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Filler Distribution as Effected by Drainage Rate and Volume

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THESIS

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Effect of Retention Aids and Drainage Rates on Filler Distribution of Titanium Dioxide

Much work has been going on in the development of increased retention of titanium dioxide. This thesis will investigate retention of titanium dioxide and drainage rates on the distribution of titanium dioxide.

The retention of titanium dioxide will be understood a little better if conditions having known effects on retention are stated. Literature states that retention of fillers increases with increased basis weight, (2) increased beating of the pulp, (1) with increased alum to a limit, (1) and decreases with interrelated machine conditions such as increased speed, vacuum in the suction boxes, and length of wire and shake. (1)

It is fairly easy to see why increased basis weight would increase retention. The thicker the filtering mat, the more chance of being trapped the particles have. So it follows that the percent titanium dioxide retained will be greater. How this is distributed throughout the thickness of the sheet is another question.

Retention of titanium dioxide increases with addition of alum up to a point. This is only true with systems where the pH is alum-dependent. (6) To understand why this is true, it is necessary to understand that maximum retention occurs in the five to six pH range. Usually, with fiber added to just plain water, three percent titanium dioxide added, based on weight of fiber, produces optimum retention. Alum hydrolyzes, when added in this amount, to give a pH between five and six. It has been observed that maximum retention always occurs when the pH values are near 5.2 when the titanium dioxide was added.

Retention of titanium dioxide increases with increased beating of the pulp. As pointed out by Willets, (19)(20) beating the pulp increases the fibrillation and decreases the porosity of the sheet. Also, it can be clearly surmised that the rate of drainage will decrease with increased beating of the pulp, due to lower porosity of the sheet. This will increase the probability that a particle of titanium dioxide will be trapped and will not "work its way completely through the sheet". The increased fibrillation also gives many more sites where the particles could be colloidally absorbed.

Retention of titanium dioxide decreases with interrelated machine conditions such as increased speed, vacuum in the suction boxes, length of wire and shake. Filtration properties will decrease with increased speed. Fibers will tend to be orientated more in the machine direction with increased speed and this in turn will decrease the porosity of the sheet. Vacuum boxes will tend to decrease the probability of a particle being absorbed in the sheet because the force required to hold a particle absorbed on a fiber does not change. A particle moving at a greater velocity will have more kinectic energy that must be absorbed before the force of absorption on the fiber will hold it at the sites. Increased wire length and shape will give a particle more of a chance of working through the entire thickness of the mat; so retention would be decreased in this case.

To give a little better understanding as to why some of the above information holds true, some of the theories of retention will be briefly discussed.

The mechanical theory of retention of titanium dioxide is essentially the following. (5) Individual particles, too small to be filtered by fibers, may be flocculated together by alum to produce floes sufficiently large to be entrapped by the fiber mat during the sheet formation. Beating the pulp also increases the internal surface area, increases the porosity of the sheet and decreases the drainage rate, as stated previously. So this gives an increased number of sites where the filler particles can become lodged in the hydrated cellulose "gel" and in the imperfections of the sheet surface. (6)

Schauman (17) showed that the rate of drainage decreases with hydration or increasing external fibrillation; therefore retention is favored. Halsam and Steele (13) also found that the fibrils appear to important as sites for colloidol absorption.

The physico-chemical theories may be broken up into two parts. The first one is commonly referred to as the charge attraction theory and may be briefly stated as follows. Some people in the pulp and paper industry (6) feel that there is a difference in sign of electro-kinectic charge between filler and cellulose. Therefore, there is an attractive force between the filler and cellulose. This attractive force may exist anywhere in the paper-making process, provided that suitable conditions are present. This is considered to be responsible for bonding the filler to fiber during sheet formation. Of course, pH would have a direct control here because of the relative ease with which the fibers and fillers could take on an electro-kinectic charge. Of course, if this theory is true, then some dispersion of the filler particles is likely to take place rather than flocculation. There is a repelling force between two particles of like charge.

The other physico-chemical theory is one of coflocculation. This theory proposes the absence of significant electro-static (6) forces on both cellulose fibers and filler particles. Therefore, the two materials may flocculate to form a common floc.

Based on past work, many investigators have concluded that the retention phenomena is probably due to the compound action incorporating both of these physico-chemical theories. (7)

Many investigations on filler distribution have been carried out. Three methods have mainly been used for this study: splitting or pulling the sheet in halves, careful abrading, and the microtome technique. (7)

Hansen (13) used the abrading technique and showed that filler content near the wire side is not caused by the influences of the table rolls, the suction boxes, nor the wet presses. The filler distribution is determined immediately after the stock has been run unto the wire. Browning, Isenberg, (3) and Mack (16) verified Hansen's findings by using the microtome technique. They found that table rolls and suction boxes only affect the filler in the immediate surface. Hansen and Mack also showed that the dandy roll causes a migration of the filler from center to topside. This increases two sidedness.

Underhay (18) used a splitting of half technique. He surmised from his data that the table rolls cause two sidedness. Hansen (13) also worked some with handsheets. He found that filler distribution is almost symmetrical, highest in the middle and decreasing as to distance traveled from each side decreases. An accurate measurement of filler distribution cannot be carried out however by just splitting the sheet in half because the increment thicknesses relative to the total thickness are not small enough.

