration of retention aids on retention. This had been a debatable issue between northern and southern paper mills because of their temperature differences.

The retention studies were performed with the dynamic drainage jar and the pilot paper machine at Western Michigan University with good agreement in both cases.

It was found that increasing temperature when using different retention aids had a considerable effect on first-pass retention. The effect of temperature on retention was found to depend on the ionic charge of the retention aid. The cationic polymer retention increased from 40°F to 70°F and then decreased from 70°F to 140°F. The anionic polymer retention decreased from 40°F to 80°F and then increased somewhat from 80°F to 140°F.

Temperature had an effect on retention drainage and many other factors which influence the wet end of a paper machine. This was shown in this study which was designed to make proper use of the theory of zeta potential - the electrokinetic charge on a colloidal particle. In the development of Britt's dynamic drainage jar, the purpose was to study the effect of colloidal factors in isolation from hydromechanical factors to the largest possible extent. In this study the charge of the polymer was shown to be the most important factor in retention as temperature increased.

INTRODUCTION

The purpose of this thesis was to study the effects of temperature on retention. To do this the system had to be well-defined. To gain maximum benefits from a retention aid evaluation, careful planning to obtain proper data was required. A historical background of previous studies was necessary to aid in development of a logical approach to the problem. In this study one needed an understanding of the theory of electrokinetic effects pertaining to flocculation, zeta potential, and retention. This property has a strong influence on retention on a paper machine. Therefore, the emphasis of this report was on electrokinetics.

The main purpose in this study was to determine if temperature increases would aid fiber and filler retention. Retention is becoming increasingly important due to rising costs of fillers and ever increasing pollution legislation.

HISTORICAL BACKGROUND

First Pass Retention

There are two ways of looking at retention. One is to minimize or ignore the first-pass retention and to depend upon recovery and recirculation of white water to achieve satisfactory overall retention in a closed system. The other is to emphasize improvement in first-pass retention by chemical-additives to the point that the recovery system has only minor quantities to recover, especially if the system is only partially closed. From Britt's article (1) the current practice is heavily weighted toward the first, with consequent build-up of the fines fraction in the headbox system. This build-up, even though it accomplishes the objective of high overall retention, can be shown to have distinctly adverse effects upon paper machine performance. The fact stands that if the first-pass retention is improved there will be less load on the recovery system. Therefore, retention aids have, and will have, a big role in the paper industry.

There are two main factors that influence first-pass retention. One is the mechanical entrapment of fine particles in the forming web which is a function of furnish composition, basis weight, machine speed, and wet-end design. Another is the colloidal attraction forces between the dispersed solids of the stock which are a function of chemical conditioning caused by additives. Machine performance is a resultant of these factors.

The first-pass retention is determined by the usual calculations from headbox and tray consistencies, while the ash retention figure is obtained by dividing sheet ash content by headbox ash content. Both are used for judging the progress during a retention aid evaluation, but they do not give the material balance type of determination needed for calculating the economics of a retention aid. Waddell (2) stated that a retention aid should be scheduled for a period when one grade or very similar grades will be running continuously for two or three days. It is difficult to obtain significant data where grade changes are frequent.

One factor stressed by Waddell that affects a given machine's first-pass retention is the location of the tray water sampling point. The evaluation of the saveall efficiency during the machine trial has a great effect. He stated this is particularly true of the flotation-type saveall, where the press water is discharged directly to a sewer system with a considerable loss of pigments. Waddell stated that the overall retention refers to the general efficiency for a longer period and includes the losses to the sewer from the savealls. It relates the materials purchases vs. all the fibers and fillers converted to saleable paper and broke. This calculation is very instructive in assessing losses of expensive titanium dioxide into broke and into recovered white water sludge from the saveall.

Britt and Unbehend (3) found that in a mat-free process in which the mechanical construction of the apparatus is a constant, there will be

a greater or lesser tendency of the fines fraction to stay with the fiber, depending upon the degree of turbulence of the system and colloidal attraction between the surfaces of the suspended particles. If a mat is allowed to form in such a system, the tendency of the fines to become mechanically entangled in the mat affects the result. Since the objective is to measure the colloidal attraction as independently as possible of mechanical entrapment, it was reasoned that the separation of retained from unretained fines should occur only through the interstices of a precisely constructed screen. Further, it was reasoned that since turbulence is always part of the sheet formation process on a paper machine, a controlled turbulence should be incorporated into the testing system. From these considerations and several years of development, Britt developed his drainage jar technique. The drainage jar procedure determines the relative tendency of the fines fraction to pass through the screen with the fluid phase under turbulent conditions. The result is expressed as retention of the fines fraction under selected and controlled turbulence conditions.

Britt's Dynamic Drainage Jar

In Figure 1 Britt's (1) dynamic drainage jar is shown. The screen in Britt's first dynamic drainage jar was of electrodeposited nickel having holes of $76\mu\text{m}$ diameter. Later it was changed to 200 mesh screen.

In Britt's study (4) the stock is diluted to 0.5% consistency and chemicals are added at this point if desired. A 500 ml sample of this

stock is placed in the drainage jar provided with an adjustable speed agitation having 2 1/2 inch blades centered in the jar and located 1/2 inch from the screen. An 80 x 68 fourdrinier screen has been adopted for normal use, although there is a wide choice in screens for use with this test. Likewise there is a choice in speed of agitation. This test can be applied to a number of samples of headbox stock. In some instances the one-pass retention of filler on the paper machine was known. In these samples the retention at 1000 rpm was approximately that observed on the paper machine. The speed range observed is 0 to 3000 rpm which represents a peripheral speed range 0 to about 1600 ft/min.

Dynamic Retention

In the performance of Britt's (5) dynamic drainage jar procedure a 500 ml sample of .5% consistency stock is used. With the agitator running the stock is poured into the jar. The filtrate is collected in a calibrated beaker. After about 200 ml of filtrate have been collected, the beaker is removed, and the content of suspended solids in the filtrate is determined. Both turbidimetric and gravimetric methods are used, with the latter generally preferred.

It is important to know the content of fines in the sample of stock. The amount of filler is known from that added and the pulp fines content is known from running a blank in the absence of filler with the dynamic test under dispersed conditions.

The retention of the fines fraction of a stock furnish by the fibers which form the structure of the sheet is greatly influenced by the degree of turbulence or hydraulic shear existing during sheet formation. Having no mat formation, we can observe the attractive forces between fines and fiber free from the difficult-to-control factor of mechanical entrapment. In the absence of flocculating agents there are extremely low forces of attraction and these are easily broken by moderate turbulence.

Various flocculating agents or retention aids have highly different degrees of effectiveness in the retention of fines under turbulent conditions. Of particular interest is that the differences among flocculating agents are shown up principally in the higher degrees of turbulence (hydraulic shear), typical of fast-running paper machines. At low levels of shear, the various flocculants are not greatly different, but at higher levels they tend to form two groups; those resisting re-dispersion of fines and those in which the flocculation is readily broken up by dispersive forces. The latter is termed soft flocculation. Britt recommended a long chain polymer, either as the sole additive, in which case it is a cationic polymer, or a two-step method in which the stock has been preconditioned to accept an anionic polymer.

It must be emphasized that maximum retention is not necessarily the best papermaking practice. High retention may be accompanied by undesirable side effects such as non-uniform formation, two-sidedness of filler content, drainage problems and low opacity due to large filler aggregates.

ELECTROKINETIC EFFECTS IN PAPERMAKING SYSTEMS

The world consists of surfaces exposed to liquid water and in this environment most materials develop electrically charged surfaces. These surface charges often result from the slight ionization of surface molecules or the absorption of ions onto the surfaces of water. Often, both negative and positive charges exist on the same surface, and then the net charge is of interest.

The historical background for this topic dates back to the 1800's. There has been much effort in this field because electrostatic forces have been found to affect many practical systems. The paper industry is concerned with the effects of charged surfaces in its study of pulp slurry drainage rate, filler retention, white water clarification, retention of wet and dry strength additives and many others. This manipulation of the electric charges which lie on surfaces of solids in water is strongly influenced by different chemical additives such as retention aids, alum and charged polymeric additives.

Electrokinetic Phenomena

The electrical consequences of a charged surface are summarized in Figure 2 which depicts a suspended electronegative particle such as a wood pulp fine or pigment. Its negative surface charge attracts a considerable number of positive counterions which tend to concentrate nearby. Those immediately adjacent to the negative surface are strongly attracted and appear almost attached to it, in a very thin layer.

Farther away there is a more diffuse, thicker layer which consists primarily of counterions but these are only mildly attracted. Still further away, in the bulk of the aqueous medium, both positive and negative ions are present in equal numbers. The presence of the charged particle produces an electric potential also shown in Figure 2. The fraction of this potential between the boundary of "attached" counterions and the bulk of the system is known as the zeta potential (6). When this particle moves through the water, only the very thin layer of strongly attached counterions tends to move along with it. Thus, the plane of shear is located at the boundary between firmly attached and the diffuse layers of counterions. If one follows the movement of this particle, one will be observing only the net effect of the particle's surface plus its thin layer of strongly attracted counterions. If this electric potential is reduced, then the repelling forces become weaker and the constant Van der Waals forces of attraction will become important. At the isoelectric point, at which zeta potential is zero, no repelling forces are active and the particles conglomerate as a consequence of the Van der Waals forces. This is very important to achieve maximum wet end retention, improved physical properties and less pollution problems.

In recent studies Moore (7) pointed out that optimum polymer and alum concentrations for drainage and retention improvement do not necessarily correlate with the charge neutralization point of the fiber surface. This does not rule out the importance of zeta potential

measurements, but suggests that indiscriminate use of such a property for controlling a papermaking furnish may not give the most desirable results. However, with a given system a given polymer may not be optimized for maximum retention at zero zeta potential. The electrokinetic state is one of several mechanisms to be considered and does not necessarily play a dominate role in any system under all possible conditions. Although the proper interpretation of electrokinetic data is often very difficult, we can hope eventually to control papermaking to a reasonable extent with the assistance of a reliable and practicable electrokinetic monitoring instrument.

Measurement Techniques

There are four types of electrokinetic phenomena. They all involve relative motion between firmly attached counterions and surrounding fluid medium, usually water (Figure 3).

Electrophoretic mobility (Figure 3) involves the motion of charged particles caused by an external potential gradient. Thus, a particle immersed in water and having a net negative surface charge will move towards the anode when a voltage is applied. The reverse of this effect, electroosmosis (Figure 3b) involves a porous plug made of this same negatively charged material but attached in the system so that it cannot move. When a voltage is applied, the fluid medium containing positive counterions in the diffuse layer adjacent to the porous plug surfaces will tend to move toward the cathode.

Sedimentation potential (Figure 3c) is developed when charged particles fall freely through a fluid and an electric potential. This effect is essentially the reverse of electrophoretic mobility. In the same way, streaming current potential (Figure 3d) and electrophoresis (Figure 4) can be regarded as the reverse of electroosmosis. If a fluid is forced to flow through the porous plug in Figure 4, a potential of the polarity indicated will be developed, because positive counterions will be swept along by the flow of the fluid through the system.

Streaming Current Detector (Hydrascan)

Operation of the instrument is based on streaming phenomena. One of the discoveries which made the instrument possible was that the walls of a capillary quickly take on the charge characteristics of colloidal particles or of other charge influencing species present in the fluid. The streaming current results from the physical separation of counterions from charged surfaces, and this occurs only in the case of charges immobilized on the surface of the boot and piston. The movement of particles (along with their counterions) through the annular space does not contribute to the signal.

The use of the annulus rather than a capillary or many capillaries permits easy cleaning since disassembly may be accomplished in few seconds and then the parts consist of a half-inch bore and a half-inch rod.

When the sample reservoir is filled so that the upper electrode remains covered, and the motor operates the piston at about four cycles per second, the sample is alternately forced up and down through the annular space between the wall of the bore and the piston. Since, in the general case, the walls possess an electrical charge, this flow results in the generation of a four-cycle streaming current.

Drift is very common because of the extreme sensitivity of the instrument plus the susceptibility of colloidal systems to influence the reading of the instrument. The nature of colloids and that of any standard makes the determination of drift very difficult. It is said by Meersman (8) that it is advisable to use a low concentration salt as an arbitrary standard to which the instrument may be checked from time to time.

It may take many samples to stabilize a new reading especially with cationic materials. Washings with distilled water and 1% starch solution (Essex Gum) can prove to be very helpful and time saving in this regard.

When the sample chamber (boot) contains only pure deionized water, the ionic double layers exist as a consequence of the unsatisfied charge on the surface of the boot and piston. It is believed that the instrument reading under these conditions is a function of the zeta potential of the boot and piston material and the dielectric constant of the liquid.

If a polyelectrolyte is added to the system, the nature of the surface charge becomes more complex. The surface of the boot and piston functions to provide absorption sites for the polyelectrolyte molecules. With macro-ions absorbed into the working surfaces of the instrument, the measured streaming current is not only characteristic of the boot and piston material and the dielectric constant of the solution but is also influenced by the adsorbed polyelectrolyte layer. The ionic double layer, and hence the streaming current, would be expected to become more positive with the adsorption of a cationic polymer and more negative with the adsorption of an anionic polymer. However, it is not all that easy since any electrolyte present in the form of salt solutions will also have their effect on the system (which according to Meersman is greater than the effect the polymer has on the system). The constant displacement feature makes the reading of the streaming current detector independent of viscosity up to a point of cavitation. The large fibers also have to be screened or the fibers will build up in the boot and plug the piston and possibly damage the system.

The reading of the streaming current detector is a function of the dielectric constant of the liquid. When attempting to correlate zeta potential with the streaming current detector readings, the readings should be divided by the dielectric constant. When attempting to correlate with mobilities they can be left as they are.

Non-aqueous samples can be handled by the instrument without problems as long as they don't attack the materials of construction.

The streaming current detector Hydrascan, based on equipment developed by Gerdes (9), is a commercial instrument which measures an empirical electrical effect related to streaming potential. The operation is summarized in Figure 5. The synchronus up and down movement of a plastic piston in a plastic cylinder containing a dilute particle suspension produces an electrical impulse which is detected by two small ring-shaped silver electrodes embedded in the inner wall of the cylinder. Since the piston moves up and down the upper electrode but never reaches the lower one, this motion produces a small electrical output, relative to the lower electrode. This signal is greatly amplified, rectified and then conducted to an output meter, where it is expressed in arbitrary units (negative or positive) with respect to a central zero point. The chief advantage of this instrument is its continuous electrical output which can be used as a simple empirical monitor of the system being studied.

Pilot Machine at WMU

The purpose as mentioned before is to simulate the dynamic drainage jar and a paper machine in respect to first-pass retention (ash). (Figures 21 and 22). It has been found that trying to duplicate a paper machine is almost impossible, but in this study the author feels if one controls the variables one can attain some pretty good data.

The author ran his experiment on a dynamic drainage jar and it is up to him to acquire the same conditions as before on the paper machine.

Parameters that Affect Zeta Potential

Cellulose fibers, which comprise the major portion of the furnish, have a negative zeta potential. According to Yurev and Pozin (10) zeta potentials of technical grades of unbleached pulps are lower than those of bleached pulps or cotton. The highest zeta potential was noted for standard cotton, (-21mV) whereas the lowest values were for unbleached sulfite (-4mV) and sulfate (-4.5mV). (This is strongly affected by the degree of purity of the cellulosic material and the degree of cooking of the pulps.) With the increase in carboxyl group content the negative value of the zeta potential tends to decrease.

At constant ionic strength according to Yurev and Pozin (10), the zeta potential of cellulosic materials at first increases with pH and then becomes practically constant at pH 5 to 6. At high acidities (pH = 3) the zeta potentials of cotton and bleached sulfite pulp were practically equal.

Also Yurev and Pozin reported the cooking strength of unbleached sulfite pulp had a considerable influence on its electrokinetic properties. As the strength of the sulfite pulp increased, the negative value of the zeta potential decreased and the surface conductance increased. Cited from Meersman (8) this is probably because of the higher content of solid lignosulfonic acid, which is very acidic, in stronger pulps.

Kamamaru (11) using wood and cotton pulps reported that the value of the zeta potential decreases as the degree of beating increased.

Polyelectrolytes, synthetic polymers which function as retention aids are available as either cationic or anionic. Since the retention aids have a higher sensitivity of use due to the charges there is less pH dependency of alum.

The zeta potential of a papermaking system is dependent on a large number of variables, including fiber type, filler type, pH, alum dosage, polymer addition, wet end additives (size, defoamers, biocides) and water quality.

The lower the pH the more positive the zeta potential becomes. This is due to the ionization of the carboxylic acid groups in the hemicellulose and phenolic hydroxyl groups in the lignin.

