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The Influence of Low Viscosity Shear of Pigments on Coated Papers Properties

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THE INFLUENCE OF LOW VISCOSITY SHEAR OF PIGMENTS ON COATED PAPERS PROPERTIES

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Submitted by:

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In preparing for this problem, interest centered on three general topics. They were the structure of clay, its' flow properties, and its' application to paper with resultant improvement in the paper's properties.

With respect to structure, kaolinite clay is crystalline. It is composed of alternate layers of alumina and silica bound together with oxygen and hydroxyl valence linkages (6). These linkages are the weakest points in the structure. Fracture at these points causes the formation of platelike particles of clay.

Clay particles with a diameter greater than two microns are generally isometric stacks. Particles with a diameter less than two microns are generally hexagonal plates. Delaminated clay particles are generally thin platelets with a narrow size distribution and an average thickness of two-tenths of a micron (1). Isometric stacks are absent in these clays. These clays also have a larger surface area per weight of clay than do conventional clays (1).

With respect to the flow properties of clay there are two situations that exist. These are dilatant and thixotropic systems.

Dilatant systems are closely packed masses which expand in bulk volume when deformed because of rearrangement of the component particles (5). The free liquid in the system is sucked into the voids created by the expansion and the system "sets up". Dilatancy has also been given the general definition as the resistance of a system to increased distortion (4). Dilatancy is not related to the rate of shear of a system (4). However, particle size is a factor in clays "setting up" and the larger clay particles tend to "set up" faster (4).

High solids content also increases the possibility of the system becoming dilatant. As the number of solids per unit volume in the system increases the voids in the system decrease in size and number, and the system becomes more closely packed. With stress this system will dilate as explained earlier.

In contrast to the undesirable dilatant system there exists the thixotropic system. A thixotropic system is a reversible sol-gel system. In this system a gel is formed with standing, but becomes fluid with stirring. Attractive forces must exist within a system for it to be thixotropic. The gel is formed due to the attraction of the particles of the dispersed system for each other. When the gel structure is sheared or distorted disruption of the bonds forming the structure takes place (4). As the rate of shear is increased the destruction of such bonds becomes more complete, and the resistance of the system to this shear is correspondingly lessened (5).

The flow properties of clay-water systems also can be shown to have a relation to the respective quantities of the two main types of particles present, plates and isometric stacks (4).

Coarse clays are very fluid at low solids content, and exhibit low viscosity even at relatively high solids content if the rate of shear is low (4). In high solids suspensions these clays are subject to shear-rate thickening and sudden shear-rate blockage, i.e. "setting up". These clays, deficient in fine particles, exhibit almost none of the thixotropic breakdown which leads to low viscosity readings at high shear rates, and to a satisfactory leveling index (4). The removal of fine particle sizes of the clay lowers the viscosity and even more so the thixotropy of a clay (4).

Clays with fine particle are more thixotropic due to their platelike structures, which are likely to have more open linkages for attractive forces. The smaller size also increases the number of probable collisions per weight of clay, and thus gives more chances for the attractive forces of the particles to become effective and form a gel structure.

Finally there is the consideration of the preparation of the clay. With respect to this shear rate and the dispersion are the key factors. Also important in the application of the clay to paper are the clays requirements for binding to the paper and the actual results the clays achieve in the final paper product.

At constant shear rate the rate of work done on a volume of fluid is proportional to the viscosity. At high solids content the rate of viscosity increase is greater than the rate of concentration increase (2).

A large increase in the surface area of a clay under shear stress shows that there is a change in particle shape rather than a breakdown of agglomerates under these conditions (2).

In dispersing clays base exchange is the controlling factor. Clay particles have a negative charge in solution due to the fracture of the primary valence bonds of the clays. These fractures occur perpendicular to the plane of the plates (6). Hydroxyl ions are preferentially absorbed at these points and water of hydration surrounds the hydroxyl ions (6).

Deflocculated clays can be handled at seventy-two per cent solids. A clay slip which is not at the maximum degree of dispersion might show thixotropic characteristics. In clays with predominate repulsive forces there will be no coagulation. Also, incomplete dispersion will give the same effect as coarse particle size in the clay (5).

In considering the binding requirements of a clay the adhesive and water removal requirements of a clay will decrease as the per cent solids of the clay increases per volume of clay. Small particle size will also decrease the adhesive requirement (7). In limiting adhesions migration pigment particle plugging is the most important single factor. This plugging effect increases as the size of the particle decreases, but the effect has its limits (7). Dilatant systems prevent particle migration to plug the pores of the rawstock.

Delaminated clays have been shown to improve certain properties of coated papers.

A delaminated clay will give improved optical properties due to a narrow thickness distribution. They give increased smoothness because of the absence of isometric particles in their composition. Also theri platelike structures have a tendency to orient parallel to the surface of the paper which also increases the bulkiness of the coating (1).

These clays can be expected to give an increased sealing effect per weight of clay because their particle size is larger than conventional clays. This sealing effect can be adjusted by adding isometric particles such as calcium carbonate or titanium dioxide to the clay (1).

Finally these clays can be expected to give a greater brightness than a conventional clay. This is possible because they have more particles per weight of clay than do conventional clays, which will increase the probability of covering the impurities present in the clay. Also the coarse clays from which delaminated clays are prepared generally have fewer impurities per weight of clay than do conventional clays.

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Abstract

This paper covers the effect of shear by a sigma blade kneader on the optical properties of a given filler clay. The object was to produce a delaminated clay with an appropriate particle size distribution that would give improved optical properties over the original filler clay and possibly another conventional coating clay at the same particle size distribution as the sheared clay.

The basic structure of clay is a thin hexagonal plate. Conventional preperations of coating clays tend to destroy these plates. It is possible to preserve these plates by using shearing forces moreso than grinding forces. These platelets occur naturally in booklets. The interplaner forces are the weakest bonding forces in these booklets. It is possible to break these interplaner bonds by shearing forces within a dilatent clay system. It was hoped the sigma blade kneader would give provide an efficeint shearing force on the given dilatent clay system discussed within this paper.