The effect of drainage rate will also be investigated in this thesis. Once a filler particle strikes a fiber, what is the probability that it will remain there. Gillespie (9)(10) and Gallily, (8) through air flow systems have shown that large particles striking a fiber with an appreciable velocity may not stick. This will be true if the energy of deformation is greater than the energy of adhesion.

Although air flow systems are not entirely the same as liquid system, it is felt that the physical theories developed for the air flow systems are applicable to liquid flow systems. Hermans and Bradee (15) suggest eight mechanisms by which aerosols can be deposited on surfaces. They are (1) inertial impaction, (2) direct interception, (3) Brownian diffusion, (4) settling, (5) electrostatic attraction, (6) sieving or plugging, (7) eddy diffusion, and (8) thermal deposition.

Davis (4) and Wong (21) consider an individual fiber in the mat relative to entrance and exit of particle concentrations. Wong's equation for describing collective properties of a fiber in the mat has been shown to be feasible. The assumptions Wong makes in his derivation are the following: (7)

1. "The fraction of material removed per fiber layer is small and can be approximated by a differential."
2. "The thickness of the mat is large compared to the thickness of a fiber layer."
3. "The amount removed per fiber layer is so small that good mixing takes place between each fiber layer."

The equation is the following:

$$\ln N_0/N_h = 4\alpha\eta h/\pi D_f$$

"where α is the fiber volume per unit volume of mat, h is the thickness of the mat parallel to the direction of flow, η is the collection efficiency, D_f is the diameter of the fibers, and N_o and N_h are the number of particles per unit volume at points $h = 0$ and $h = h$, respectively." (7) The above equation also assumes that remain constant over the entire mat thickness.

Gillespie, (9) using an air flow system, found that large particles could be detached by increasing the air flow. This would happen if the fluid drag force exceeds that of adhesion. So the particles could rearrange and migrate as the high rate of flow continues.

Grace (12) extended these concepts to liquid systems; direct sieving appears to be the main controlling mechanism. A cellulose fiber mat has many "channels" in it. At first the channels are fairly large but particles lodge in these channels, the resistance to flow increases. This causes the fluid to seek out those "channels" with less resistance to the flow. But this causes more particles to go through these channels and increases the probability of particles lodging. There is a point where all channels will have approximately the same flow resistance. The rate of flow will then decrease the probability of retention would increase still further. At this point, the retention of fine filler particles will be increased due to reduction in flow rate.

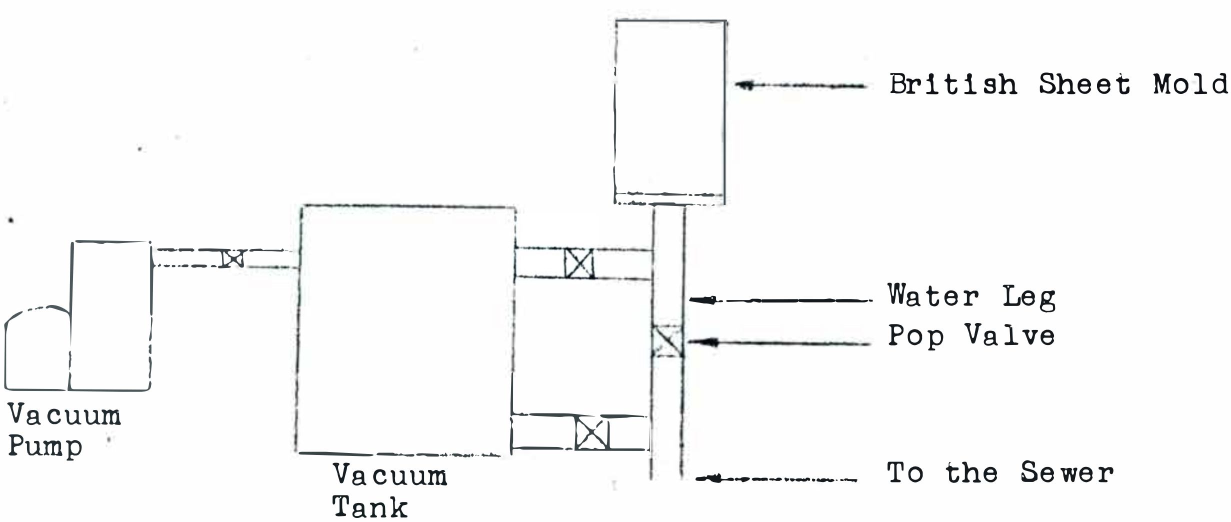
Ghosh (11) and Eliassen (5) studied the clarification of water through sand bed filters and their results indicate that the amount of material retained is greatest on the upstream side.

Some fine particles also went completely through. This seems to indicate that although retention is a function of particle size, it is also complicated by system geometry, hydraulic forces, and collodiodal forces.

Thesis

A mixture of 50 percent hardwood kraft and 50 percent softwood sulfite was beaten in a standard T.A.P.P.I. beater until the Canadian Standard Freeness was approximately 420 ml, for all handsheets. Titanium Dioxide was used as the pigment and it was experimentally determined that under these conditions approximately seventy percent based on weight of dry fiber must be added. If less than this amount was added, the retention decreased to less than 10% which was unfavorable. The titanium dioxide was added to the beater after the beating was finished, and circulated for five minutes with no load on the bed plate. This insured a uniform mixture of pigment and fiber. In two liter batches, this mixture was blended for 30 seconds to insure adequate dispersion. Handsheets were made using essentially T.A.P.P.I. procedure. The following apparatus was built to vary the drainage rate.