Anionic polymers with high alum, low pH systems is an important usage as a polymeric retention aid. Polymers increase retention by bridging one particle to another. Zeta potential is used to measure the proper charge type and optimum level for usage. Too much polymer will redisperse the system and reduce retention.

Wet end additives, particularly rosin size, greatly affect the zeta potential of the stock. Rosin size is an anionic emulsion but is used in conjunction with alum to form a size precipitate. The precipitate forms on the fibers and in doing so causes more alum to be retained by the pulp, which makes the zeta potential more positive.

The quality of the process water is also important in controlling zeta potential. Dissolved salts will cause the zeta potential to decrease in magnitude toward zero. Polyvalent ions are much more effective than monovalent ions and therefore, water hardness and sulphate ion concentration become important parameters in the control of zeta potential. The Ca^{++} and Mg^{++} ions are available for absorption on the negative particles. The cationic polyelectrolyte will be in competition with these adsorbed ions and be less effective. By figuring out the hardness of the water, chemical additions to the water can be related to pure water.

There are many parameters which can change others in ways that seem impossible to predict zeta potential. If an experiment is well controlled one can ascertain reliable data.

The application of electrokinetic monitoring to a practical papermaking process is both desirable and feasible. By measuring the surface charge of the pulp furnish at various stages in a paper mill, one can often establish useful correlations between surface charge and process improvements. This application has been demonstrated both by fundamental mobility measurement and by simultaneous monitoring with an empirical continuous output device. Although the proper interpretation of electrokinetic data is often very difficult, we can hope eventually to control papermaking to a reasonable extent with the assistance of a reliable and practicable electrokinetic monitoring instrument.

Bridging

To reduce the high negative charge given off by the cellulose fiber

and fillers, cationic retention aids are added. They serve as a dual function of charge neutralization and bridging (12). Bridging refers to a long chain polymer molecule that is in contact with adjacent solid surfaces. Pulp fines show much better retention than filler when the retention mechanism is simple filtration, but when flocculating polymers are added to the system, the improvement in filler retention is far more dramatic than with pulp fines. This is evidently because bridging is more effective and perhaps also because the larger pulp fines present a greater target to the flow of water of agitation (13). Bridging exhibits itself by improved tenacity against redispersion by hydraulic shear forces.

The work by LaMer and his co-workers (14) has led to the conclusion that bridging of particles by high molecular weight polymer is the principal mechanism in producing flocculation. In this type of polymer-solid interaction, only a segment of the polymer attaches first, by forming physical or electrostatic bonds. The remaining free end of the polymer then adsorbs onto another particle that has a free adsorption site. Formation of the polymer bridges can occur even against appreciable electrostatic charge barriers. This type of mechanism is predominant in affecting flocculation.

Temperature

There are many factors to consider when deciding to increase the temperature on a paper machine. Temperature affects the physical and

chemical properties of the papermaking system. These properties are fiber, water, retention aids, and other additives, which all affect retention.

Increasing temperature on a paper machine will increase drainage because of the decrease in viscosity.

Changing temperature will affect cellulose fibers by decreasing their surface area when heat is applied. This has been proven on a Pulmac Tester. Temperature increase gives less surface area for the polymer (retention aid) and other additives to act upon due to an exothermic reaction. Also, the negative charge that the fiber possesses will have a smaller net charge density (15).

As temperature increases the net charge density of a polymer decreases; therefore, there is more flocculation and higher retention (15). Net charge density is the net charge per unit volume.

Also, when temperature increases, the surface charge density increases; therefore, the repulsive forces decrease and flocculation increases. This denotes the total surface charge density; that of the diffuse layer and that of the compact layer.

Additives are also affected according to their charge and physical state. Fiber, polymer retention aids, and additives are all affected by a temperature increase which affects electrokinetic properties.

EXPERIMENTAL

Experimental Design

The purpose of this experiment is to show the effect of temperature on retention using various concentrations of retention aids. The retention aids used are manufactured by Hercules. Cationic high molecular weight - Reten 210, anionic high molecular weight - Reten 421, and cationic low molecular weight - Reten 304 are used at 1 lb., 2 lbs., 3 lbs. per ton. By using different charges and concentrations, one can have a better understanding of how temperature affects retention. The effects on retention were studied on both the dynamic drainage jar and the pilot paper machine at Western Michigan University.

The dynamic drainage jar was used in this study because it compared very well to the colloidal factors on the paper machine. To obtain good results on both the dynamic drainage jar and the paper machine the conditions such as pH, agitation, furnish, hardness of water, retention and dosage, and temperature had to be controlled. Temperature was the only variable per dosage of polymer that was changed to determine the effect this had on first-pass retention and the Hydrascan charge - zeta potential. The temperature change for each retention aid dosage was from 40°F to 140°F.

In comparing the dynamic drainage jar and the paper machine the author chose treatments of 2 lbs. per ton high molecular weight cationic polymer and also the two-step system in which 1 lb. per ton high molecular weight cationic polymer, Reten 210, is adsorbed onto the solid surfaces

of the stock, followed by a 1 lb. per ton high molecular weight anionic polymer. The purpose was to compare first-pass retention and the Hydrascan charge - zeta potential. The pH in this experiment was maintained at 4.5.

The author divided this study into two sections, the dynamic drainage jar and the paper machine. In each section the conditions will be discussed in further detail.

Preparation of Pulp

The preparation of pulp was the same for the dynamic drainage jar and the WMU pilot paper machine. Bleached softwood and hardwood kraft (50/50) with 10% solids of TiO_2 was used in the base stock. Hard water was used in both cases at a pH 7.8. The pulp was beaten to a freeness of 450 CSF. The dynamic drainage jar pulp was beaten by the Tappi Standard Method in a Valley Laboratory Beater and the pulp for the pilot paper machine was refined by the double disc refiner. Both stocks were diluted down to a .5% consistency on the wire.

Calibration and Standardization of the SCD (Hydrascan)

The instrument was standardized after each sample by washing with deionized water and 1% Essex Gum solvent. The sensitivity selector switch located in the front of the electronic indicator was set at 32 X, the most sensitive setting. All readings throughout the experimentation were taken after five minutes had elapsed.

Dynamic Drainage Jar

The purpose of using this dynamic drainage jar is to simulate what actually goes on a paper machine in reference to the colloidal properties. It is impossible to simulate the mat formation, therefore the retention tests must be performed without mat formation. If a mat forms, this can affect the result in an uncontrolled way. This is why the design of the dynamic drainage jar was important in this study.

This design was developed from Britt's ideas and ideas the author picked up from Hercules and American Cyanamid. The jar in Figure 1 is made from a durable plastic lemonade pitcher which was used to withstand high temperatures. At the bottom of the pitcher was a 1 inch hole for free drainage. The purpose of the hole was to plug the container for initial mixing. At the bottom of the container was a synthetic wire (58 x 74) mesh which was supported by a wire supporter with a snug fit. There was a 1 1/2 inch propeller about an inch from the wire that rotated approximately 525 rpm. At this speed the author felt there was good correlation to the 70 feet per minute on the pilot plant machine. This speed was used throughout the experiment.

The following procedure was used to operate the dynamic drainage jar.

1. Take 1 liter of representative sample at pH 4.5.
2. Add retention aid to sample.
3. Heat sample 5-10°F above temperature requirement.
4. Pour in drainage jar with stopper in.

5. Turn agitator on to 525 rpm for 1 minute.
6. Pull plug and collect 100 ml of white water.
7. Use this 100 ml sample for determining the first-pass retention.
8. Repeat steps 1 through 5 and collect a 250 ml sample.
9. Use this 250 ml sample for the Hydrascan Streaming Current Detector.

Retention Aids

In using the dynamic drainage jar three retention aids were used: Reten 210 (cationic high molecular weight polymer), Reten 304 (cationic low molecular weight polymer), and Reten 421 (anionic high molecular weight polymer). The three polymers were used at 0.5, 1, 2 and 3 lbs. per ton respectively at a 0.5% concentration.

The polymers were added one at a time. In each case they were added before heating by the use of a pipette except for the sequential addition study. In this case the cationic high molecular weight polymer was added before heating and the anionic high molecular weight polymer was added after heating. In doing so the cationic polymer would have a chance to act upon the stock solution before the addition of the anionic polymer. The agitation of the propeller would mix the polymer for a 1 1/2 minute to give a uniform mixing.

Heating

The one liter sample was placed in a metal container and heated

in a steam jacket. The first-pass retention sample was heated 5-10°F above required temperature due to the cooling of the solvent. For the Hydrascan zeta potential analysis, the temperature was slightly higher. In both cases with the Hydrascan and Retention sample, the reading and test was taken at the required temperature.

pH

Stock pH is an important variable. In running the dynamic drainage jar, Reten 210 high molecular weight cationic polymer was run at pH 7.5 and 4.5. The other two polymers were run at pH 4.5. Sulphuric acid was added to reduce the pH.

Paper Machine

The pilot paper machine was run with the same furnish, pH, concentration of polymer, temperature, freeness, consistency, hardness of water, "agitation", etc. One possible difference was in the refining. The pilot paper machine stock was refined by a double disk refiner and the dynamic drainage jar stock was refined by a Valley Beater. Both were refined at 350 freeness.

The paper machine was run at 70 ft. per minute at a basis weight of 35 lbs.

The holding chests at this speed could only last 3-1/2 hours. Since this was the case, the experiment was run with two retention aids - Reten 210 high molecular weight, cationic polymer and the sequential (cationic and anionic high molecular weight polymer). The temperature range was as follows: 70, 90, 110, 130, 140°F.

We found that our steam added to our white water collection box took about five minutes to increase our temperature 10°F. The samples were taken at each temperature range.

Before running the machine a blank was run. There was a 10 minute waiting period to standardize conditions.

Once the temperature and conditions were met, a sample was taken from the headbox and the white water tray. Also a paper sample was taken. There was enough sample from the headbox and the tray to run a first-pass retention and a Hydrascan streaming current detector analysis.

Retention Aids

Due to the limited time to run the experiment on the paper machine, two different polymers at 2 lbs. per ton were used. The first was Reten 210 and the second was a sequential addition in which 1 lb. per ton of Reten 210 is adsorbed onto the solid surfaces of the stock, followed by a 1 lb. per ton addition of Reten 421. Reten 210 was added at the stuff box and Reten 421 was added at the fan pump.

The retention aids were prepared at .5 concentration, as was the dynamic drainage jar.

pH

The pH of the paper machine was controlled by using sulphuric acid. On the start up a pail of acid was dumped in the white water box to bring down the pH to 4.5. Once this was achieved the automatic controller would adjust the pH to 4.5 automatically.

RESULTS AND DISCUSSION

In this study the level of turbulence, temperature, sulphuric acid addition, pH, concentration of Retention Aids at different weights were selected as the parameters to be studied. The high and low molecular weight polymers with cationic and anionic charges were used throughout the study. The following series of figures and tables presented in the back of the thesis will aid in summarizing the author's study.

In (Figure 6) first-pass retentions were made on Holt's dynamic drainage jar at varying temperatures using no retention aids. At pH 4.5 retentions were higher than pH 7.8 from 40 - 140°F. Notice on the graph that the percent retention decreased then increased at increasing temperatures. This is probably due to the electrokinetic properties of the sample, which will be proven later.

In (Figure 7) percent retentions on the dynamic drainage jar were again tested under the same conditions as before (Figure 6), except this time a .5 lb. per ton Reten 210, a high molecular weight cationic polymer, was added. The same occurred in both (Figures 6 and 7). The percent retention decreased to about 100°F, then increased up to 140°F. The difference between (Figure 6) and (Figure 7) was that the addition of Reten 210 increased the percent retention considerably. This again was caused by bridging action and increasing electrokinetic charge of the polymer to the stock suspension.

In (Figures 8-10) the same study was made except this time the retention graph was opposite of (Figures 6 and 7). As the temperature increased, the percent retention increased to about 80°F then decreased

somewhat to 140°F. Again, to remind us, the results were from Holt's dynamic drainage jar. The author feels that the .5 lb. per ton in (Figure 7) wasn't quite enough to surpass the charge of the furnish. That was why (Figure 7) did not agree with (Figures 8-10).

In (Figures 11 and 12) percent retention was again run like (Figures 8-10), except that the tests were taken at pH 4.5 using .5 lb. and 1 lb. per ton of Reten 304, a low molecular weight cationic polymer. Also the percent retention as before (Figures 8-10) increased to about 60°F then decreased to 80°F and then it increased. The percent retention in (Figures 11 and 12) using a low molecular weight cationic polymer was lower than the higher molecular weight polymer (Figures 8-10).

In (Figures 13 and 14) the percent retentions decreased and then increased at increasing temperatures. The percent retention had an opposite effect as did the cationic polymers. The reason for this was due to the negative charge. The sequential dosage of positive and negative ions seemed to set up an opposite charge to enhance fiber to fiber flocculation and filler and fines retention. This is why the 50/50 percent sequential addition of Reten 210 - cationic polymer and Reten 421 - anionic polymer had a much higher percent retention than the cationic polymers.

In (Figure 15) the viscosity of water is shown. The purpose was to compare this graph to the graph on (Figure 6). The graphs do compare somewhat. Both decrease in retention as temperature is increased but then the blank increased around 110°F. So one might say that viscosity has a slight effect on retention but not when electrokinetic

charges are introduced. The important characteristic about [increasing] viscosity is its faster drainage.

The author would like to point out that percent retention is discussed, but actually first-pass retention was used. First-pass retention was used because there was no fiber mat formed when using a dynamic drainage jar. The retention was tested from what had first passed through the wire.

In (Figures 16 and 17) the purpose was to compare first-pass retention and percent retention. In (Figure 16) using a cationic polymer and (Figure 17) using a sequential addition of 50/50 percent cationic and anionic addition, there was a very close similarity between the two curves. Again in (Figures 16 and 17) one can see that the two graphs go in opposite directions due to the opposite charge. As (Figure 16) increased up to 120°F and then decreased, (Figure 17) decreased down to 90°F and then increased.

In (Figure 18) the cationic high molecular weight polymer was summarized using the dynamic drainage jar. As temperature increased the percent retention using the 1, 2, 3 lb. per ton of polymer increased to 60 to 80°F and then decreased. The lowest percent retention seemed to be at the lowest temperature. Also as the lb. per ton dosage increased, so did the percent retention, respectively.

In (Figure 19) the retention on the dynamic drainage jar using cationic low molecular weight polymer was summarized. The maximum percent retention seemed to occur at 60°F and 120°F. The percent retention in (Figure 19) was lower than the high molecular weight retention (Figure 18). In this study it showed that a higher molecular

weight polymer caused more bridging action and also had a stronger electronegative charge which gave a higher percent retention.

In (Figure 20) the percent retention using 50/50 percent Reten 210 and 421 (high molecular weight cationic and anionic polymer) was summarized. Again the highest percent retention was shown at 40°F and 100-120°F. It appeared that the amount of dosage seemed to have a considerable effect in percent retention with increased temperature.

Up to now only the dynamic drainage jar was used to determine the effects of temperature on retention. In (Figures 21 and 22) the graph shows that the dynamic drainage jar (Holt's) simulates very closely to the pilot paper machine at Western Michigan University. In both graphs (Figures 21 and 22) cationic and anionic polymers are used. In these figures the dynamic drainage jar had indeed correlated very well to the paper machine.

In (Figures 23-25) the graphs showed that the zeta potential using the Hydrascan zeta meter by Hercules had a significant influence on the percent retention. For example (Figure 23) using a cationic system, the highest first-pass retention occurred at 100°F, which had around a 0 electronegative charge. At 70°F the graph showed that the percent retention was at a minimum but the Hydrascan charge was very high (+150). Also at 125°F the percent retention decreased and also the zeta potential was very low (-90).

Another example (Figure 24) was shown using a sequential addition of cationic and anionic polymer. At 70°F the highest percent retention did not have a 0 zeta potential. The author felt he didn't read it at a low

enough temperature or it might have been closer to 0 zeta potential. At 95°F the lowest percent retention had a low zeta potential. At 123°F the author couldn't figure what had happened except maybe there was an error.

In (Figure 25) the percent retention and zeta potential was determined using no retention aids at pH 7.8. At 70°F maximum retention had a +30 zeta potential. The lowest percent retention occurred at 100°F with a very low zeta potential.

The author felt that temperature can affect the papermaking system which can have a significant influence on zeta potential and percent retention. It was shown in previous examples that one attains maximum retention near a 0 zeta potential and a minimum percent retention at a low or high zeta potential. The author is not saying that temperature will have a significant effect in all cases, which I'm sure it won't. But in depth study of his variables, one can use temperature as a controlled variable to attain maximum retention.