Theoretically the delaminated clays should give improved optical properties over the original clay due the favorable change in the particle distribution toward particles with a smaller effective diameter and smaller particle size distribution. The platelets which are preserved by this technique should improve the brightness of the clay due to better coverage of impurities and a more effective coverage of the paper due to the presence of more particles per weight of clay than in the original filler clay, and in a comparable conventional clay.

The opacity should improve due to the formation of more effective planer surfaces within a given thickness of the clay. The smaller particle size and narrower distribution should also improve the smoothness and gloss by giving a more uniform coating surface. The ink holdout should improve since the larger platelets will have a smaller edge to surface ratio and the booklets will have been eliminated from the sheared clay. Finally, according to the theory of relative sediment volume, the adhesive demand of the sheared clay should show a decreased adhesive demand from that of the original clay.

The absolute viscosity of the clay should also increase as a result of the formation of the finer particles by this technique.

Experimental Procedure

The clay was sheared for ten and twenty hours respectively. The particle size distribution was determined for these clays and for the original clay by TAPPI Standard TS 649 sm-54.

Drawdowns of the original clay and the clay with twenty hours shear were prepared. Three solid and adhesive levels were used with each clay. The starch' levels were ten, twenty, and thirty percent by weight of dry pigment. The solids' levels were thirty, forty, and fifty percent dry solids.

A sixty pound base stock was used for all the samples, and starch was used as the adhesive in all the samples.

Approximately an eighteen pound coat weight was applied to all the samples. The samples were then calendered at forty pounds pressure for four nips.

Brightness, opacity, gloss, K&N ink, smoothness, Dennison wax, opacifying power, and basis weight of the respective clay samples and the base stock were determined.

The absolute viscosity of the clay slips with and without adhesive wre determined by use of the Hercule's viscometer. Brookfield viscosities of the same samples were also recorded.

The clay was sheared under dilatent conditions at approximately sixty-five percent solids. Tetrasodiumpyrophosphate was used as the dispersing agent in these clays.

Results and Discussion

The most significant results were the marked increase in the ink holdout of the sheared clay over that of the original clay, and the marked increase of the opacifying power of the clay with shear. These appear to indicate the formation of platelets as desired. A comparison of this clay's optical properties and surface properties with those of a clay of the same particle size distribution prepared by a conventional technique would verify this.

The smoothness showed a decrease which was not expected. This is believed to be the result of insufficient screening of the sheared clay slips, and the fact that the impurities that were initially present in the filler clay and released by shearing the clay were not removed to any large extent. This decrease in smoothness is believed to also be the cause of the decreased gloss in the sheared samples.

The brightness and opacity showed only slight increases. Again the presence of the above mentioned impurities may have been significant in the final results.

The absolute viscosity of the samples increased markedly with shear at forty percent solids. At fifty percent solids the absolute viscosity decreased. The increased viscosity with shear would seem to indicate the formation of finer particles of clay. The decrease in viscosity I cannot account for.

The efficiency of the sigma blade with respect to shearing force placed effectively on the clay decreases markedly with a decrease in the amount of large clay particles present in the given clay system.

Apparently the optical properties of a delaminated clay do not change significantly when the percent of particles in the clay with effective diameters of less than two microns is increased from sixteen to forty-one .

The increased ink holdout, the increase in the opacifying power of the clay with shear and the increase in the opacity and brightness of the clay with shear are indications that a filler clay can be improved within the mill by the use of the sigma blade kneader. The economics of the operation would have to be considered though.

It has been indicated that delaminated clays are significantly better than conventional clays at particle size distributions with greater than fifty percent of the clay particles having an effective diameter of less than two microns. Perhaps sufficient amounts of a delaminated clay with greater than eighty percent of the particles less than two microns could be added to the sheared clay with the final clay mix having a particle size distribution with fifty percent of the particles having a diameter of less than two microns. This procedure could give an economical quality coating clay if the cost of the power input in shearing the initial filler clay to the desired particle size distribution was sufficiently low, and the long time of shear required was not a critical factor.

Data

Particle Size Distributions

Hours of Shear	% less than 2 microns *	% 2 to 5 microns	% 5 to 10 microns	% greater 10 microns
0	16	30.5	34.5	19
10	35	33	32	0
20	41	21	38	0

Brookfield Viscosities
(centipoises)