DIAGRAM OF LAB. EQUIPMENT



By controlling the degree of vacuum in the tank, the drainage rate could be controlled. The tank was large enough so that the pressure change, due to the water flowing into the tank, was small. The tank was drained after each handsheet was made.

Not only drainage rate, but the effect of changing the actual volume of water used in forming handsheets was studied. Some handsheets were made with 7.2 liters passing through, while in the remainder, only 3 liters were used.

All sheets were air dried on rings in the constant humidity room. The sheets were lightly calendered before sectioning.

An American Optical Company Spencer 860 Sliding Microtome was used to section the papers. This entire operation was carried out at a constant humidity (50% R.H.) and temperature (72°F.). A microbalance was used for the weighings while size 00000 crucibles with matching covers were used for the ashing of the paper samples.

To hold the paper in position during the sectioning, small wooden blocks of soft pine (10 x 15 x 20 mm) grain long, were used. Small rectangular pieces of paper were cut and glued to the top of these blocks, using Duco Cement as the adhesive.

The wooden block was clamped into the microtome and leveled by gradually raising the block 5 μ increments. Care had to be taken not to slice too much off the block at once, since this dulls the blade very quickly. To the leveled block surface, Duco Cement was applied and the pre-cut paper sample was placed with the appropriate side up. A flood lamp was used to dry the glue very quickly.

The sample was raised gradually by 5 μ increments until the knife just contacted the paper. The sample was sliced into 15 increments. The maximum number from any one side was four. To take more than this number would disturb the results because of glue penetration. A camel hair brush was used to brush the sections into their respective crucibles.

The rest of the procedure consisted of a gravimetric determination of the ash content, with the weighings made accurately to .00001 gram. The paper samples were ashed in a muffle furnace for thirty minutes at approximately 1000^{o}F. All weighings were made in equilibrium with the atmosphere in the constant humidity room.

Experimental Results

Sheet	Ash Content for Individual felt 15 μ slices	Ash Content for Individual Wire 15 μ slices	Ash Content of Sheet
2.2 sec 25 in vacuum 3 liters	(1) 10.61% (2) 11.86% (3) 14.08%	(1) 10.32% (2) 11.27% (3) 12.52%	12.18% Figure I
3.3 sec 10 in. vacuum 3 liter	(1) 10.29% (2) 12.41% (3) 14.53%	(1) 12.93% (2) 13.86% (3) 17.59% (4) 14.81%	13.45% Figure II
13.0 sec 0 in. vacuum 7.2 liters	(1) 10.28% (2) 12.39% (3) 14.16%	(1) 13.91% (2) 14.77% (3) 14.61% (4) 14.20%	13.82% Figure III
9.0 sec 10 in vacuum 7.2 liters	(1) 8.07% (2) 11.13% (3) 12.03%	(1) 10.80% (2) 11.32% (3) 14.00% (4) 12.89%	11.52% Figure IV
3.7 sec 0 in. vacuum 3 liters	(1) 9.57% (2) 14.92% (3) 16.59%	(1) 18.96% (2) 19.55% (3) 18.89% (4) 18.11%	16.95% Figure V
3.7 sec.(check) 0 in. vacuum 3 liters	(1) 12.72% (2) 14.81% (3) 16.19%	(1) 18.68% (2) 19.32% (3) 18.62% (4) 17.58%	16.95% Figure VI