CONCLUSIONS

This study is by no means a conclusive theory of retention aids, since there are many variables and factors that affect the chemistry of a paper machine. The drainage jar is one method to attempt to study a particular system.

Temperature change had a large influence on first-pass retention and was found to affect the charge of the system. Viscosity variation did not affect retention considerably. It was also shown that increase in concentration of retention aids also increased retention. Both cationic low and high molecular weight polymers had a maximum retention around 60 to 80°F and anionic around 40°F and 100°F. Also shown was that cationic and anionic polymers seemed to vary in opposite directions because of opposite charge indicated by the Hydrascan zeta potential analysis. First-pass retention seemed to compare very well to percent retention on the paper machine.

There was better retention at pH 4.5 than pH 7.5 for a cationic retention aid.

By optimizing the temperature there can be an increase in production and less load on the saveall. But one must study the effects on formation, drainage and the economic feasibility of heating the stock with respect to increase in performance.

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TABLES AND FIGURES

TABLE I

First-Pass Retention-Filler Using Reten 210
(High Molecular Wt. - Cationic Polymer)

<u>Temp (°F)</u>	<u>Blank (0)</u>		<u>.5#/ton</u>		<u>1#/ton</u>		<u>2#/ton</u>		<u>3#/ton</u>	
	pH 7.8	pH 4.5	pH 7.8	pH 4.5	pH 7.8	pH 4.5	pH 7.8	pH 4.5	pH 7.8	pH 4.5
40	40	58.0	59.0	86.0	68.2	81.6	71.6	75.4	70.2	85.8
60	34.0	36.6	82.6	84.2	63.4	84.2	72.4	44.4	85.4	73.8
70	32.4	47.0	49.6	71.8	80.6	86.0	73.4	92.0	89.2	92.2
90	14.2	68.2	44.2	64.4	60.4	81.8	62.8	91.2	88.8	92.6
110	11.2	43.8	50.8	80.8	67.4	80.0	27.8	83.6	75.4	89.2
120	21.6	54.2	53.2	64.4	63.6	76.2	58.4	84.8	77.6	89.6
140	78.4	62.0	65.4	71.2	52.0	68.4	60.2	88.8	79.4	75.8

TABLE II

First-Pass Retention-Fiber Using Reten 210
(High Mol Wt. - Cationic Polymer)

<u>Temp (°F)</u>	<u>Blank (0)</u>		<u>.5#/ton</u>		<u>1#/ton</u>		<u>2#/ton</u>		<u>3#/ton</u>	
	pH 7.8	pH. 4.5	pH 7.8	pH 4.5	pH 7.8	pH 4.5	pH 7.8	pH 4.5	pH 7.8	pH 4.5
40	94.4	93.4	92.8	90.0	92.2	94.1	94.4	94.6	94.2	94.8
60	92.2	92.5	98.7	96.7	89.9	96.7	92.1	99.9	94.9	92.4
70	97.0	94.1	95.0	98.2	92.2	92.4	95.6	97.1	98.8	98.3
90	90.5	91.9	92.6	95.5	94.3	89.7	94.6	97.0	94.1	99.2
110	94.2	92.0	91.9	98.2	92.6	90.2	91.9	95.6	95.7	95.7
120	96.0	93.4	91.4	98.0	92.7	95.2	92.7	96.8	96.8	96.0
140	81.2	95.7	95.3	97.0	92.6	94.9	94.3	95.3	95.6	93.6

TABLE III

First-Pass Retention-Filler Using Reten 304
(Low Mol. Wt.-Cat. Polymer)

<u>Temp (°F)</u>	<u>1/2#/ton</u>	<u>1#/ton</u>	<u>2#/ton</u>	<u>3#/ton</u>
	pH 4.5	pH 4.5	pH 4.5	pH 4.5
40	60.0	69.8	70.4	81.4
60	71.6	59.4	85.8	82.0
80	62.8	70.6	65.4	75.6
100	63.8	72.8	68.6	81.0
120	71.0	65.8	73.6	79.8
140	64.0	73.4	74.0	79.8

TABLE IV

First-Pass Retention Fiber Using Reten 304
(Low Mol. Wt.-Cat. Polymer)

<u>Temp (°F)</u>	<u>1/2 #/ton</u>	<u>1#/ton</u>	<u>2#/ton</u>	<u>3#/ton</u>
	pH 4.5	pH 4.5	pH 4.5	pH 4.5
40	95.0	96.0	96.4	94.1
60	95.0	90.4	96.8	96.9
80	80.5	94.6	97.2	95.8
100	91.5	94.9	93.9	97.4
120	93.5	93.1	95.6	97.0
140	92.7	94.2	93.6	95.4

TABLE V

First-Pass Retention-Filler Using 50/50% Reten
210 & 421 (High Mol. Wt.-Anionic Polymer)

<u>Temp (°F)</u>	<u>1/2#/ton</u>	<u>1#/ton</u>	<u>2#/ton</u>	<u>3#/ton</u>
	pH 4.5	pH 4.5	pH 4.5	pH 4.5
40	93.6	93.8	96.1	97.8
60	82.0	90.4	87.6	92.8
80	83.2	86.6	72.2	79.2
100	79.0	91.2	75.6	89.4
120	86.4	71.6	79.4	81.8
140	72.6	89.4	71.2	92.0

TABLE VI

First-Pass Retention-Fiber Using 50/50%
Reten 210 & 421 (High Mol. Wt.-Anionic Polymer)

<u>Temp (°F.)</u>	<u>1/2#/ton</u>	<u>1#/ton</u>	<u>2#/ton</u>	<u>3#/ton</u>
	pH 4.5	pH 4.5	pH 4.5	pH 4.5
40	96.2	97.1	96.3	96.4
60	92.9	95.2	96.2	94.4
80	92.5	95.7	92.5	91.4
100	94.0	96.2	93.1	92.0
120	94.8	92.1	91.0	94.0
140	92.6	93.5	90.8	92.1

TABLE VII

First-Pass Retention & % Retention Using 2#/ton
Reten 210 (High Mol. Wt.-Cat. Polymer) @ pH 4.5
On the Pilot Paper Machine at WMU

() Hydrascan Charge

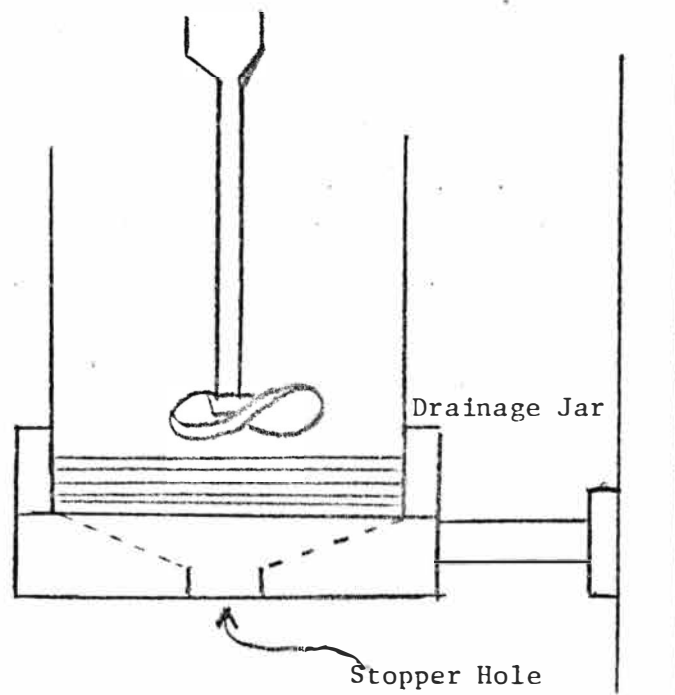
<u>Temp (°F)</u>	<u>1st Pass Retention</u>	<u>% Retention</u>
70	54.8 +(154)	55.5
90	78.1 (+61)	69.8
110	82.3 (-61)	85.6
120	56.8 (-93)	78.9
130	80.0 (-93)	85.3
140	81.4 (-26)	79.5

TABLE VIII

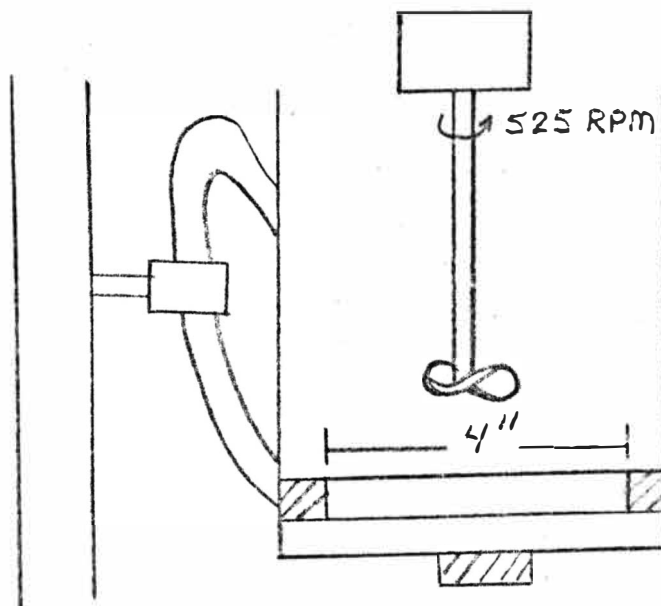
First-Pass Retention & % Retention Using 2#/ton
50/50% Reten 210 & 421 (High Mol. Wt.-Anionic
Polymer) @ pH 4.5 on the Pilot Paper Machine at WMU

() Hydrascan Charge

<u>Temp (°F)</u>	<u>1st Pass Retention</u>	<u>% Retention</u>
70	82.5 (+147)	66.6
90	65.4 (-80)	64.4
110	69.6 (-11.2)	70.7
120	75.2 (-109)	64.3
130	73.8 (-122)	67.1
140	73.1 (-93)	65.0



A. Britt's Dynamic Drainage Jar



B. Holt's Dynamic Drainage Jar

Figure 1. Dynamic Drainage Jar

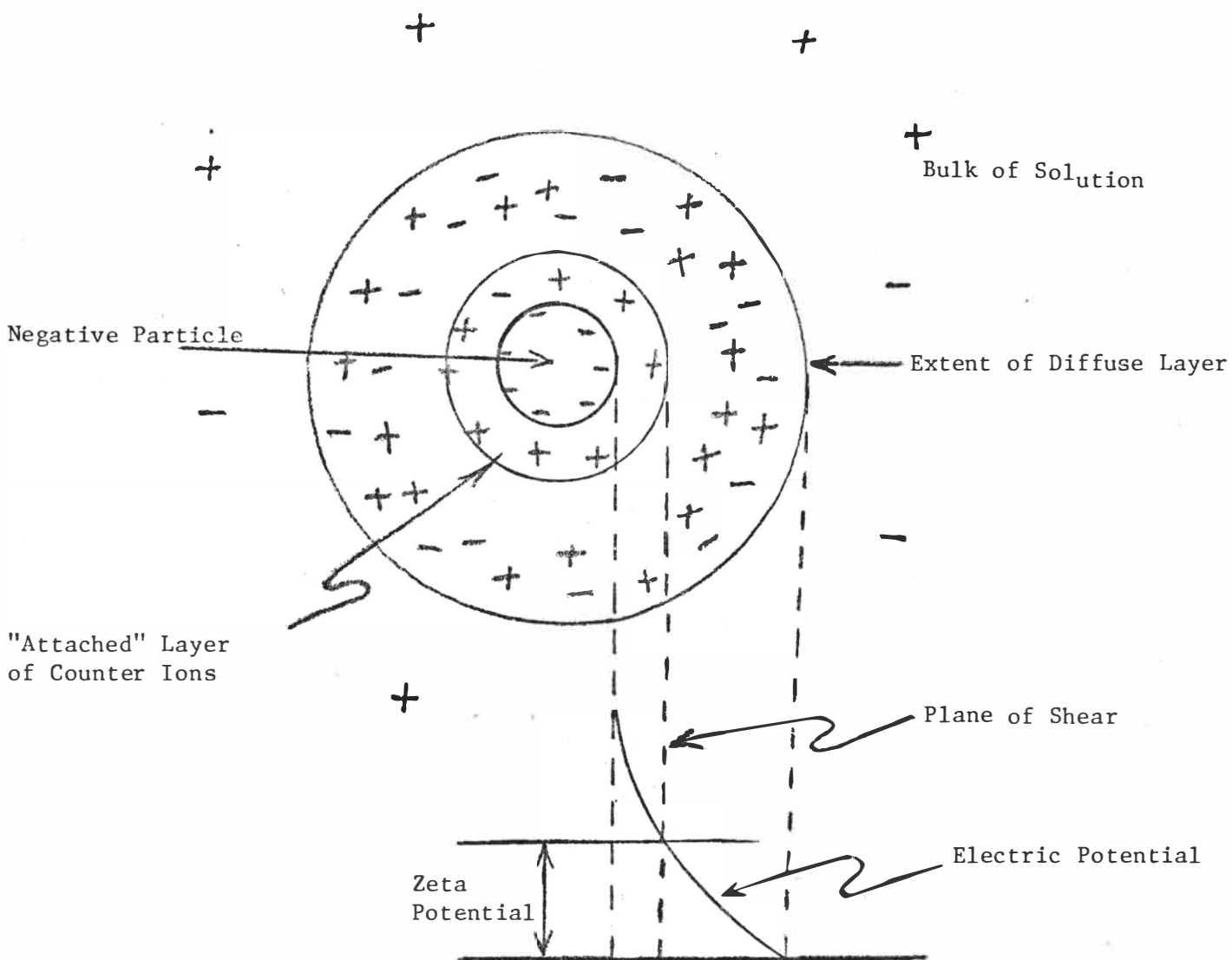
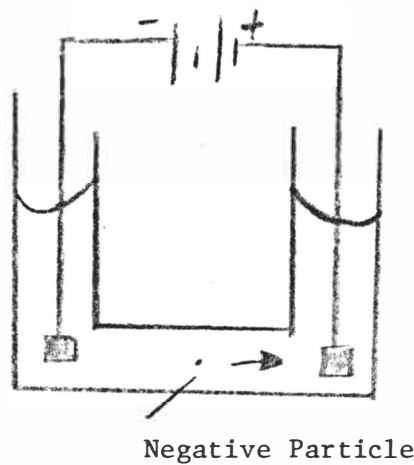
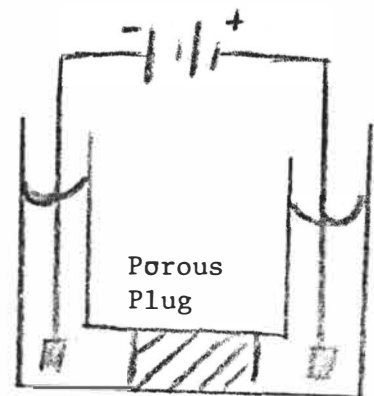


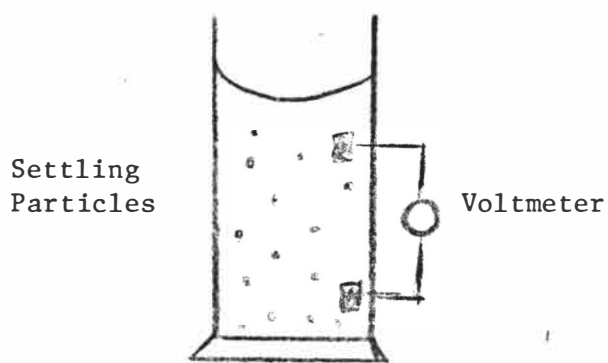
Figure 2. Electronegative Particle and Double Layer