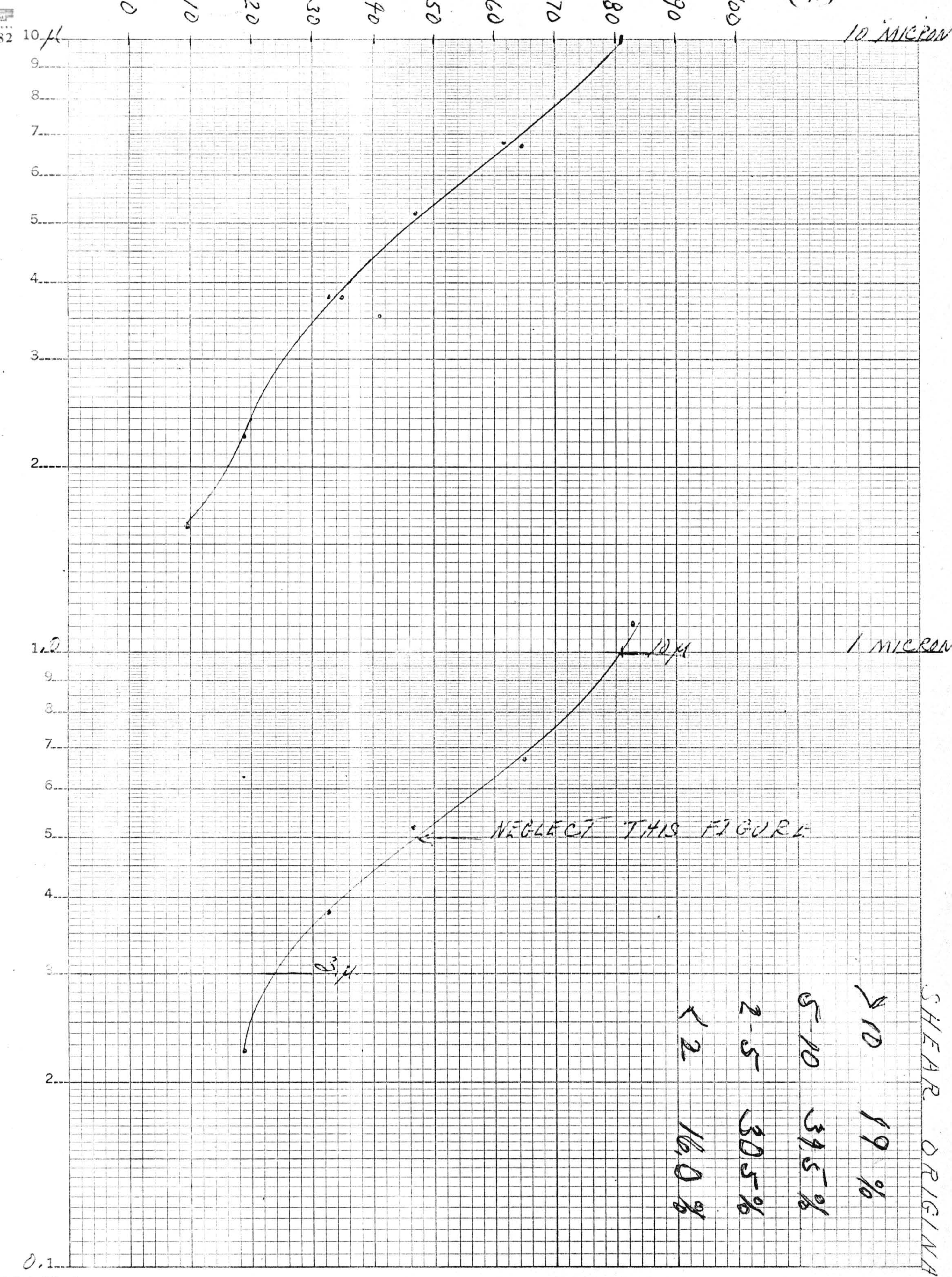
% Starch	Hours of Shear	Percent Solids							
		40%				50%			
		10	20	50	100rpm.	10	20	50	100rpm.
0%	0hrs.	20	14	16	20	40	30	34	44
	20	20	12	14	32	40	30	32	40
10%	0	200	130	81	82	768	514	308	252
	20	120	88	75	84	600	400	275	220
20%	0	620	442	268	215	2288	1830	x	x
	20	280	210	154	162	3900	2600	1580	1250
30%	0	1236	856	496	344	x	x	x	x
	20	960	408	748	x	x	x	x	x

Data:

Optical and Surface Tests

Test	Hours of Shear	Percent Solids						
		40%			50%			
		10	20	30	10	20	30	Percent Starch
Brightness (G.E.)	0	82.7	83.0	84.5	82.5	81.0	80.0	
	20	82.3	83.2	85.0	86.0	84.5	x	
K & N Ink (% loss in Brtness 2 min. test)	0	65	50.3	36	62.5	47.4	35.5	
	20	36.3	26.9	x	36.1	30	x	
Opacity (%)	0	90	89.5	88.2	91	87.5	88.0	
	20	93	93	90	92	90.5	x	
Gloss (%) (Bausch & Lamb)	0	39	24.5	17.5	37.5	25	16.7	
	20	30.5	22.5	14.5	33.5	19.0	15.0	
Beck Smoothness (seconds)	0	331	261	189	364	273	153	
	20	295	187	88	331	218	x	
Dennison Wax	0	3	8	x	3	7	10	
	20	6	8	10	3	8	8	
Opacifying Power (S)	0	0.38	0.13	0.26	1.05	0.22	1.87	
	20	5.20	5.62	1.84	8.50	2.69	x	
Absolute viscosity	0	15.0 x	23.85 22.95	50.3 45.0	47.7 38.9	104.0 77.7	x x	initial equil.
	20	17.65 15.85	41.5 32.6	95.4 70.6	x x	82.1 59.1	x x	