FIGURE I

VACUUM: 25 in.
VOLUME: 3 L.
DRAINAGE TIME: 2.2 sec.
ASH: 12.18%

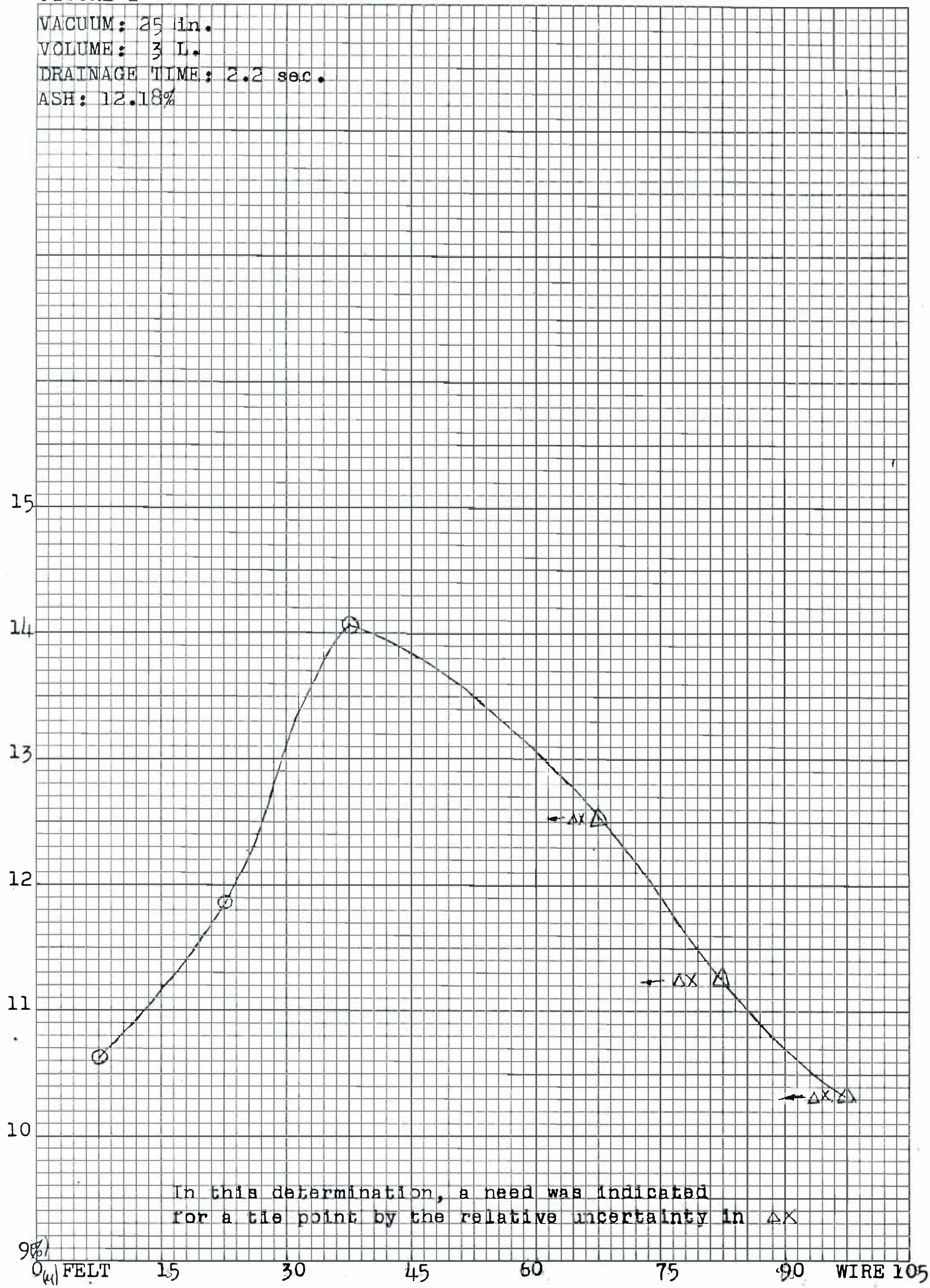


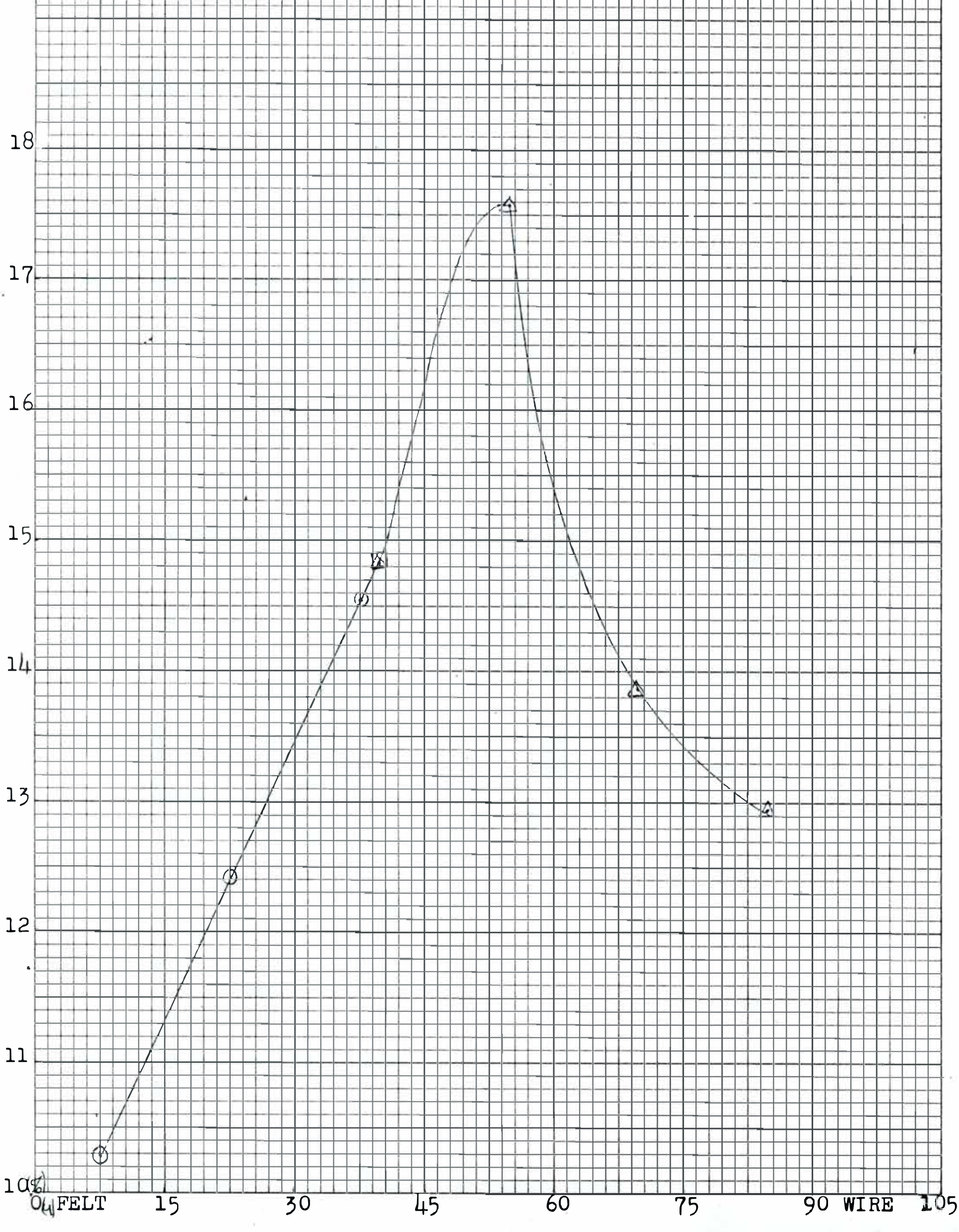
FIGURE II

VACUUM: 10 in.

VOLUME: 3L