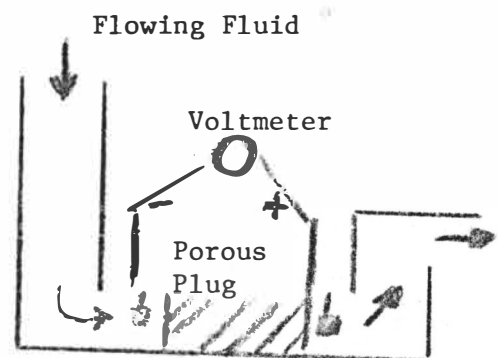
a) Electrophoretic Mobility



b) Electroosmosis



c) Sedimentation Potential



d) Streaming Potential

Figure 3. Electrokinetic Phenomena

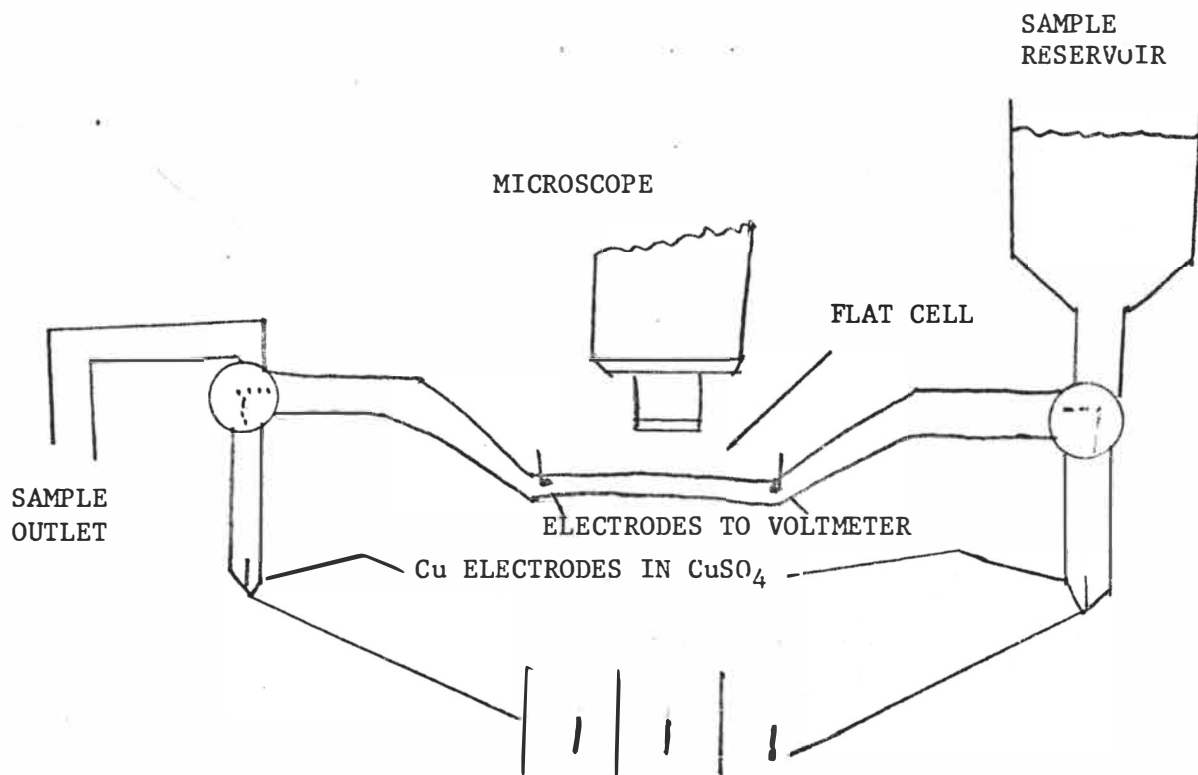


FIGURE 4. Briggs' Microelectrophoretic Mobility Tester

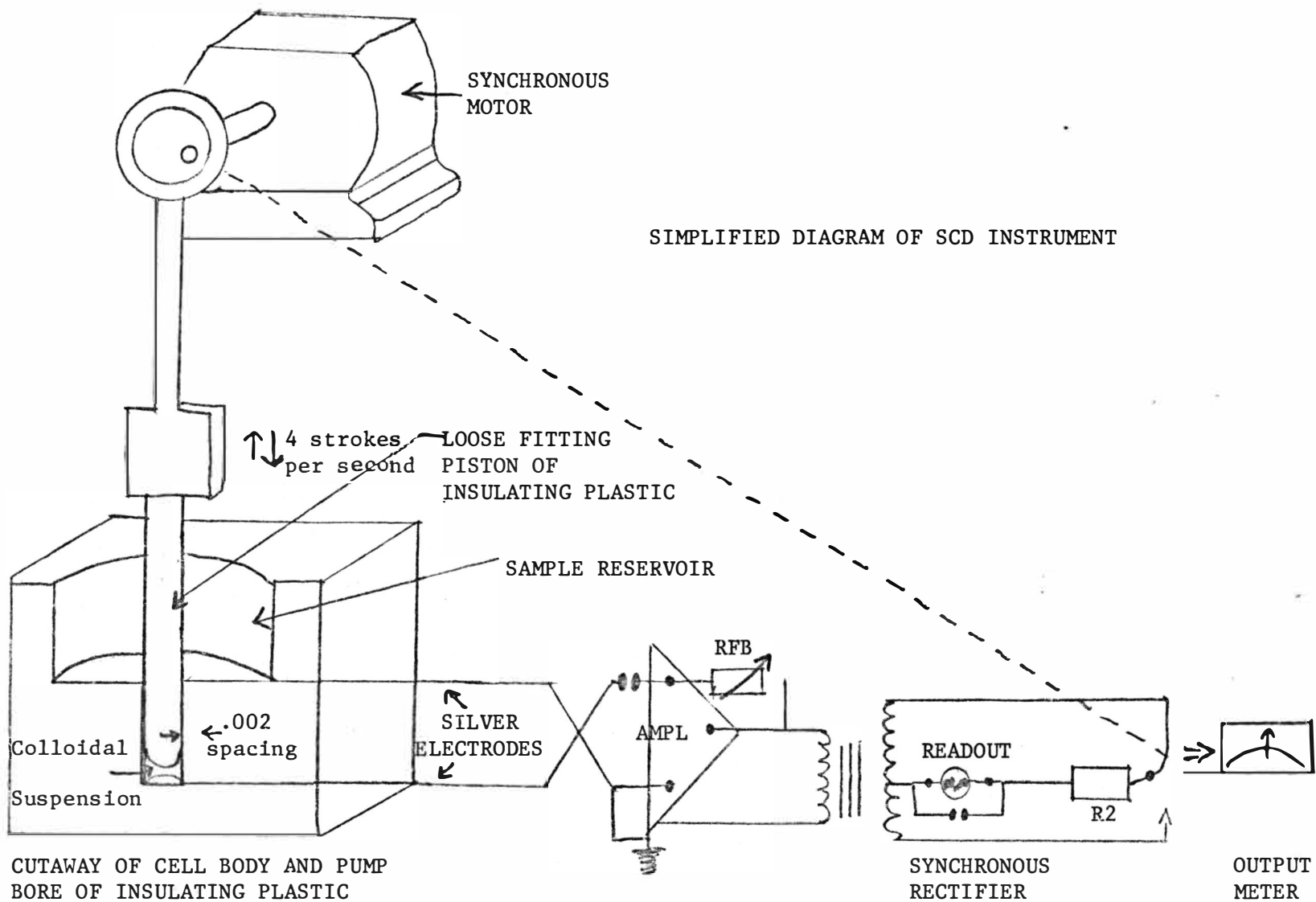


FIGURE 5. Simplified Diagram of SCD Instrument

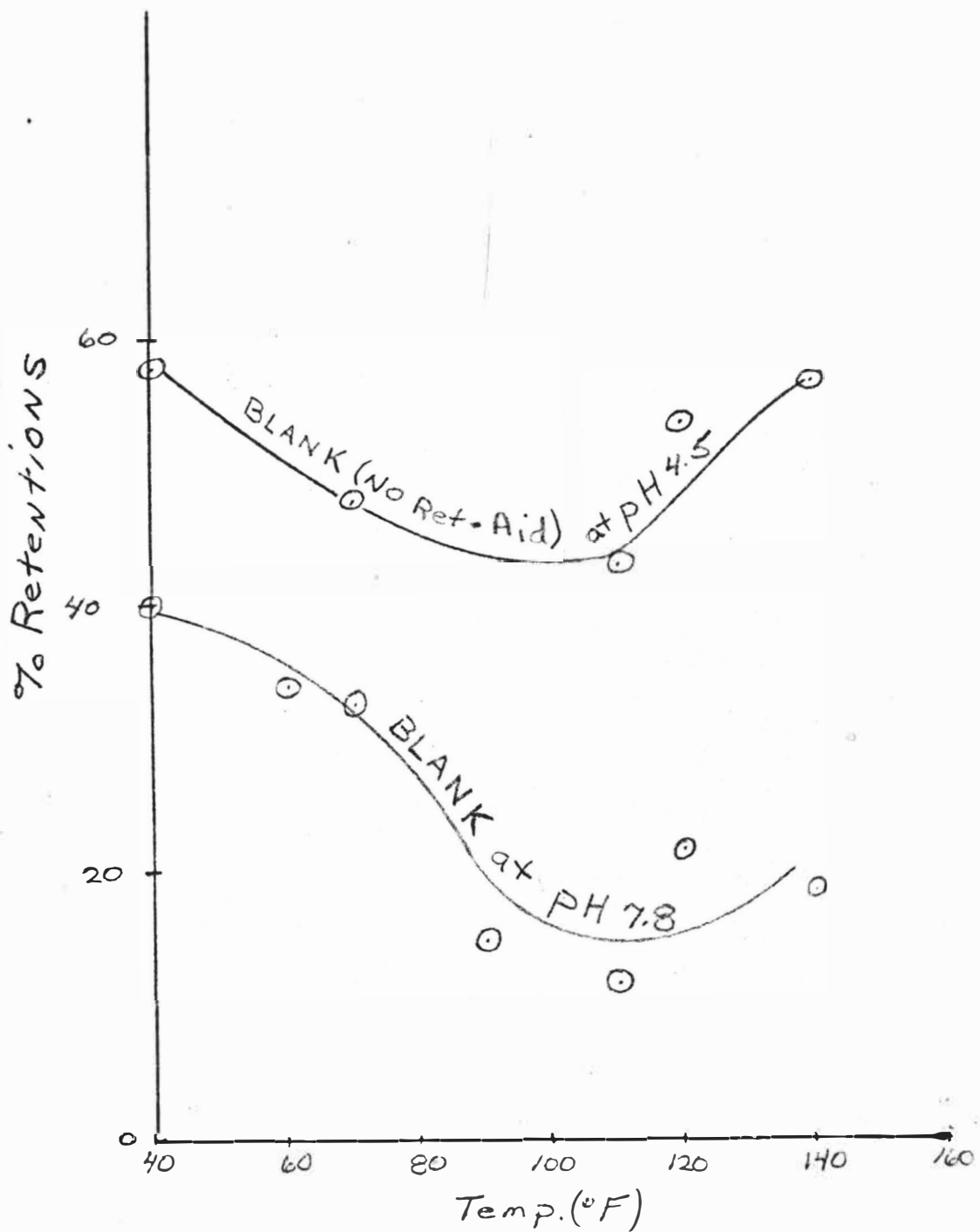


Fig. 6 Retentions on Dynamic Drainage Jar at Varying Temps Using No Ret. Aid.

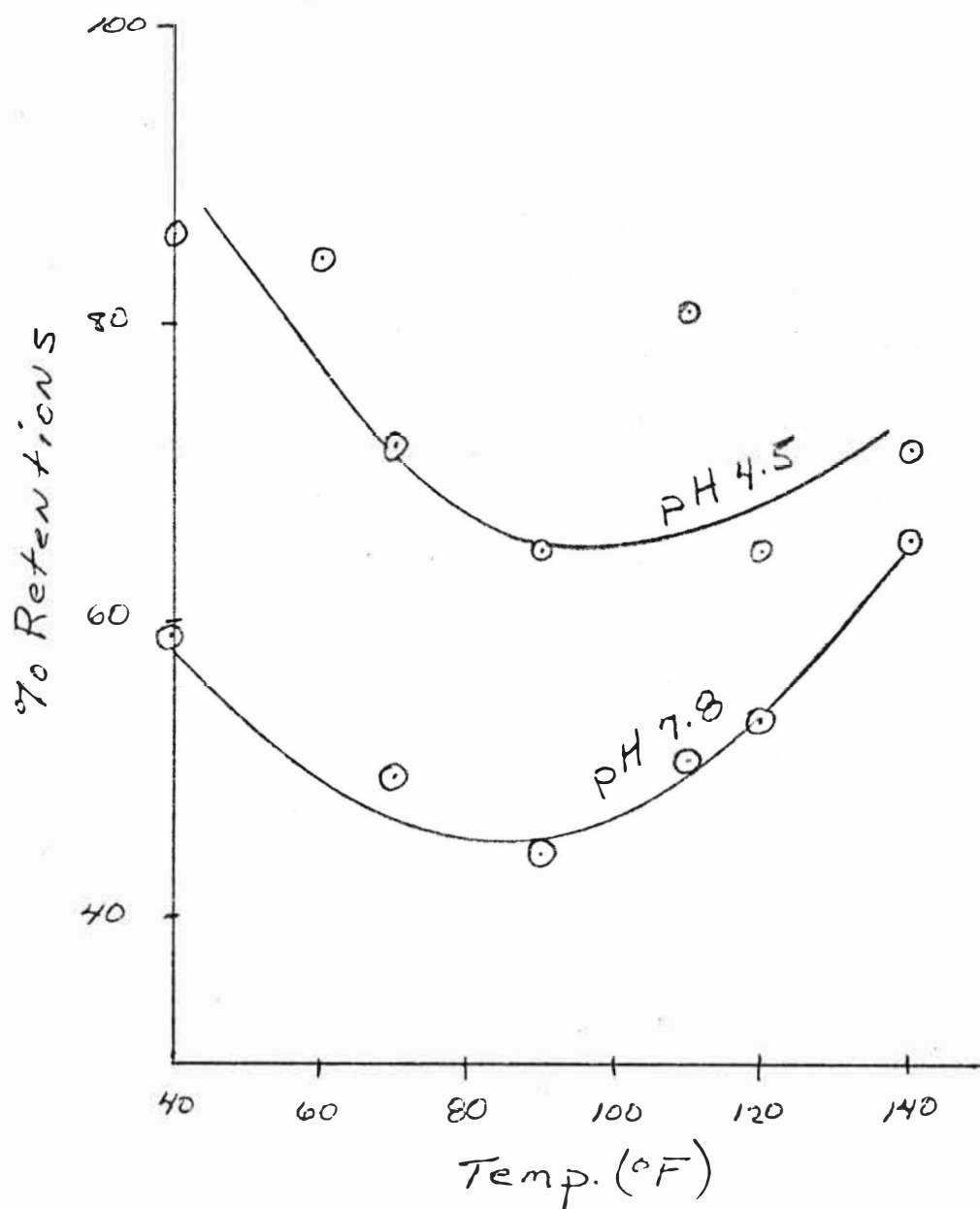


Fig. 7 Retentions on Dynamic Drainage Jar at Varying Temps. using .5 #/Ton Reten 210 (High Mol. Wt Polymer - Cationic)

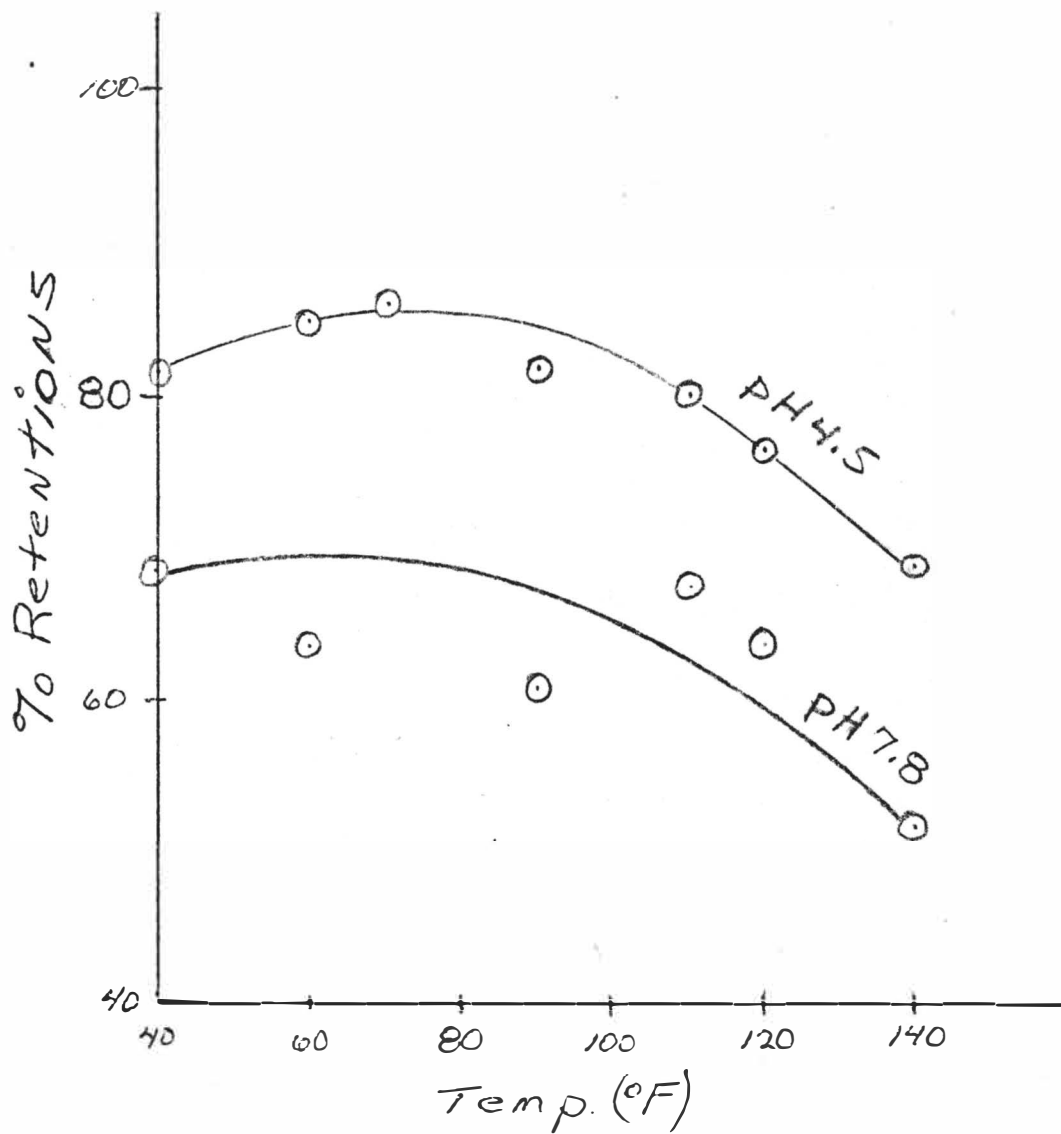


Fig. 8. Retentions on Dynamic Drainage Jar at Varying Temps. Using 1[#]/Ton Reten 210 (High Mol. Wt.)