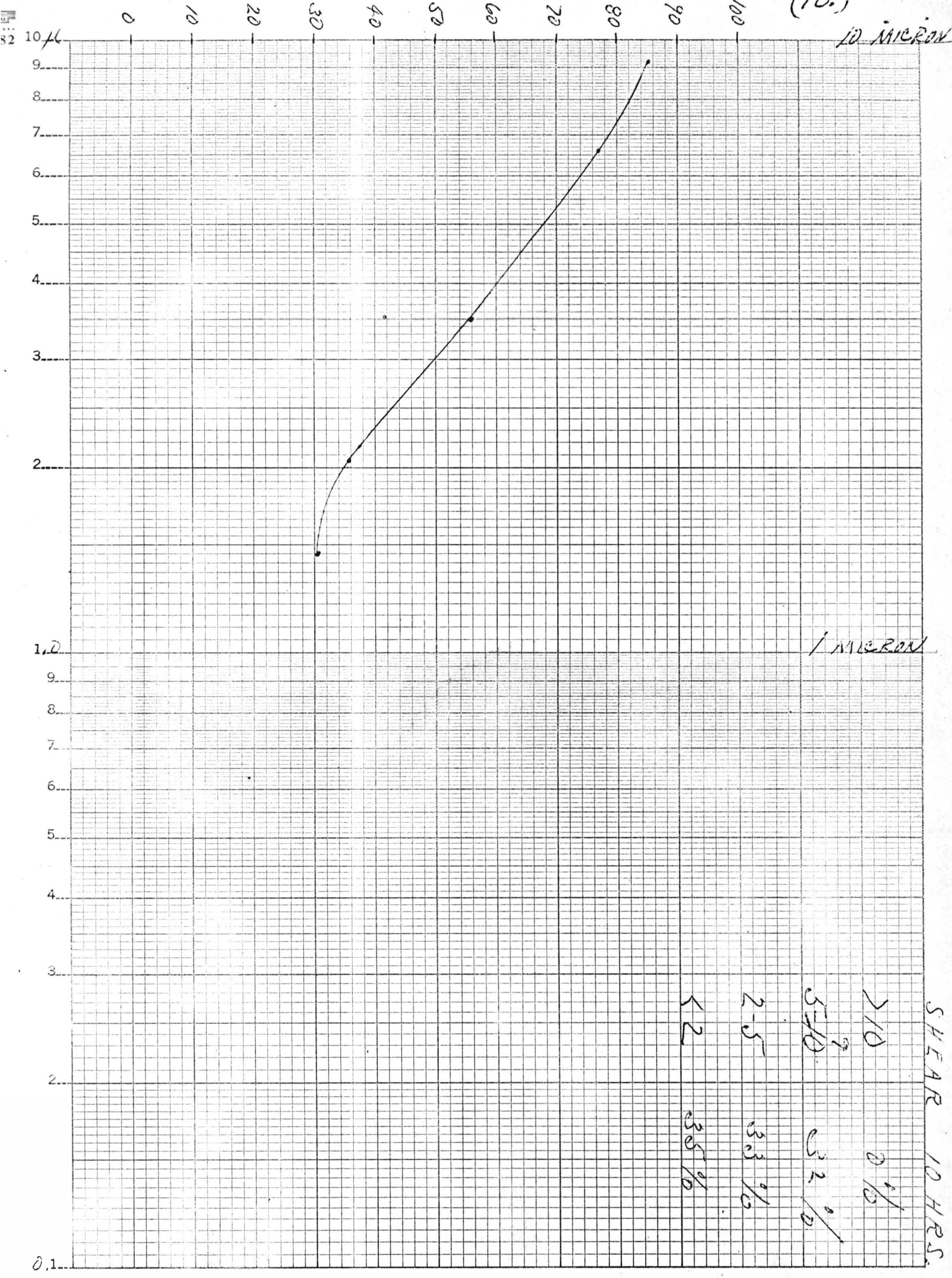
FIGURES OF PARTICLE SIZE DISTRIBUTIONS



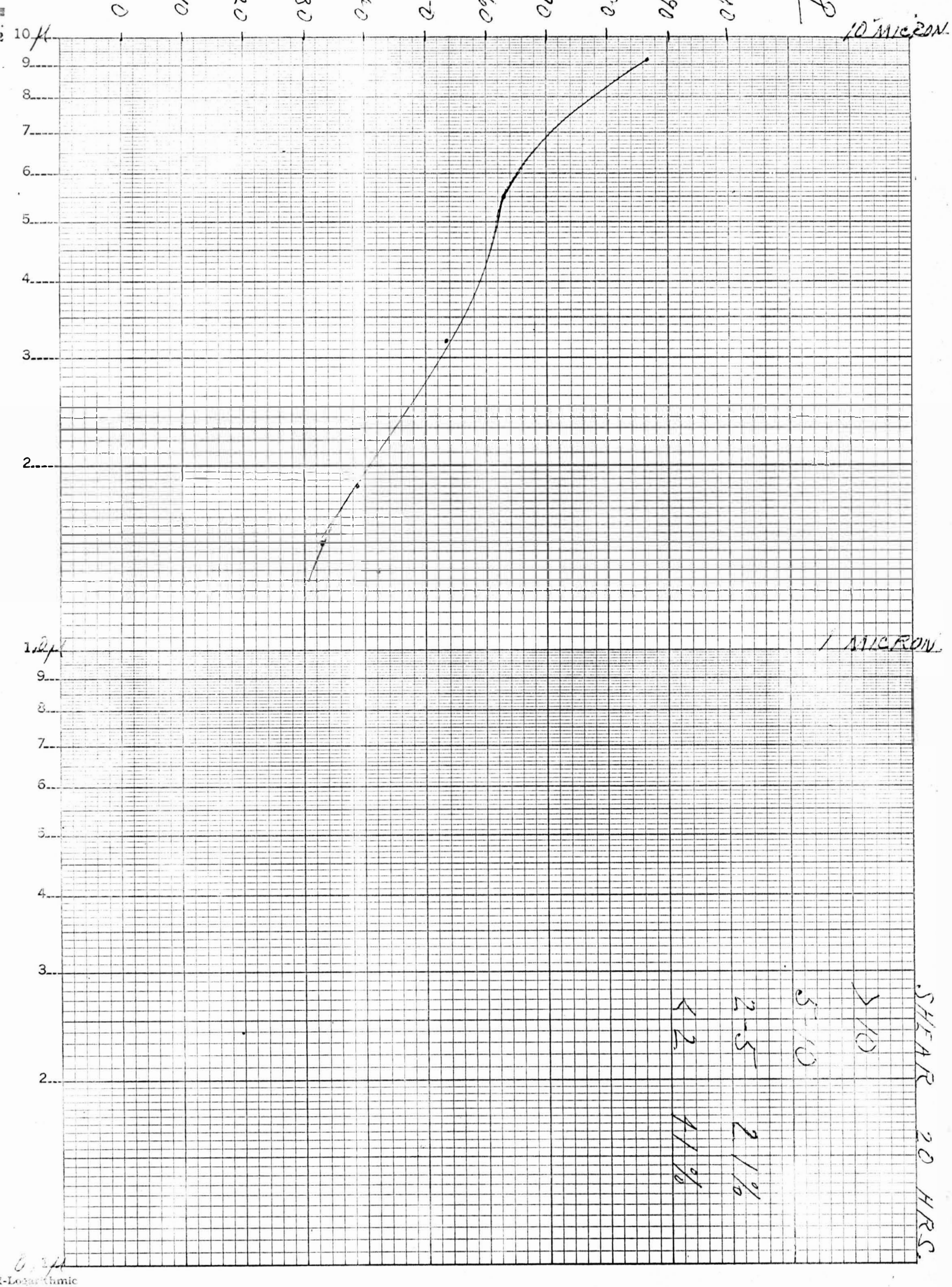
SHEAR ORIGINAL

> 10	19%
5-10	39.5%
2-5	30.5%
< 2	16.0%

mi-Logarithmic
es x 10 to the inch