DRAINAGE TIME: 3.3 sec.

ASH: 13.45%



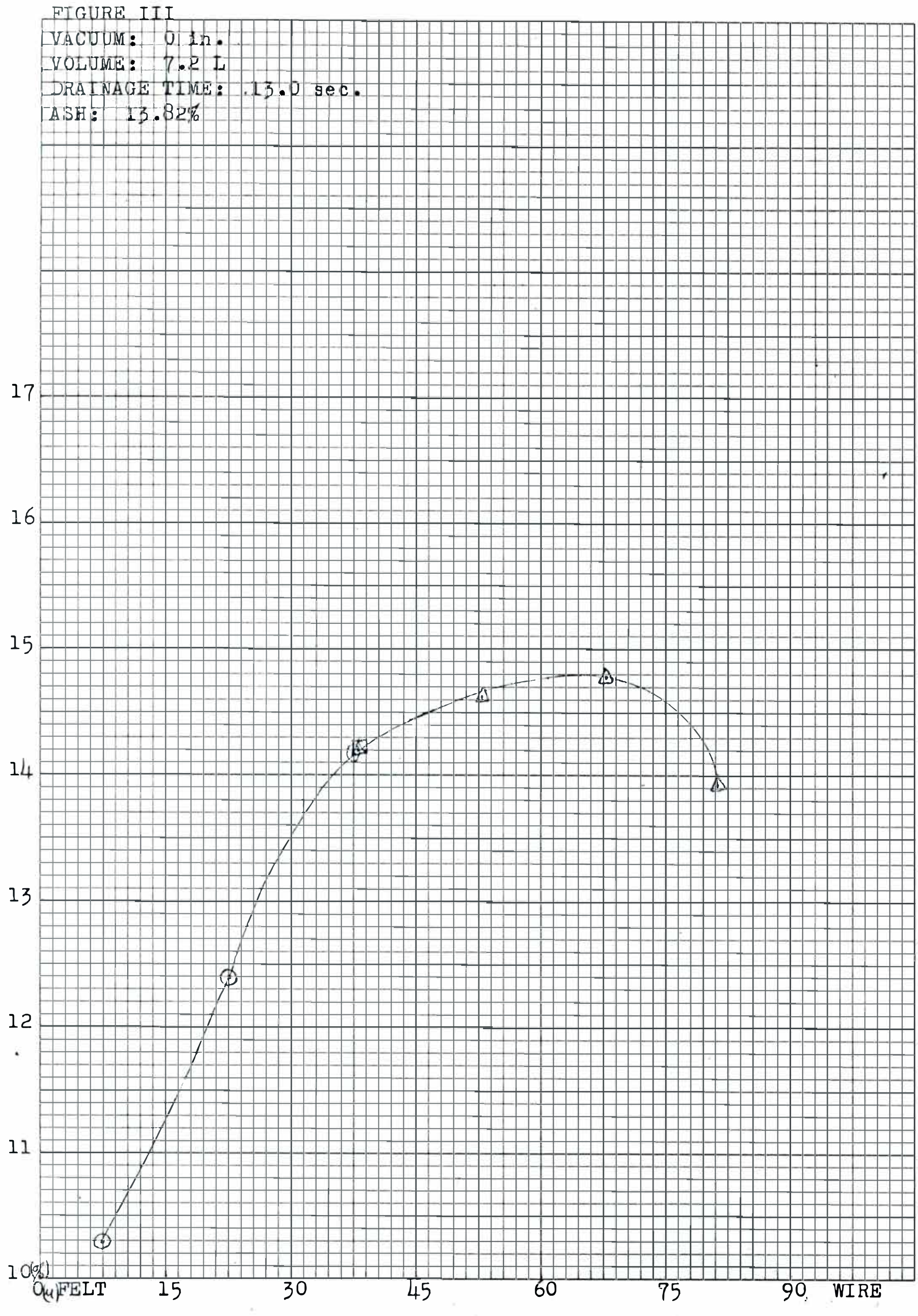


FIGURE III
VACUUM: 0 in.
VOLUME: 7.2 L
DRAINAGE TIME: 13.0 sec.
ASH: 13.82%
17
16
15
14
13
12
11
10(%)
0(u)FELT
15
30
45
60
75
90
WIRE