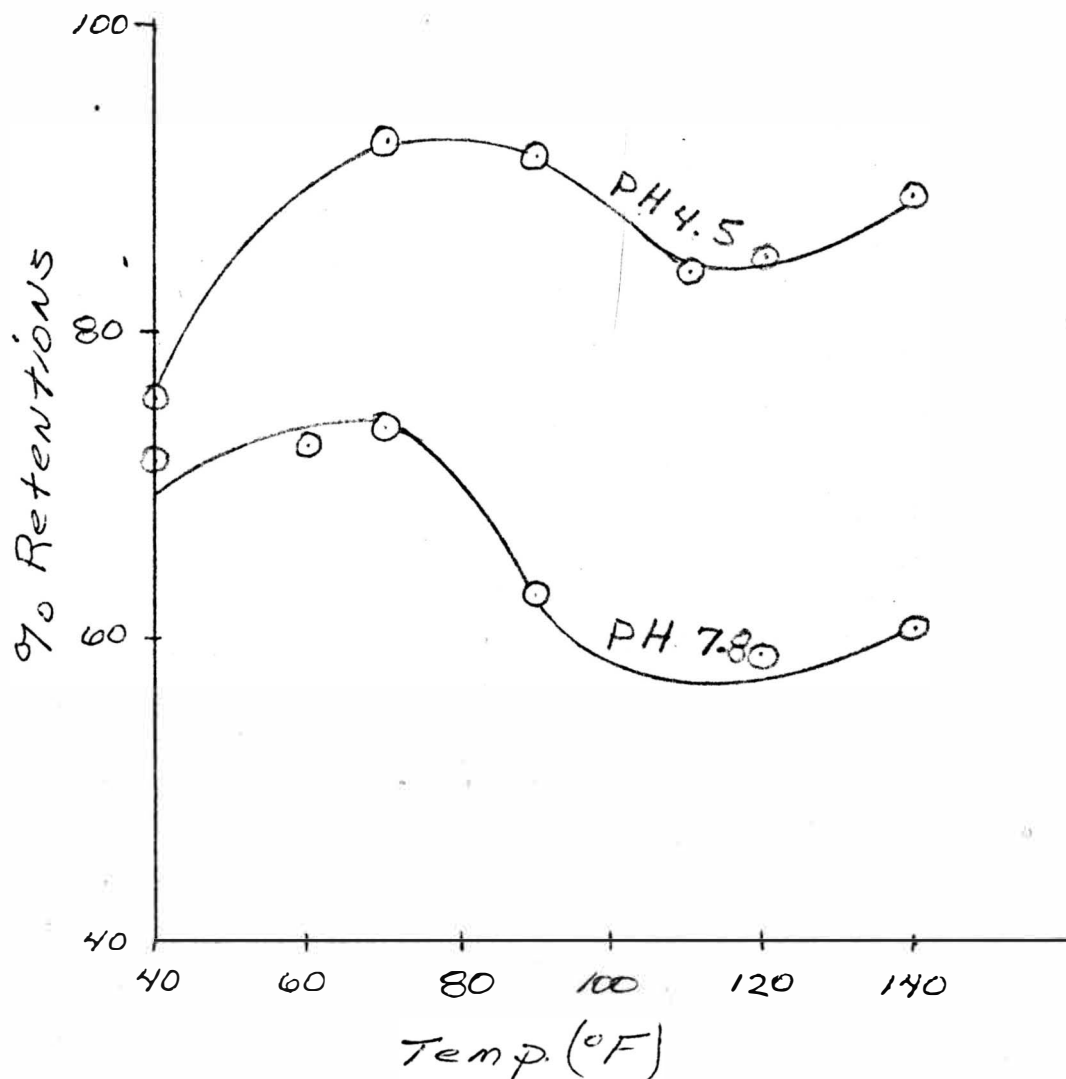


Fig. 9. Retentions ON Dynamic Drainage Jar at Varying Temps. Using 2[#]/TON Reten 210 (High Mol. Wt.)

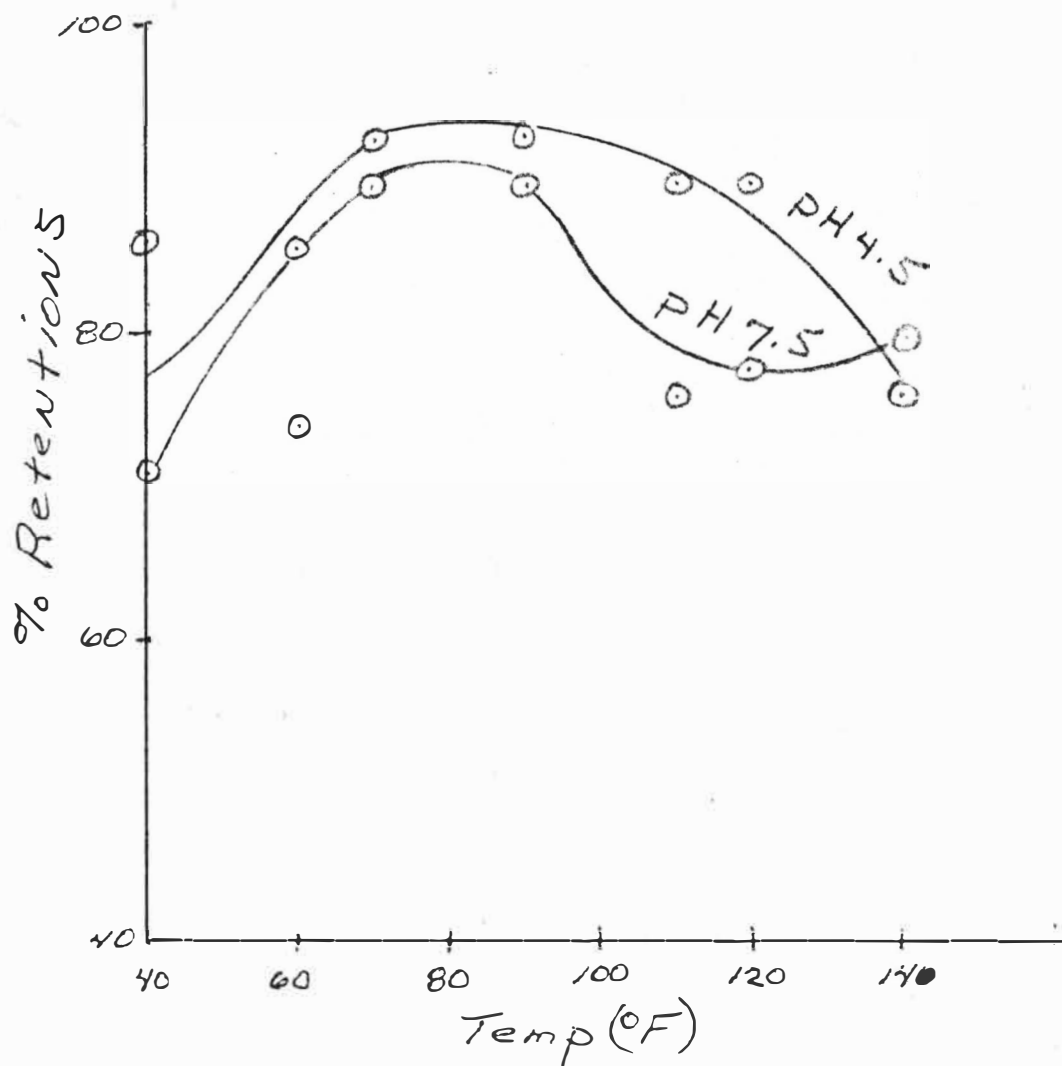


Fig. 10. Retentions on Dynamic Drainage Jar at Varying Temps. Using 3#/Ton Reten 210 (High Mol. Wt.)

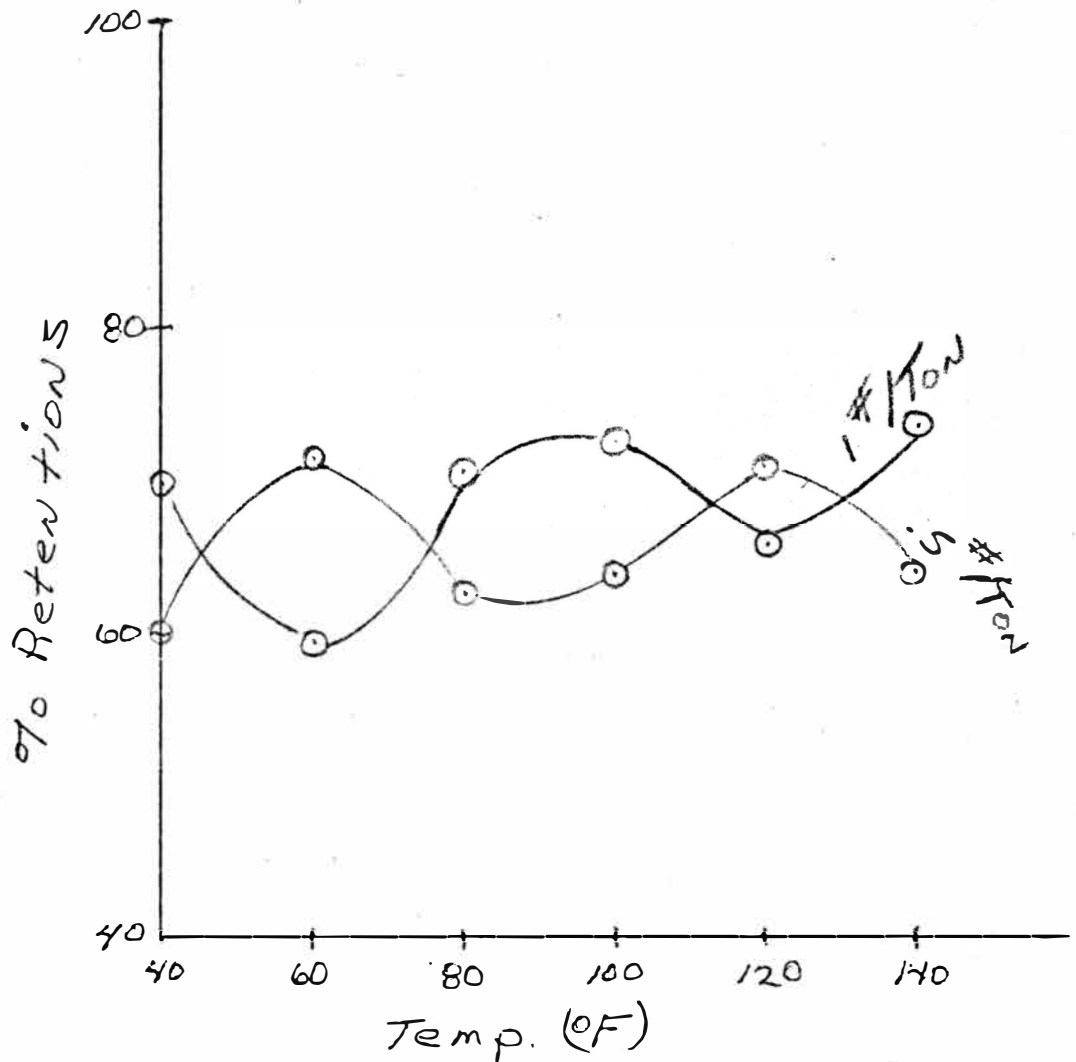


Fig. 11. Retentions ON Dynamic Drainage Jar at Varying Temps. Using .5 & 1#/Ton Reten 304 (Cationic LOW mol. Wt.)

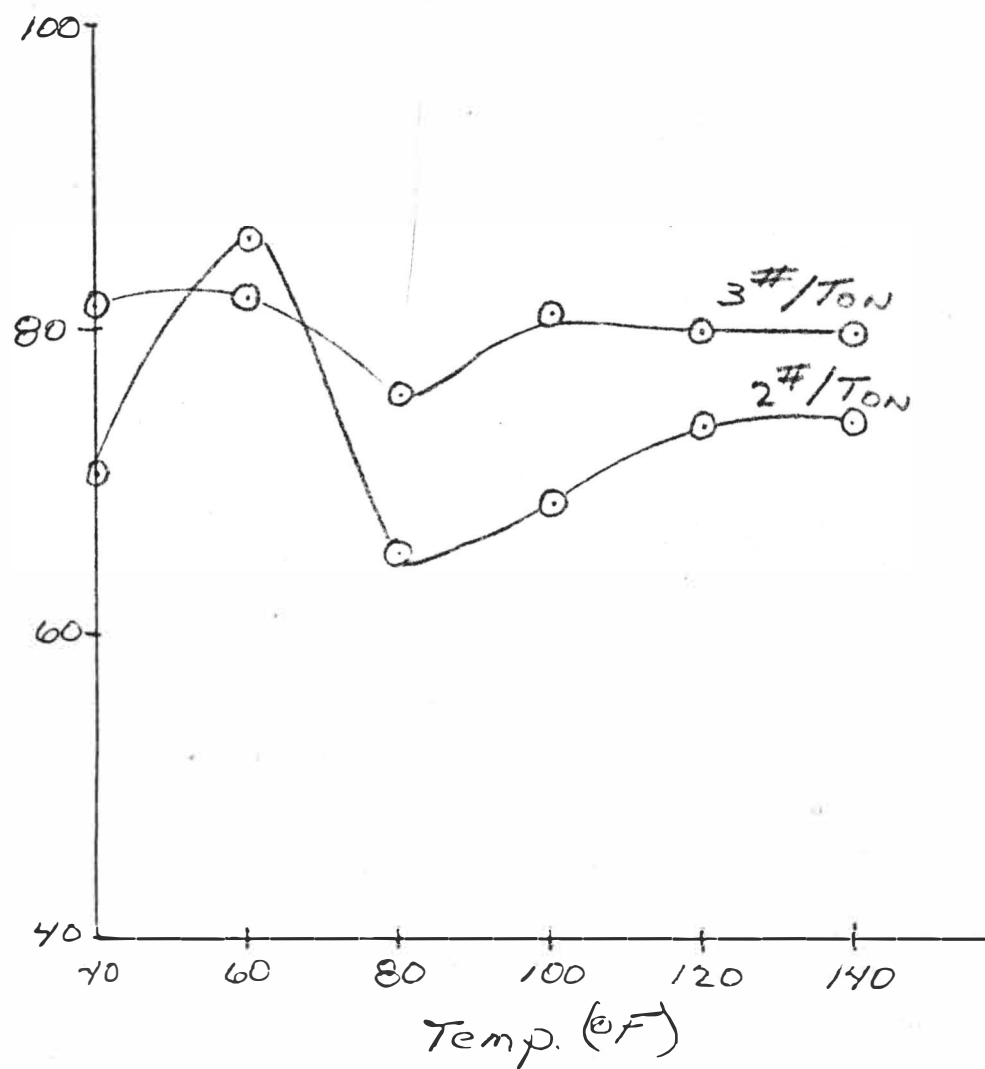


Fig. 12. Retentions on Dynamic Drainage
Sar at Varying Temps. Using 2 & 3
#/TON (Cationic low Mol. Wt.)