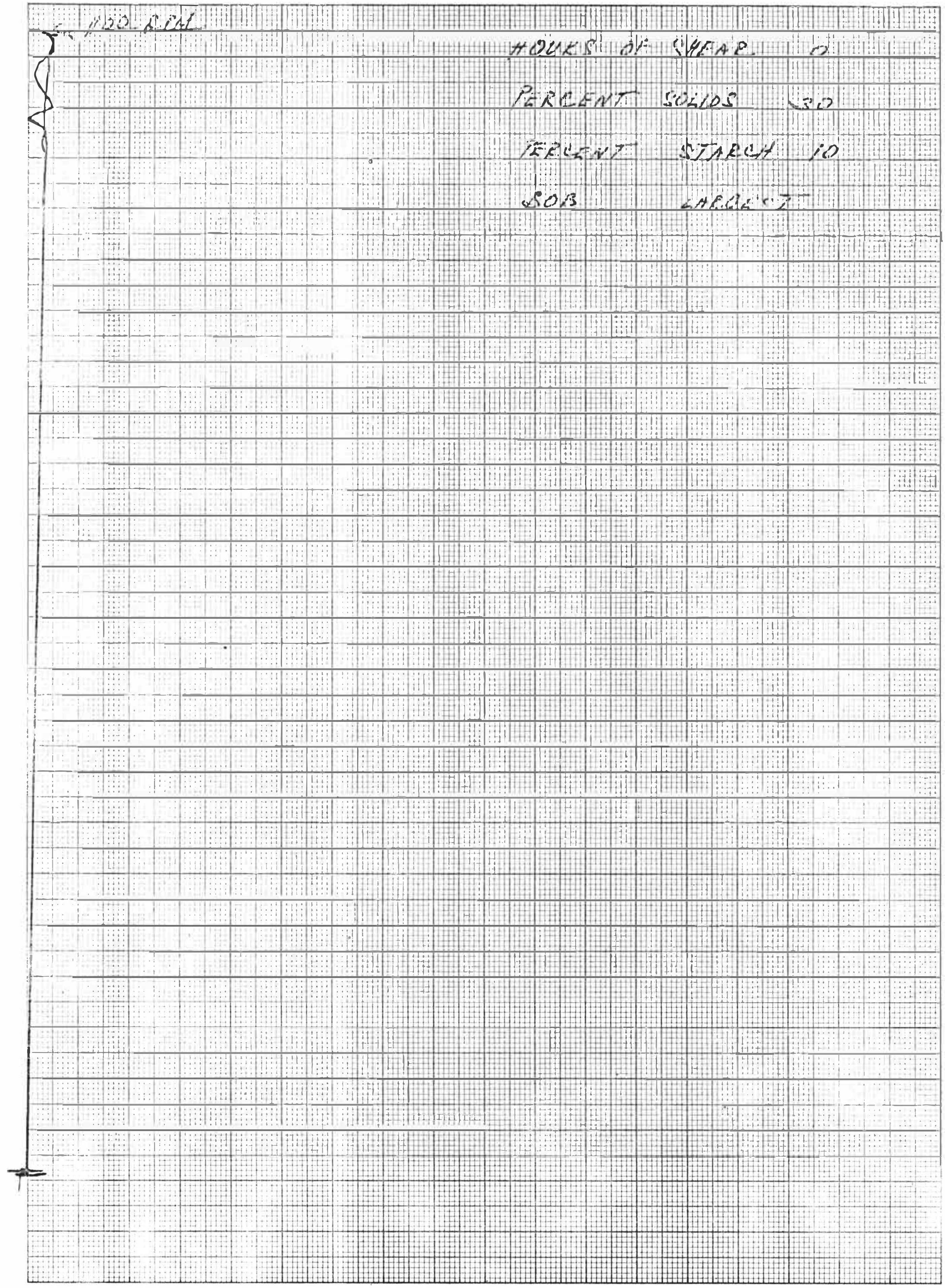


mi-Logarithmic
es x 10 to the inch


10 μ
9
8
7
6
5
4
3
2
1.0 μ
9
8
7
6
5
4
3
2
0.1 μ
10 MICRON
1 MICRON
SHEAR 20 HRS.
<2
2-5
5-10
>10
41%
21%
-Logarithmic
s x 10 to the inch