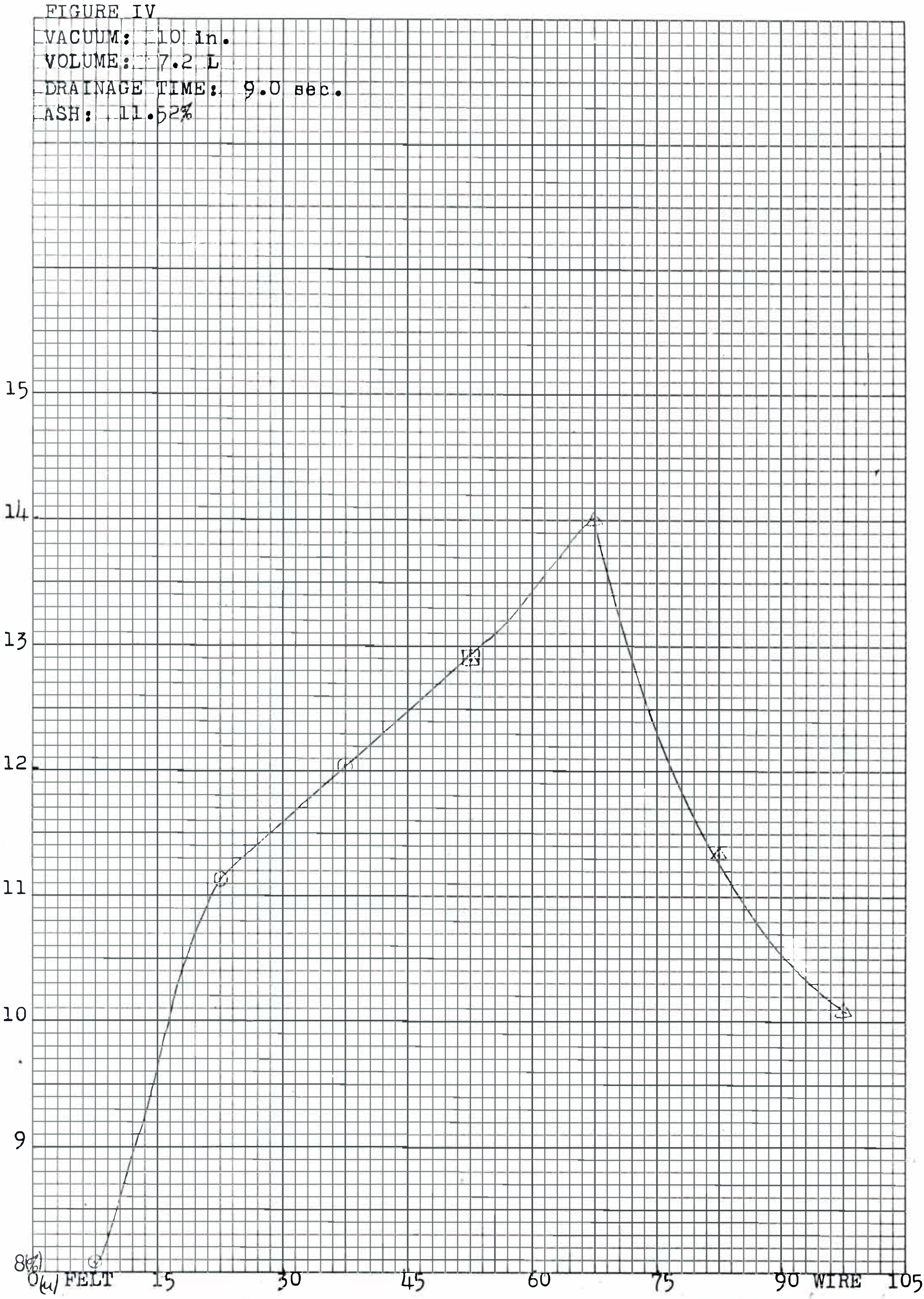


FIGURE IV
VACUUM: 10 in.
VOLUME: 7.2 L
DRAINAGE TIME: 9.0 sec.
ASH: 11.52%
15
14
13
12
11
10
9
8(%)
0(μ) FELT
15
30
45
60
75
90 WIRE
105

FIGURE (V)