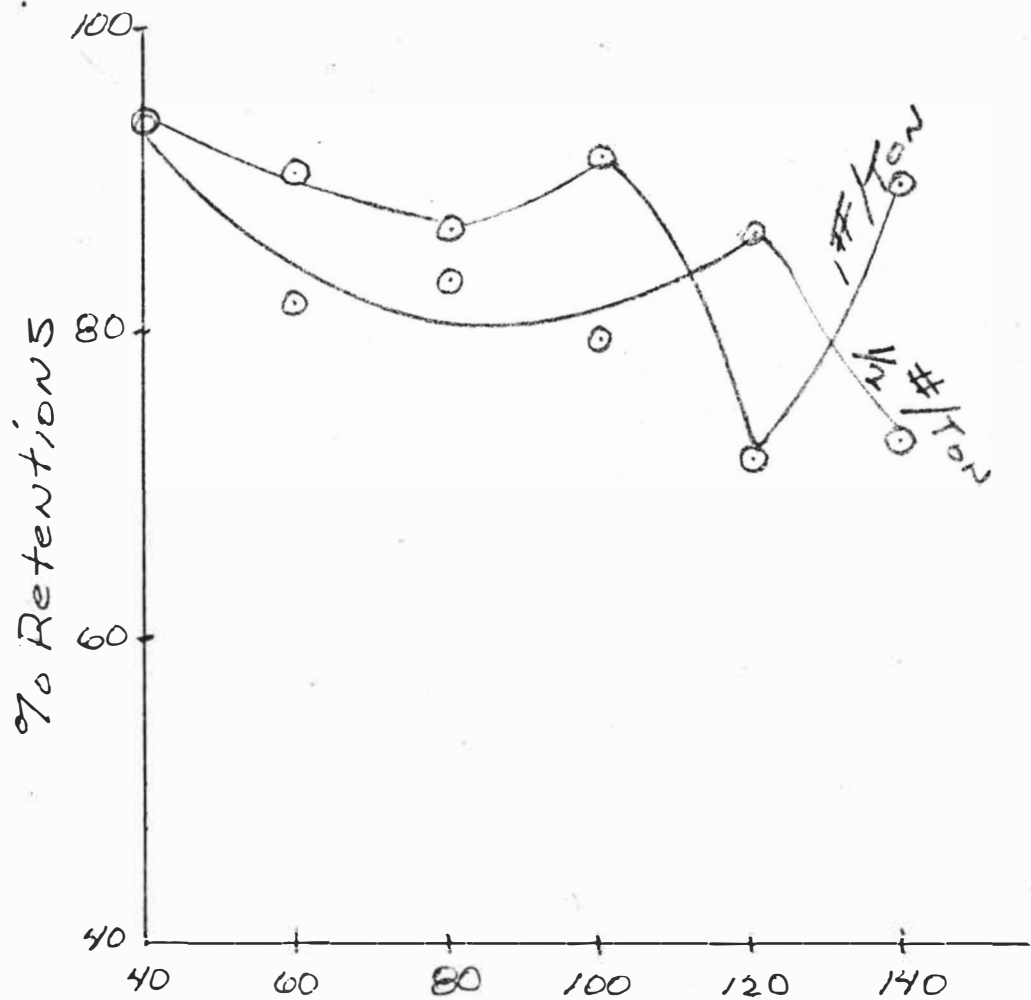


Fig.13. Retentions On Dynamic Drainage
 Jar at Varying Temps. Using 50/50 %
 Mixture Reten 210 & 421 (Cat. & Anionic
 High Mol. Wt. Polymer)

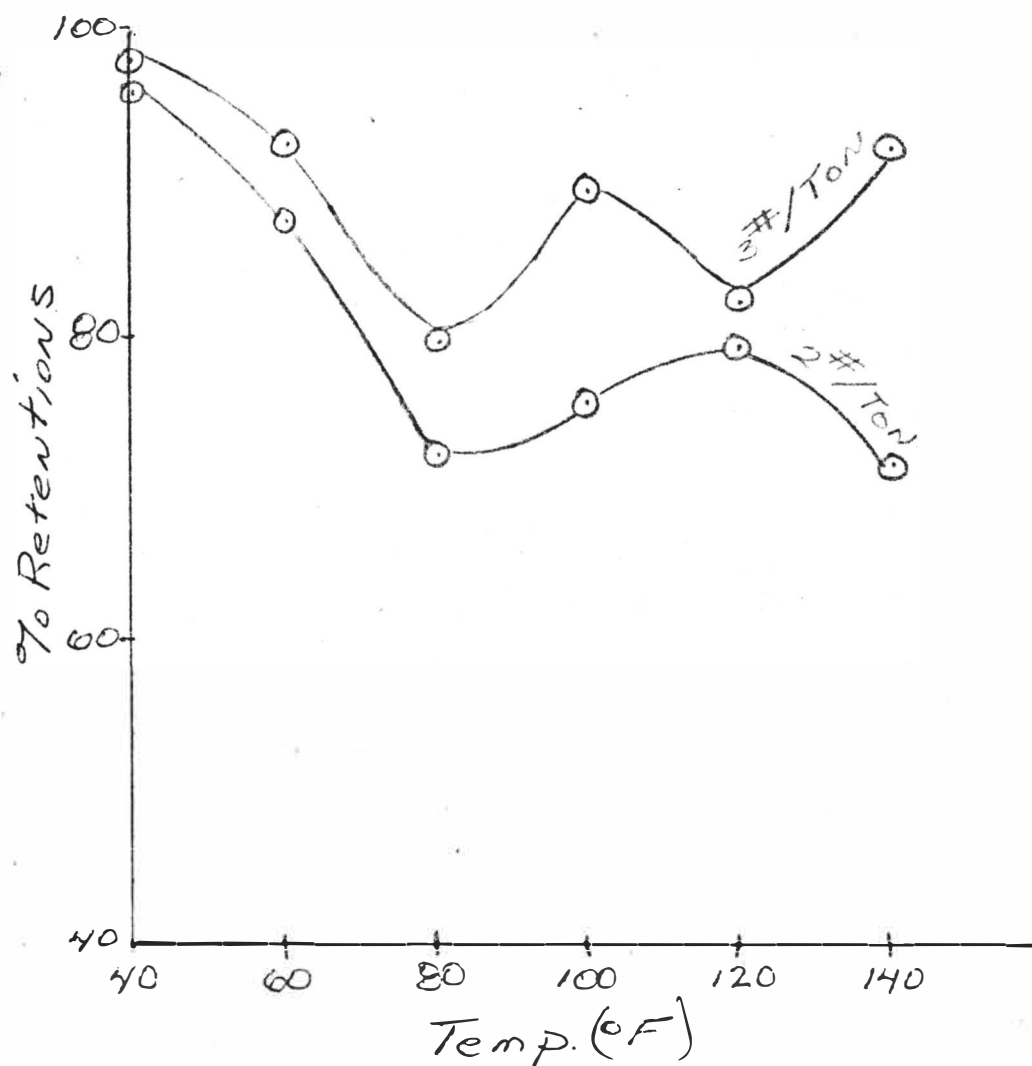


Fig. 14. Retentions on Dynamic Drainage Tar Using 50/50% Mixture 421 & 210 (Cat. & Anionic High Mol. Wt. Polymer)

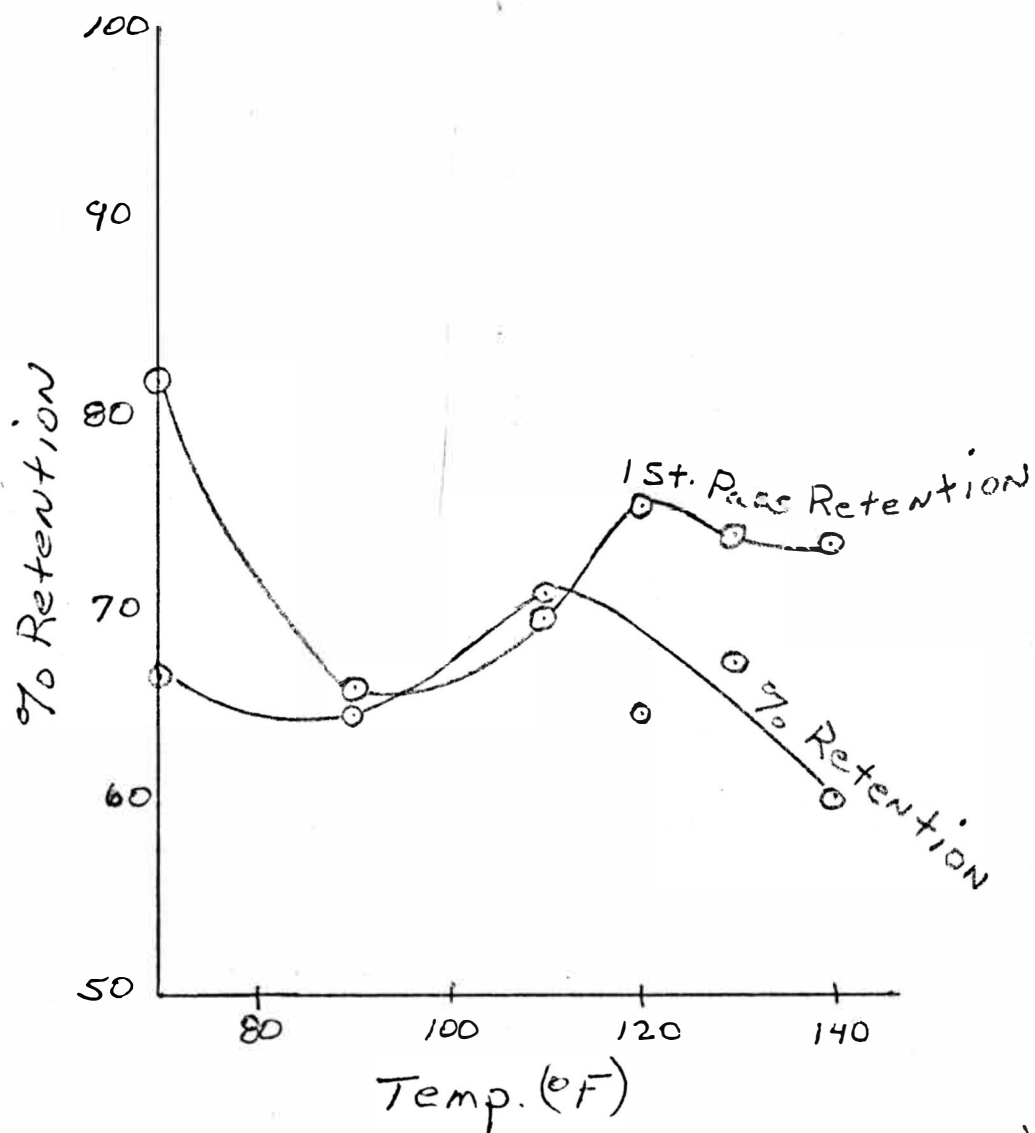


Fig. 17. Retentions on Paper Machine at WMU Using 50/50 % Reten 210 & 421 (Cationic & Anionic High Mol. Wt. Polymer)

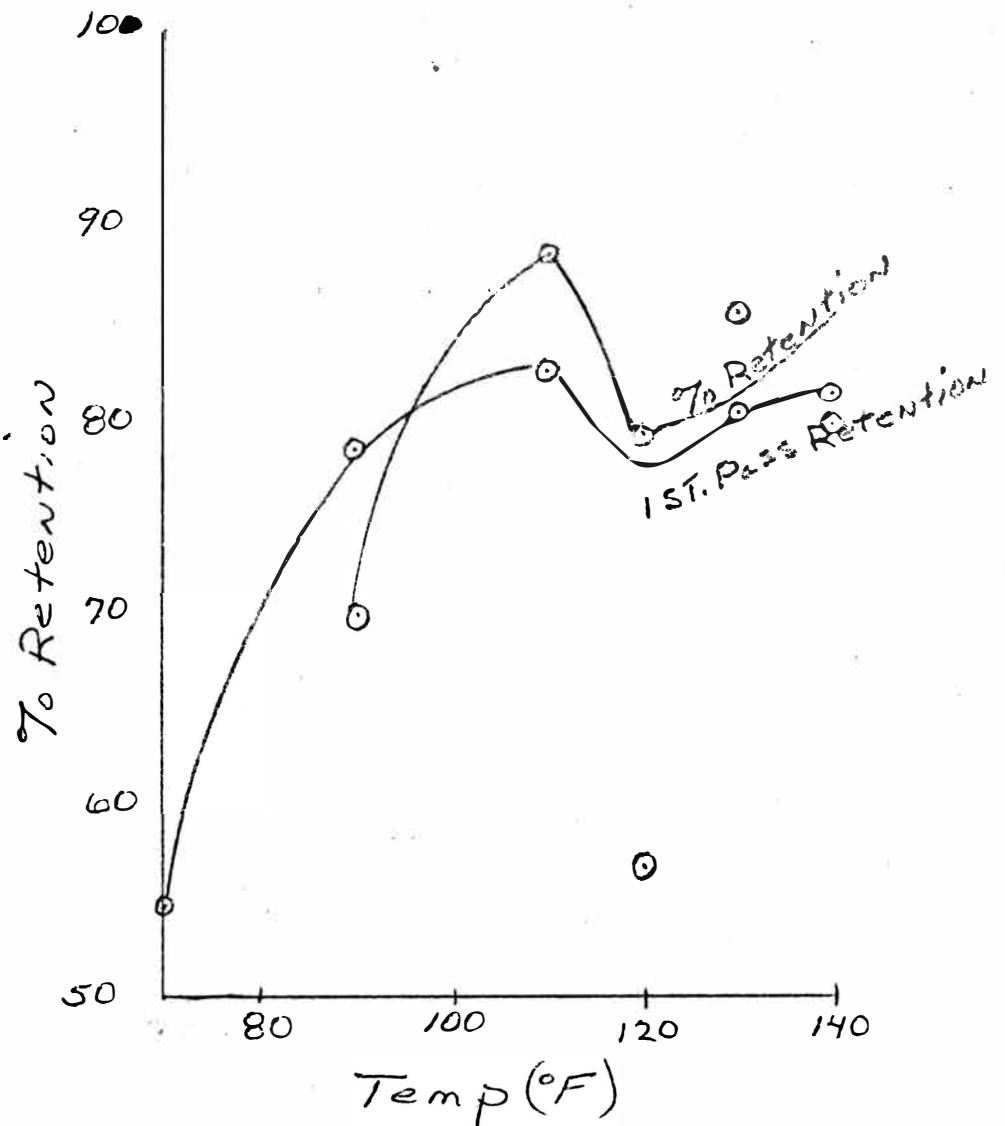


Fig. 16. Retentions on Pilot Paper Mach.
at U.M.U. Using 2 # / Ton Reten 210
(Cat. High Mol. Wt. Polymer)