RHEOGRAMS FROM HERCULE'S VISCOMETER FOR DETERMINATION OF ABSOLUTE VISCOSITY

-188



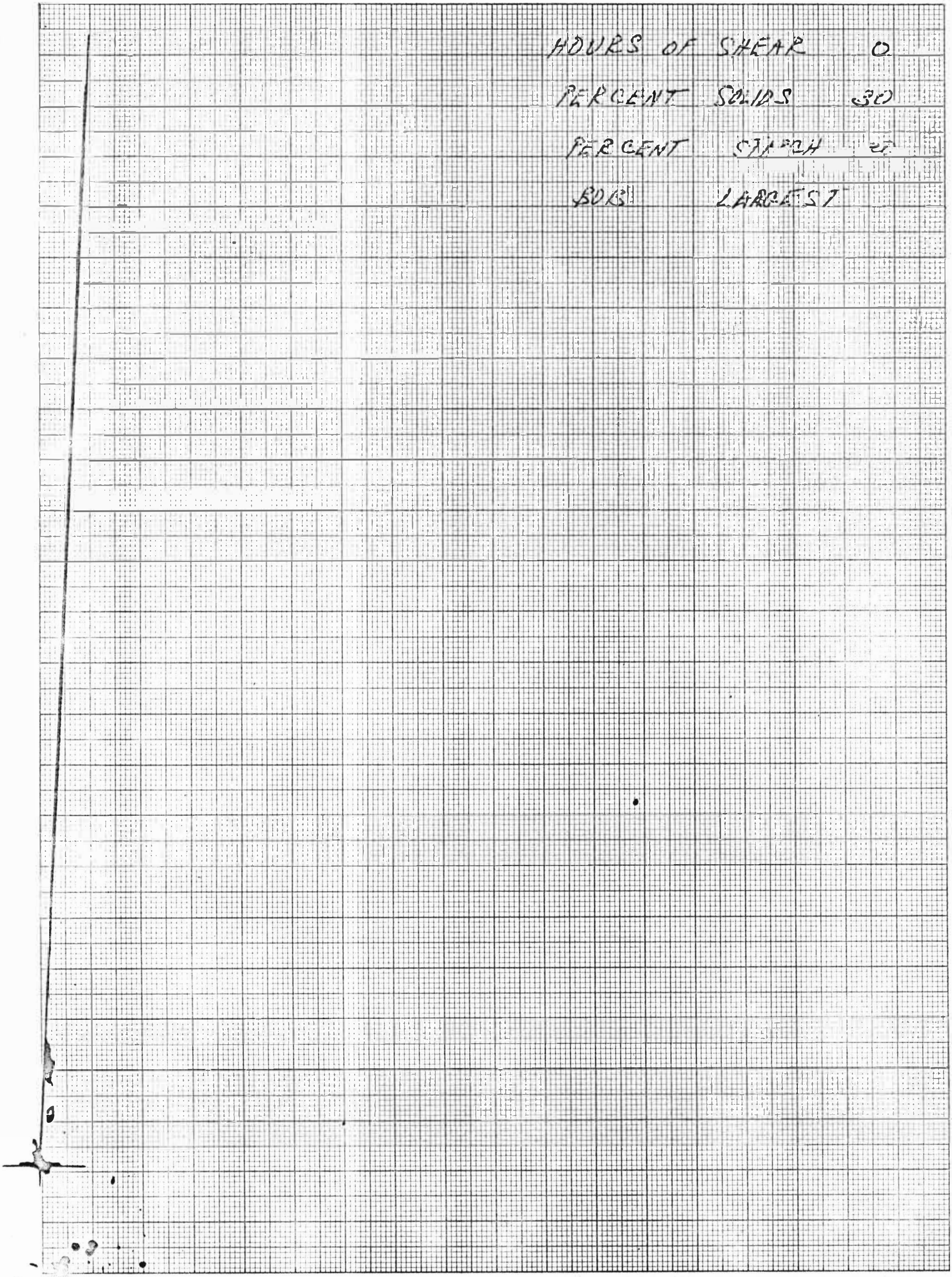
Millimeters to the Centimeter

HOURS OF SHEAR 0

PERCENT SOLIDS 30

PERCENT STARCH 20

BOB LARGEST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