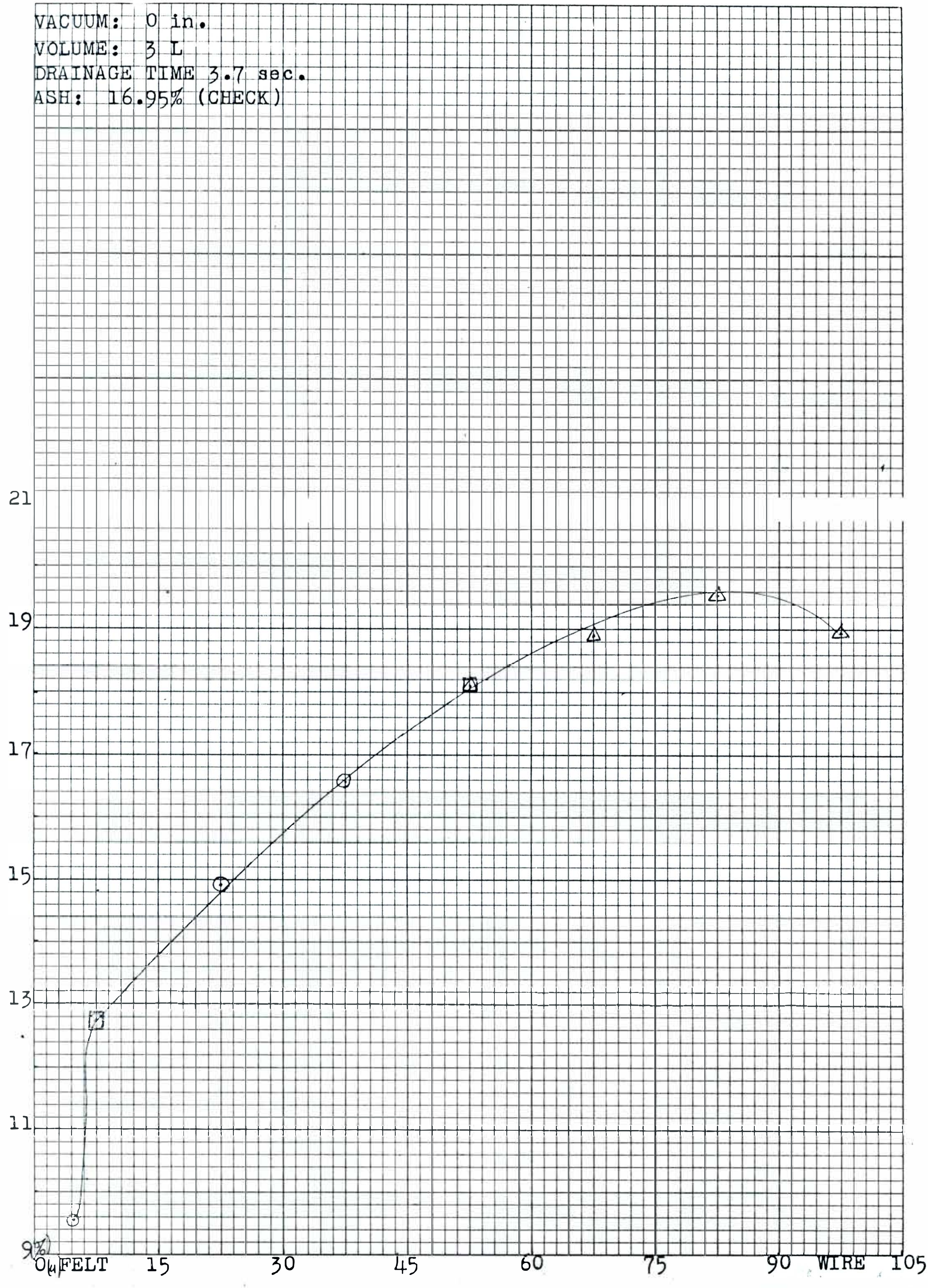

VACUUM: 0 in.
VOLUME: 3 L
DRAINAGE TIME 3.7 sec.
ASH: 16.95% (CHECK)
21
19
17
15
13
11
9%
0
FELT
15
30
45
60
75
90
WIRE
105