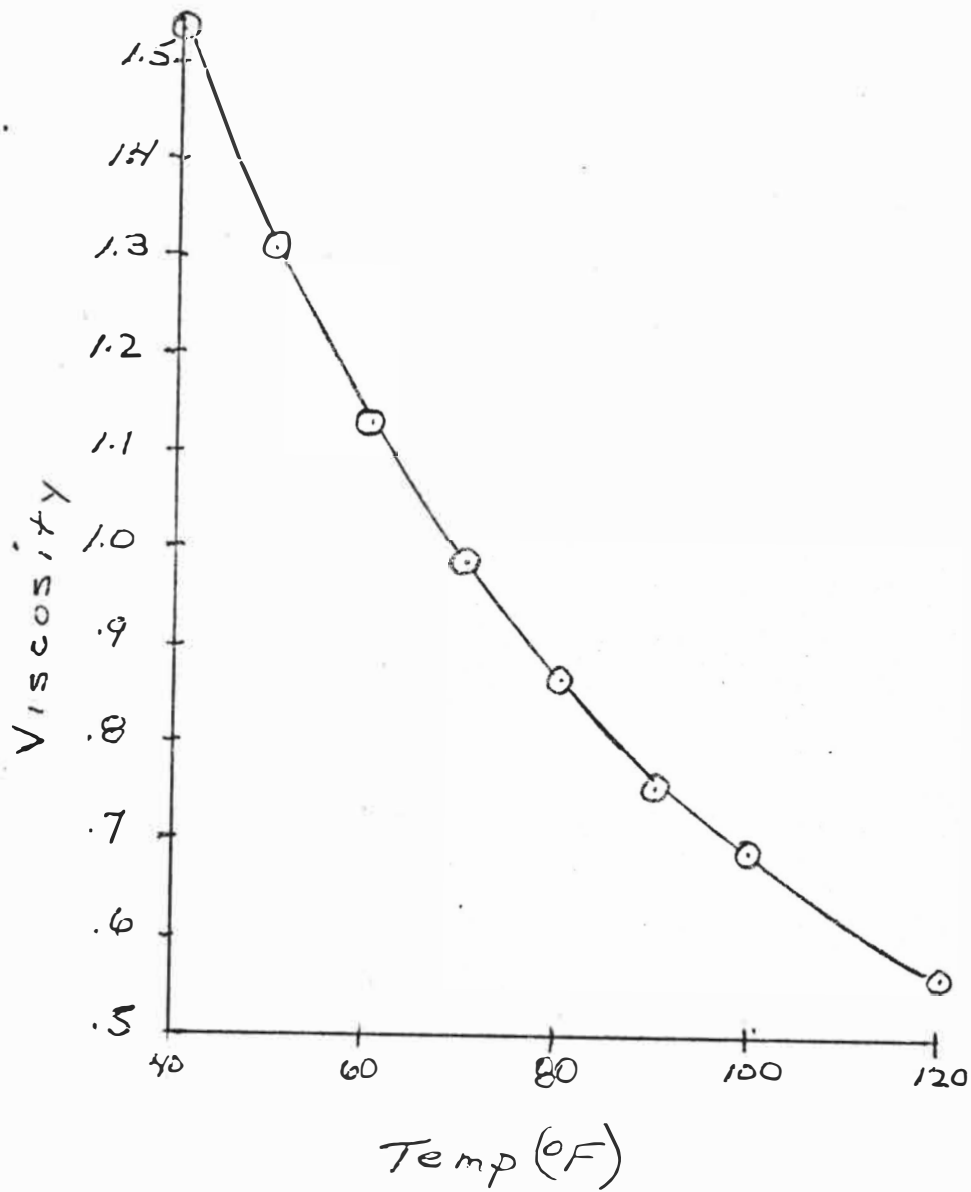


Fig. 15. Viscosity of Water

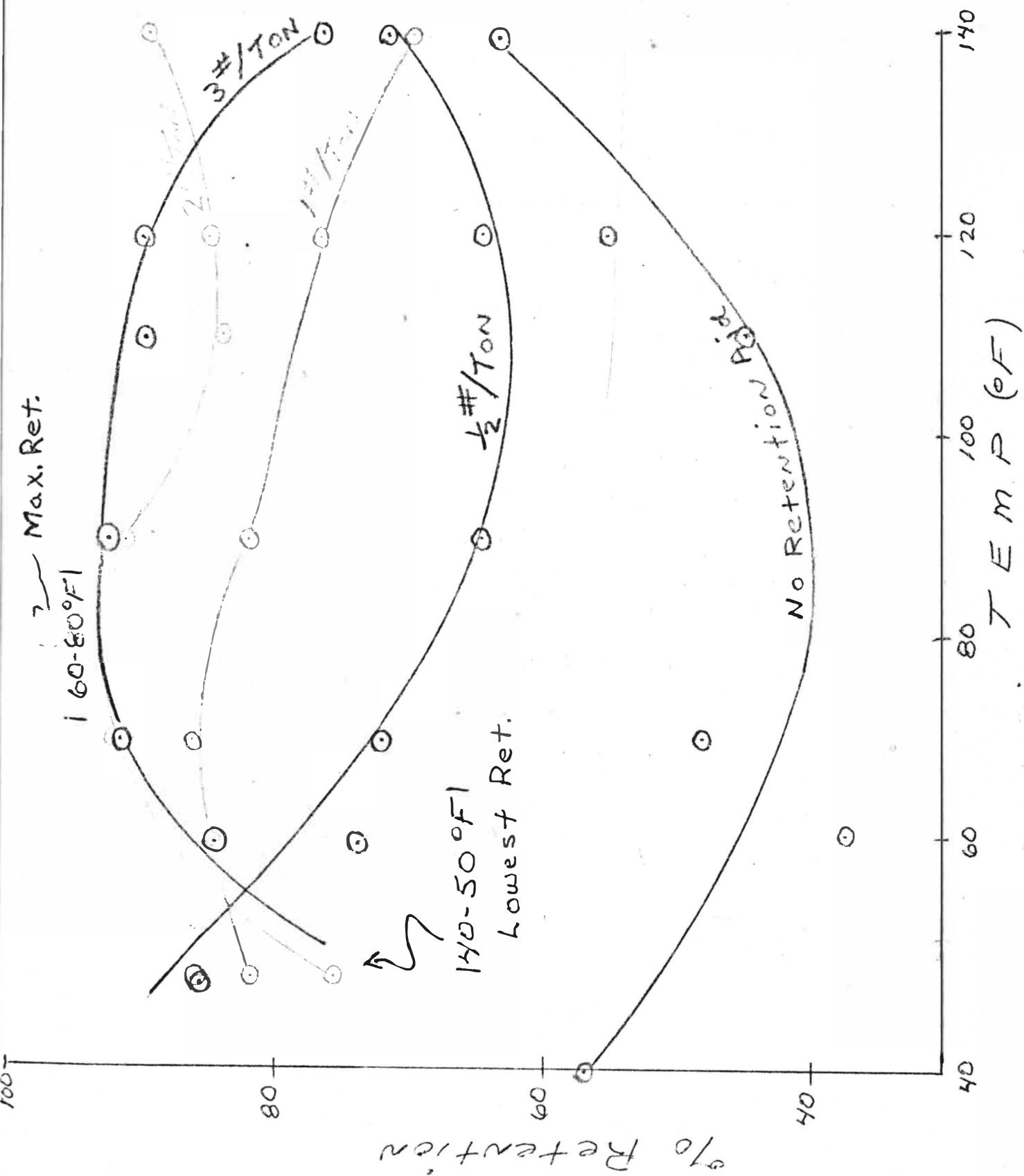


Fig. 18. Retentions on Dynamic Drainage Tar
USING RETEN 210 (Cat. High Mol. Wt. Polymer)

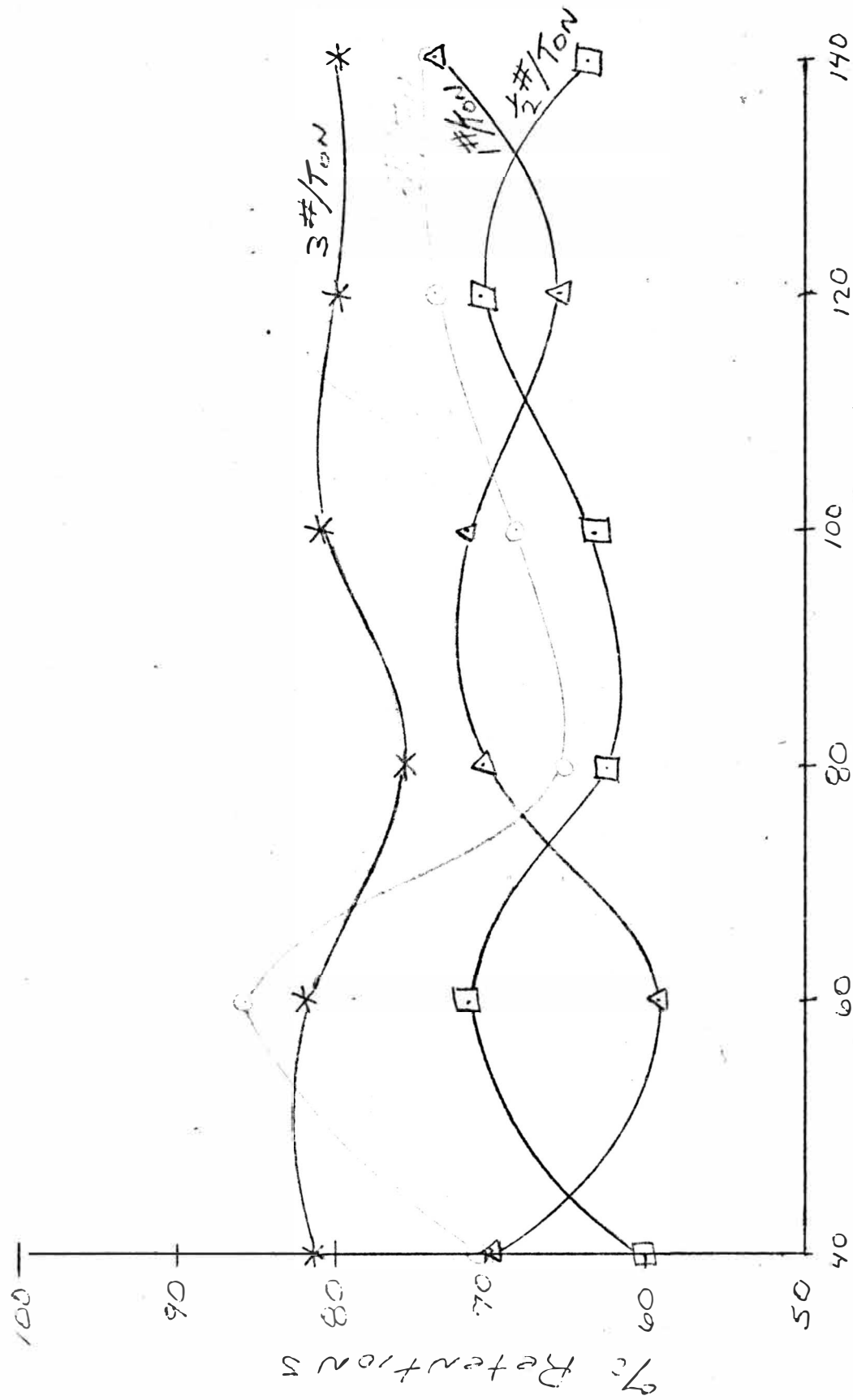


Fig. 19. Retention On Dynamic Drainage Jar at Varying Temps. Using Reten 304 (Low Mol. Wt. - Cat. Polyme

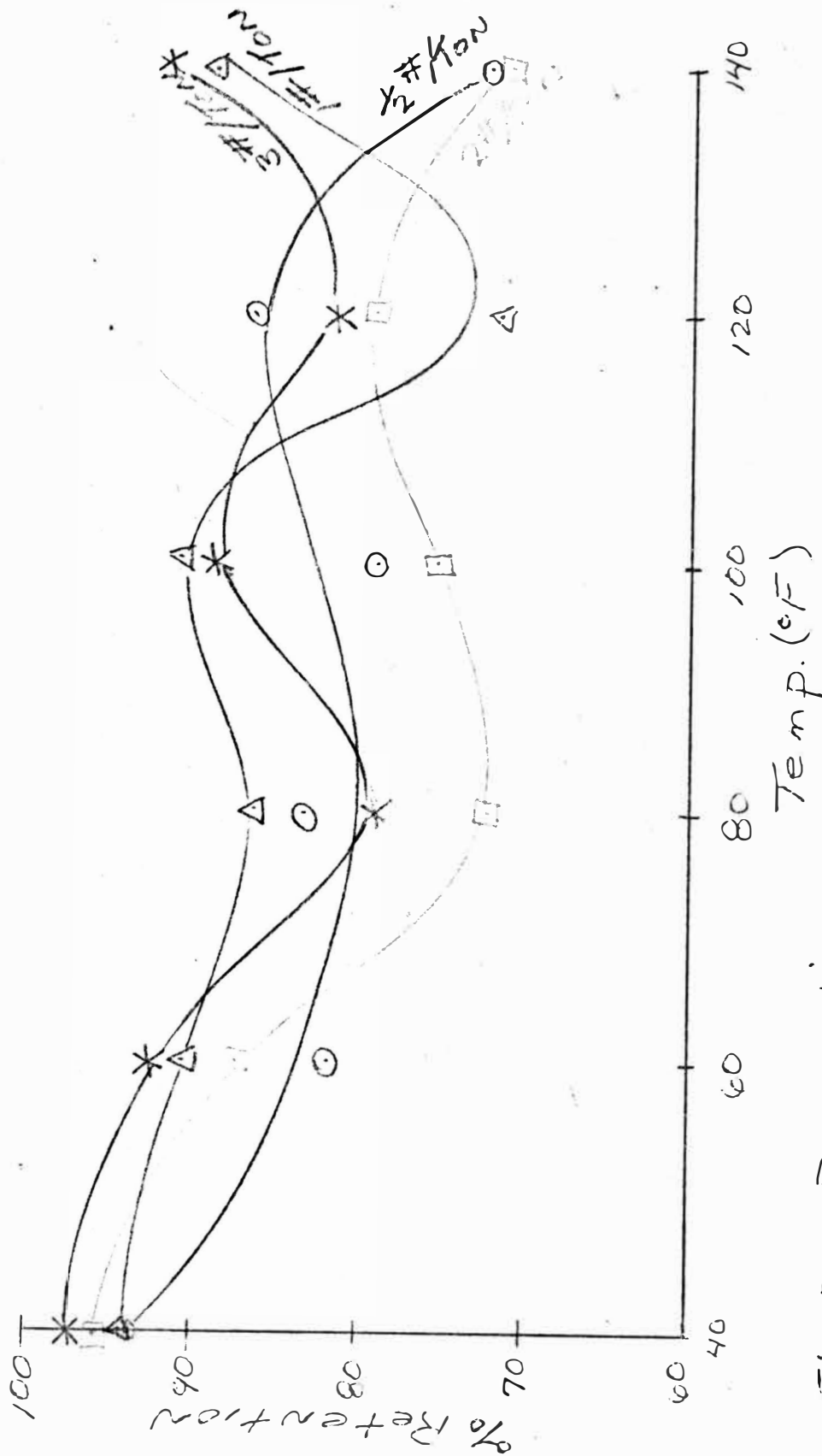


Fig. 20: Retentions on Dynamic Drainage Tar at Various Temps. Using 50/50 % Reten 210 & 421 (High mol. wt - Anionic Polymer) at pH 4.5

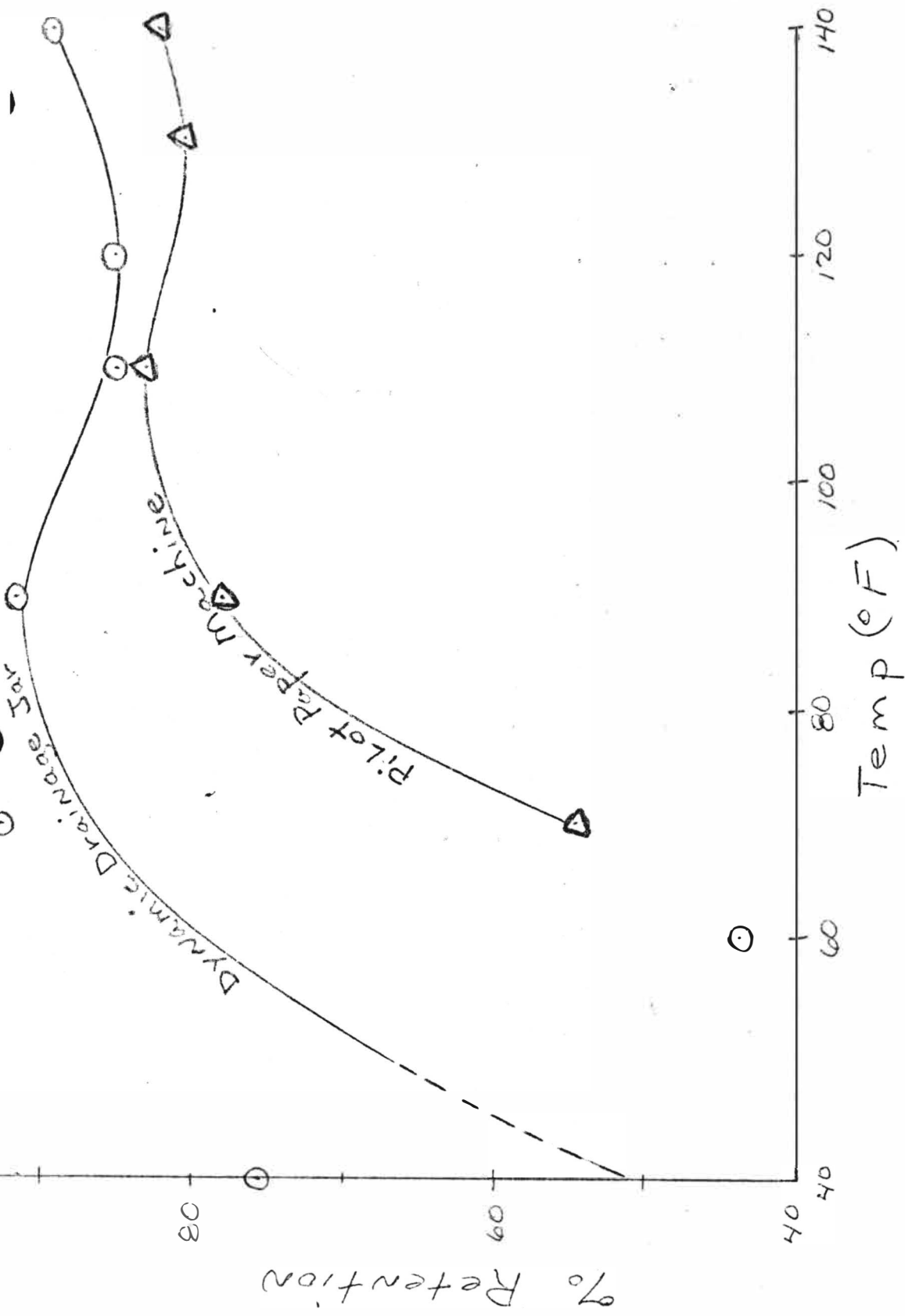


Fig. 21. Retentions on Dynamic Drainage Jar & Pilot Paper Machine (Wmu) at Varying Temps. using 2 lb. per Ton of Reten₂₁₀.