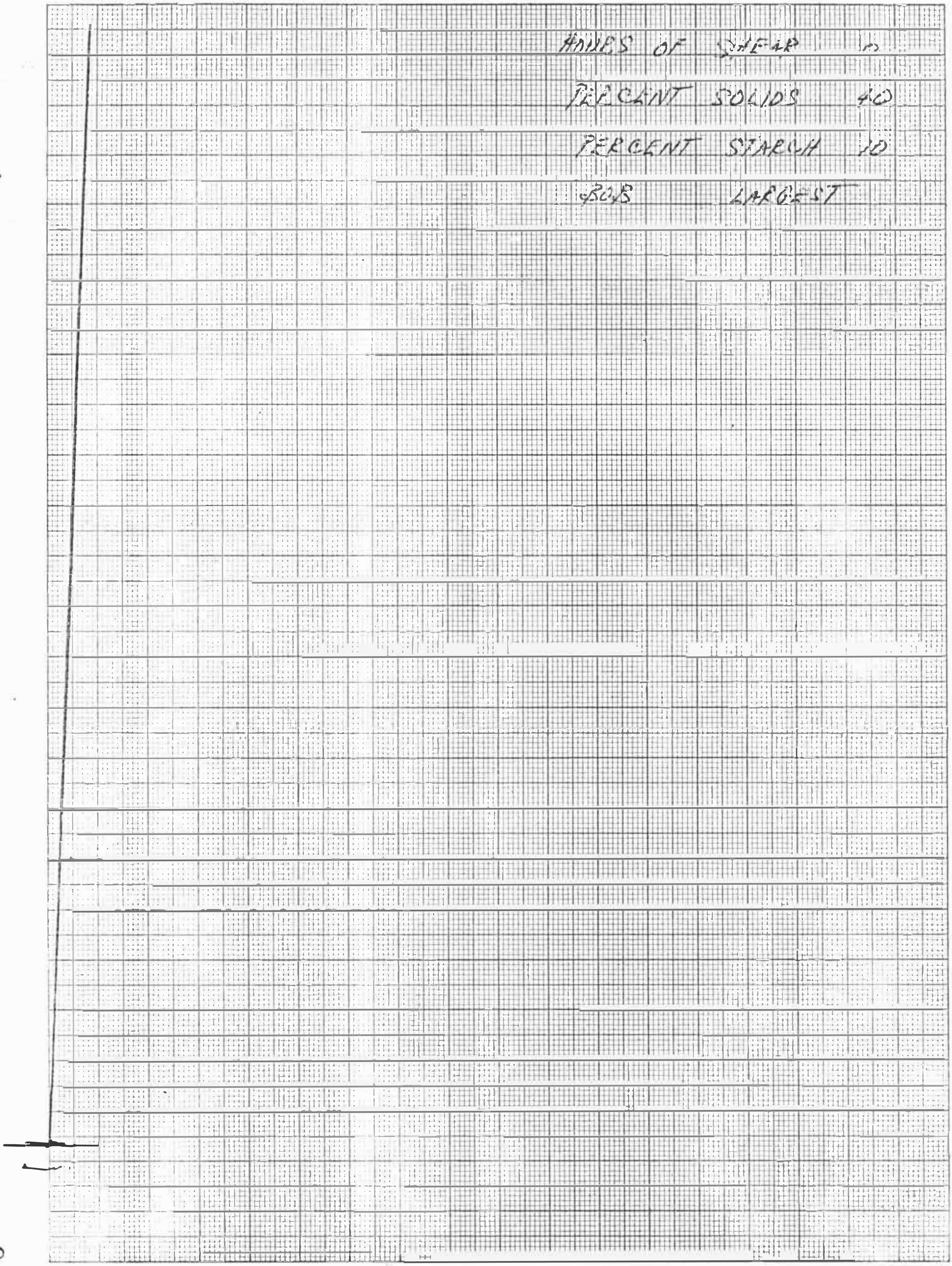
PERCENT SOLIDS 30
PERCENT STARCH [illegible]
BOX LARGEST
0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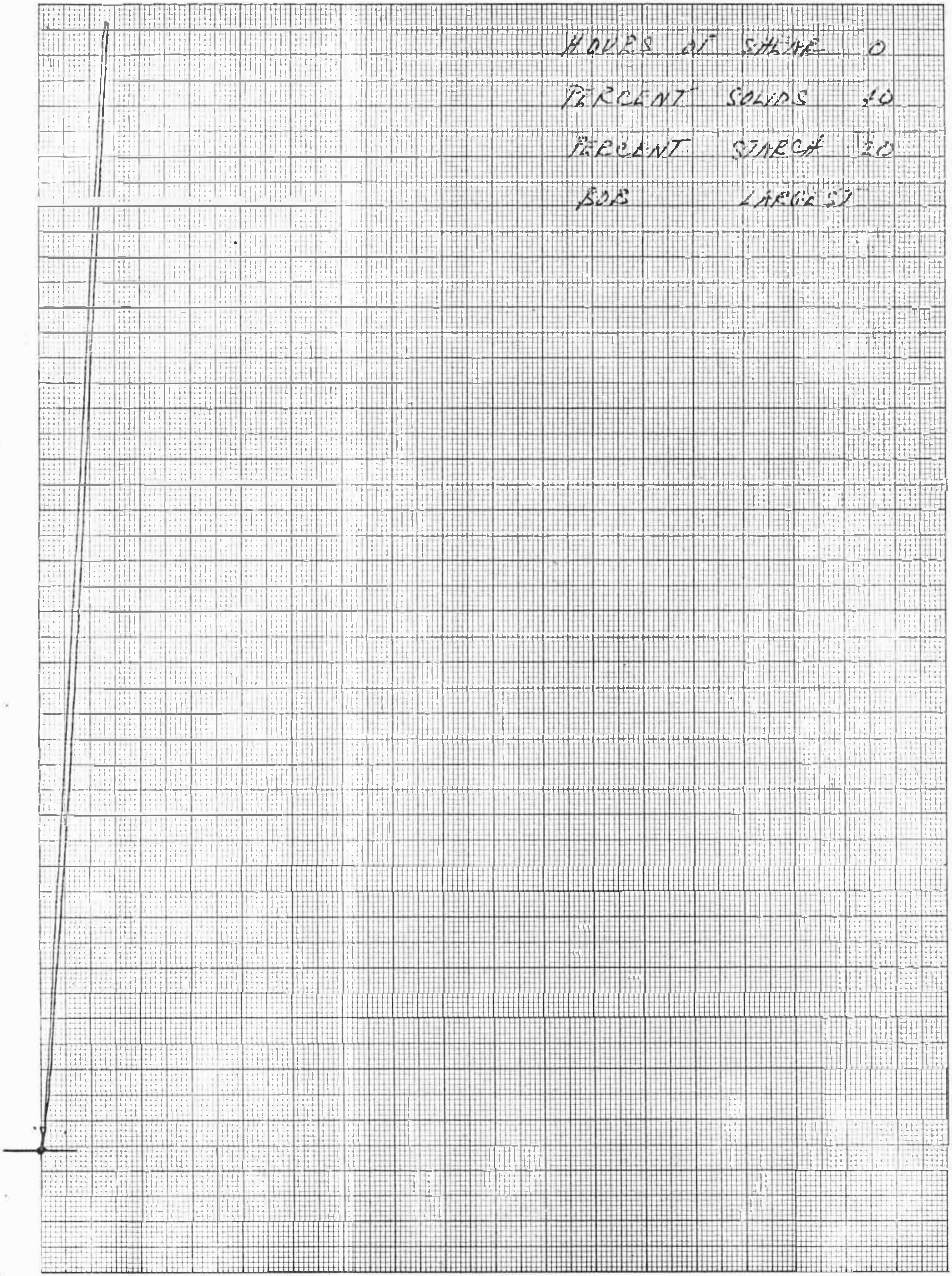
PERCENT SOLIDS 40
PERCENT STARCH 20
BOYS LARGEST