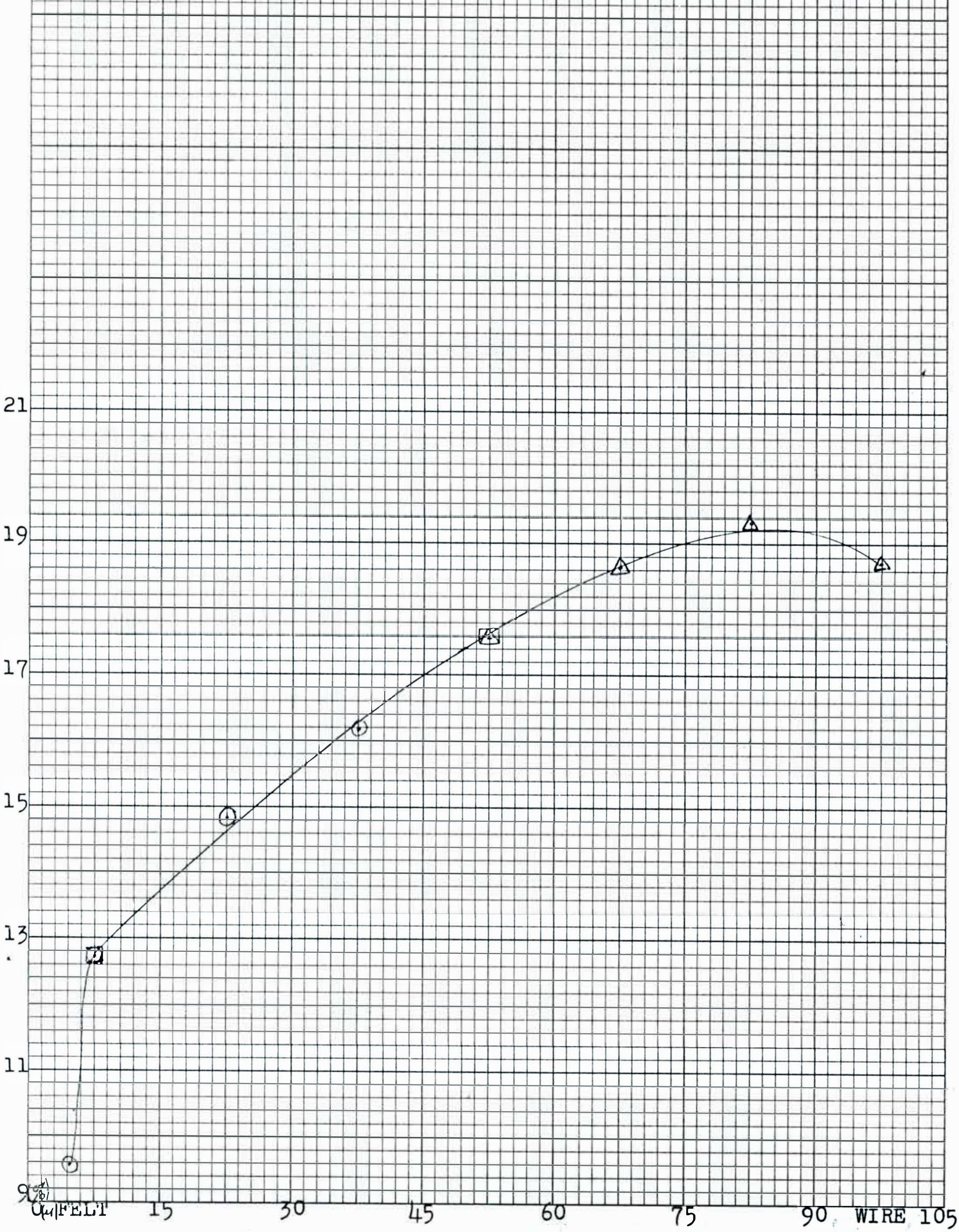
FIGURE VI

VACUUM: 0 in.

VOLUME: 3 L.

DRAINAGE TIME: 3.7 sec.

ASH: 16.95%



Presentation of Experimental Results

It can be seen from the results, that a greater flow rate tends to equalize the usual two sided filler retention. A greater flow rate reduces overall retention. Both of these factors may be explained from an energy standpoint. Water having a greater flow rate will exert more of a drag on the particles, both from an electro-static and frictional viewpoint. Each time a titanium dioxide particle sticks to a fiber it will stay there until enough force is supplied to overcome the adhesive force. This could be thought of as a potential energy "hump", where in order for the particle to move on, enough energy must be supplied to get over this hump. The particle then goes on hitting other fibers until it is "caught" or trapped again. When this happens, the above process repeats. The water may or may not be flowing fast enough to break the particle loose from any given position. However, the greater the flow rate, the greater will this probability be. This explains why there is relatively less retention with the greater flow rates.

As mentioned above, with a greater flow rate, usual two sidedness decreased; however had it been possible to effect some greater flow rates than in this study, it follows that gradually the maximum would be shifted far enough over that two sidedness would again be prevalent. However, in this case, the greater retention would be on the felt side. This trend is easily seen if the figures for the successively greater flow rates are examined. On figure I, the felt initial slice is already seen to be a little higher than the wire initial slice.

In this study, two water volumes were used in the British Sheet Mold forming process - 7.2 liters and 3 liters. With the same drainage rate, the "three liter" handsheets showed the greatest retention. From the previous energy discussion, it follows that a greater volume of water will pull more of the titanium dioxide particles through. There are two factors influencing this. The handsheet is gradually forming as the water flows through the wire gradually depositing fibers and some of the pigment on the mat. In the case of the larger volume of water, the average resistance encountered by the titanium dioxide particles from the fibers is much less per liter of water passing through. It follows the average "trapping power" of the fibers per particle will be reduced.

The other factor is due to the longer total time for the larger volume of water to flow through at a comparable rate. Therefore, the particle will be exposed to the dragging forces, both frictional and electro-static, for a correspondingly longer time. This factor also increases the probability that the particle will ultimately end up farther from the felt side.

In the treatment of results, the distribution of the titanium dioxide was plotted as a continuous curve throughout the sheet. The distribution had to be determined in two steps, one from each side of the sheet. In order to treat the results in this way, a "tie value" - a value which overlaps or that almost overlaps the increment thickness from the opposite side, was found most helpful. This point was merely plotted to fit into the trend and the rest of the values spaced 15 apart. These values are indicated on the graphs by a triangle-square combination enclosing the point. The circles indicate the determinations made from the felt side and the triangles - from the wire side. In the case where a check was made on the method, it was found that the first layer may not be exactly 15 thick. This was due to the slight roughness of the paper surface and also to the slight amount that must be sliced off before the actual section may be made. It was attempted to make the first actual section less than 15μ so that the first "skimmings" plus this would equal approximately 15μ . Therefore it was necessary to have another "tie point" in this region of the check. But it was found that the method is very reproducible and accurate.

In this study, it has been shown that filler distribution in handsheets can be objectively examined by controlling the flow rate of the British Mold and by using the microtome method. This method has proven to be accurate and reproducible under these conditions.

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