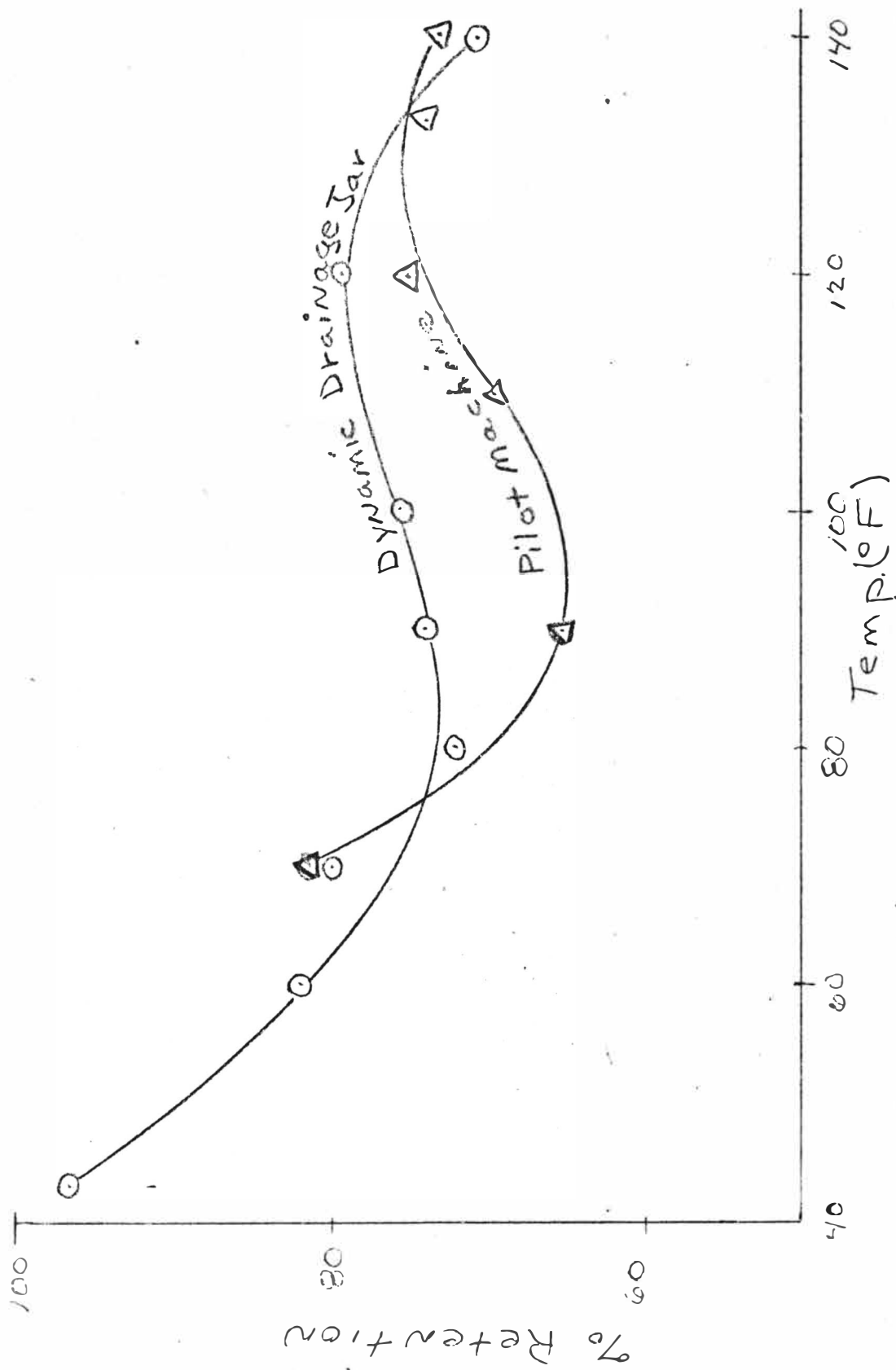


Fig. 22. Retention On The Dynamic Drainage Jar & The Pilot Paper Machine Using 50/50% Reten 210 & 421 (High Mol. Wt. - Anionic Polymer) at 2#/Ton

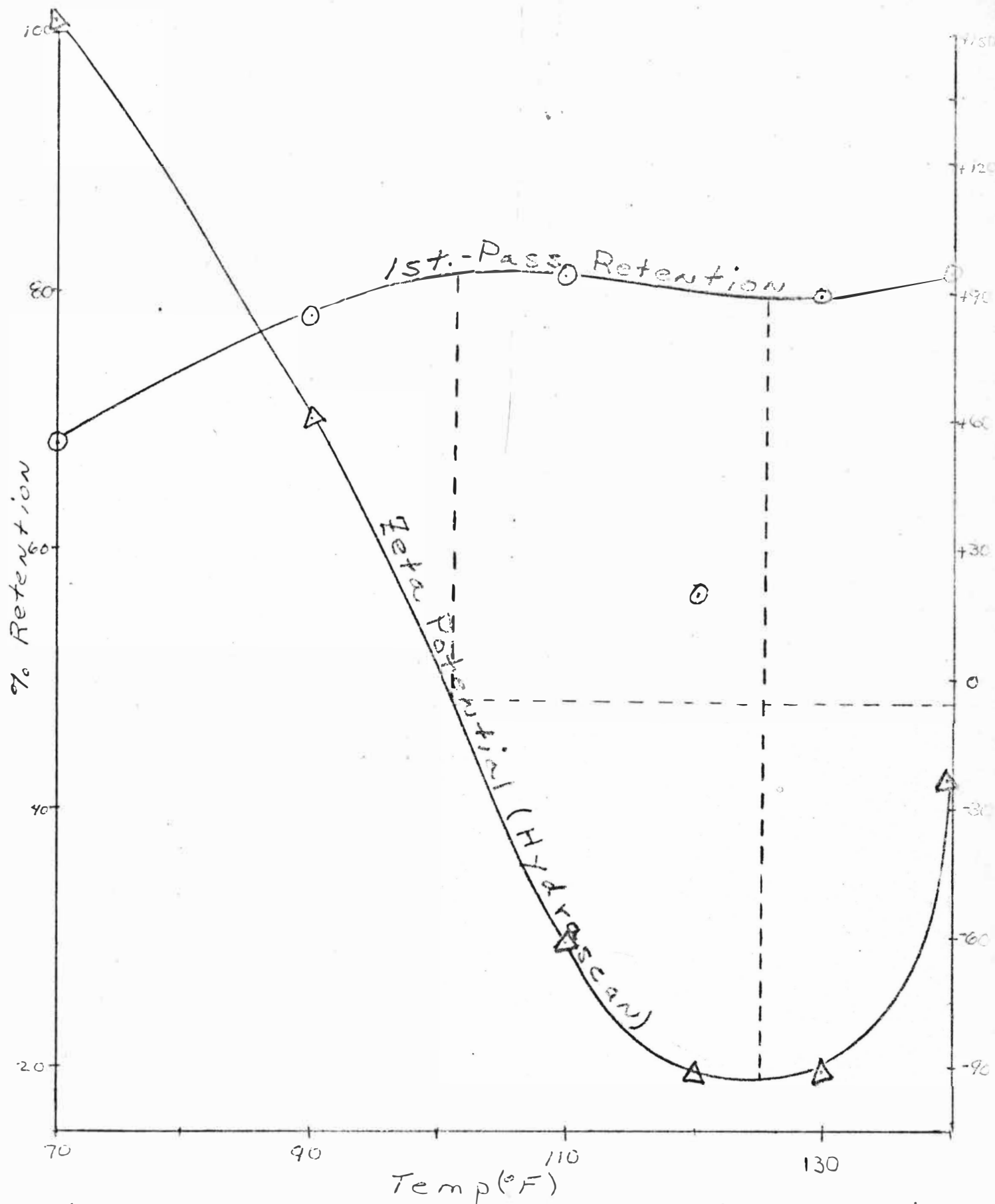


Fig. 23. Retentions on the Pilot Paper Machine at Various Temps. Using 2#/Ton Reten 210

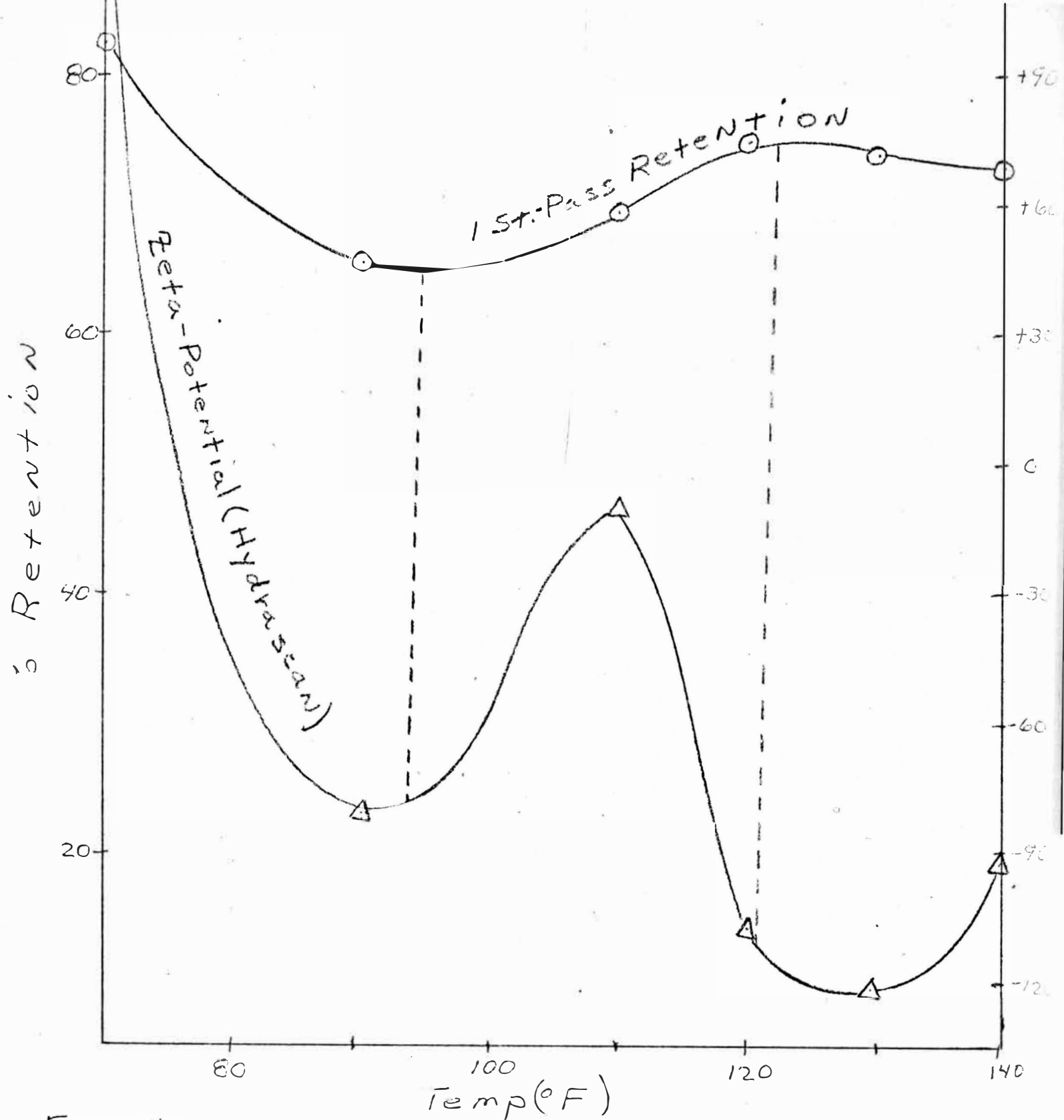


Fig. 24. Retentions on The Pilot Paper Machine USING 50/50% Reten 210 & 421 (High Mol. Wt. - Anionic Polymer) at 2#/Ton

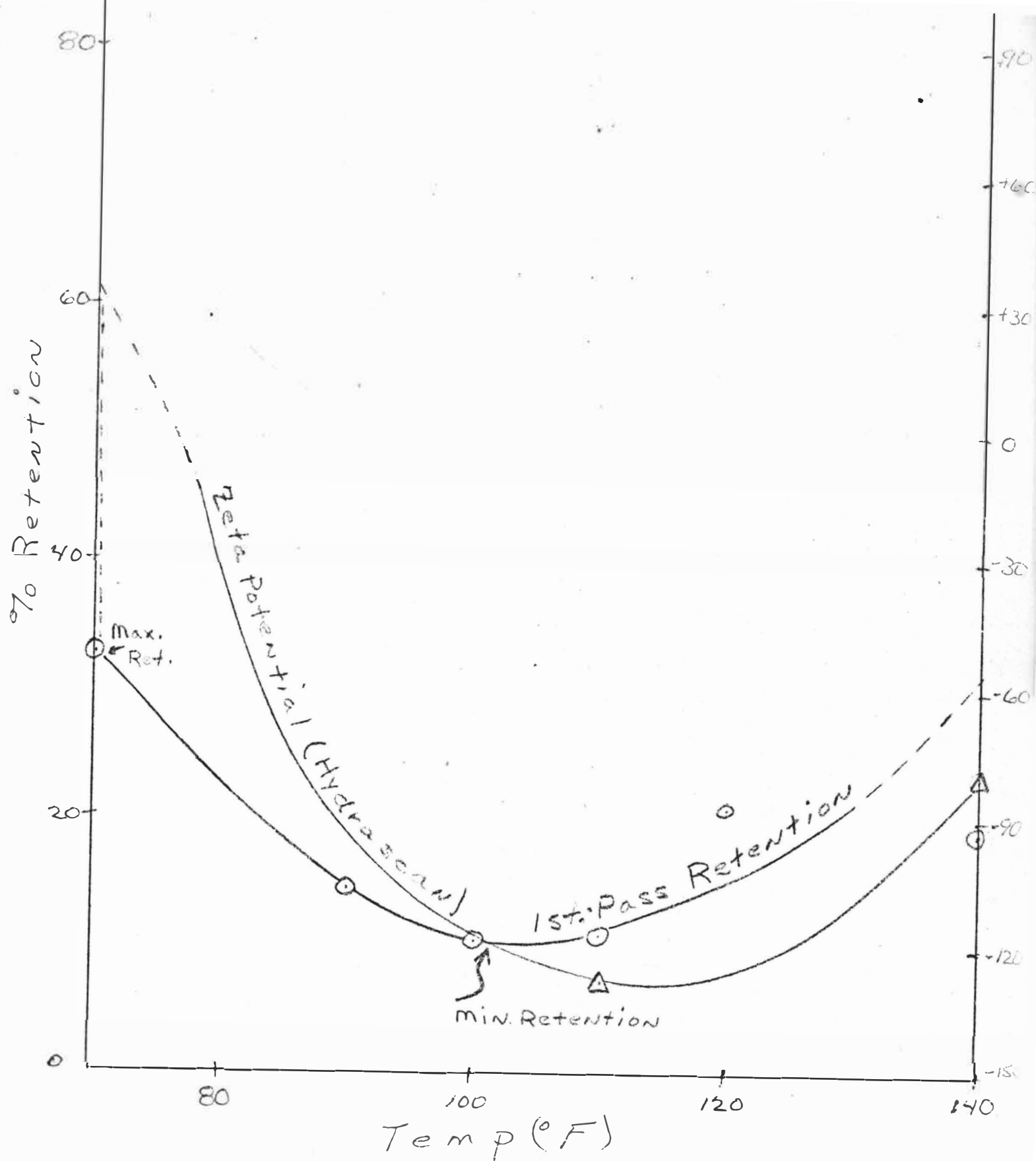


Fig. 25 Retentions on Dynamic Drainage Tar at Varying Temps. Using No Ret. Aid at pH 7.8