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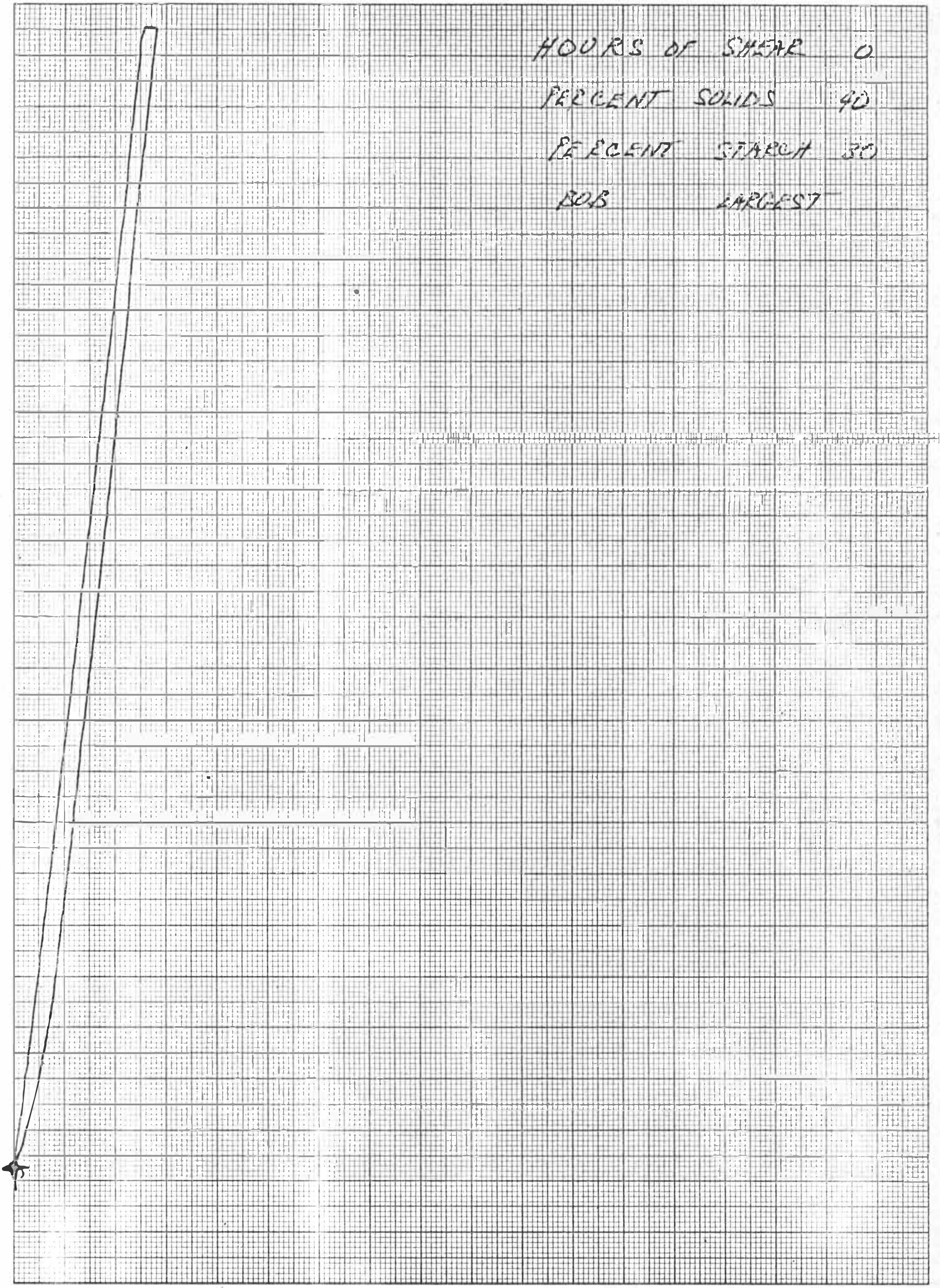
Millimeters to the Centimeter

188



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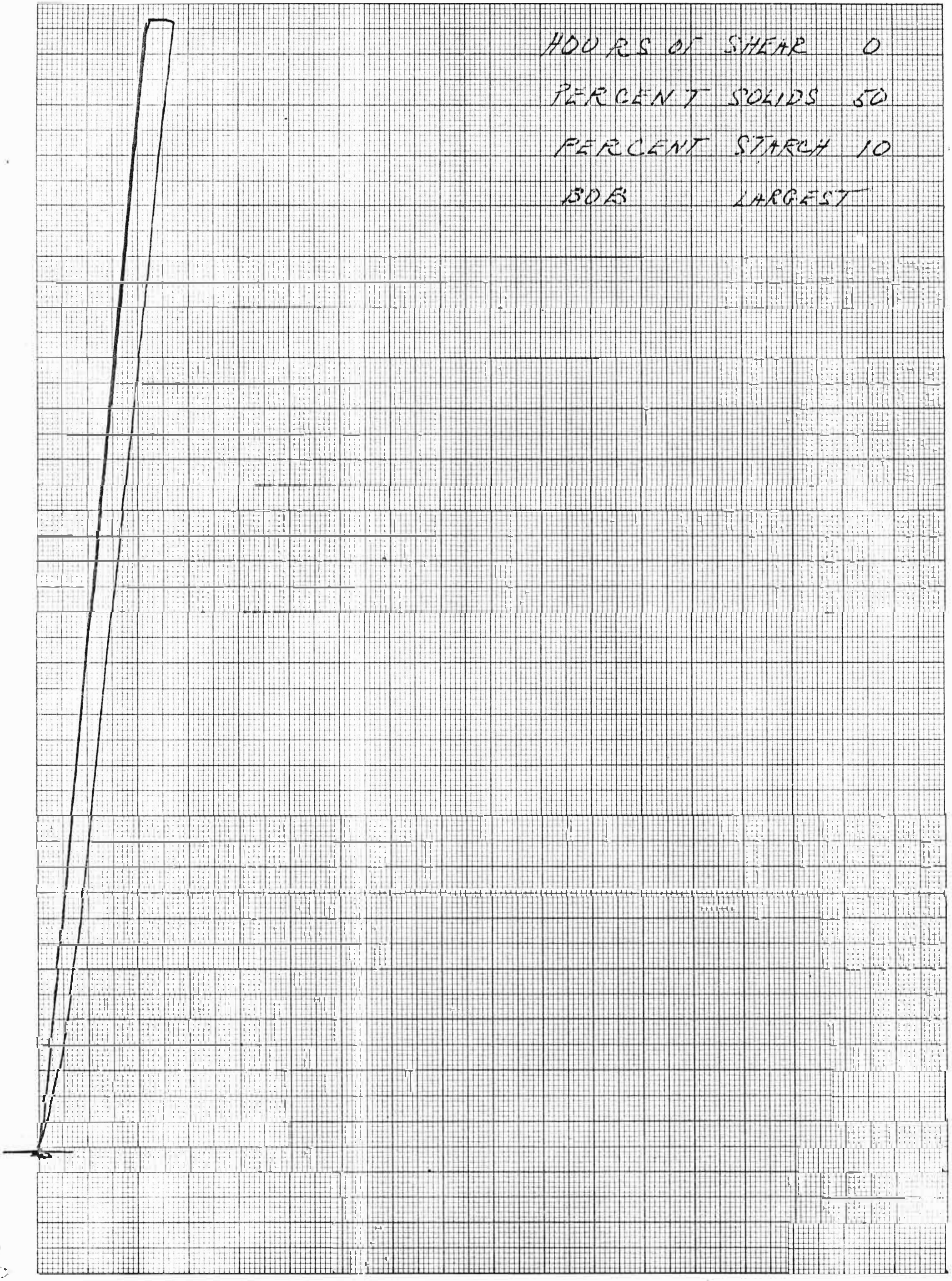
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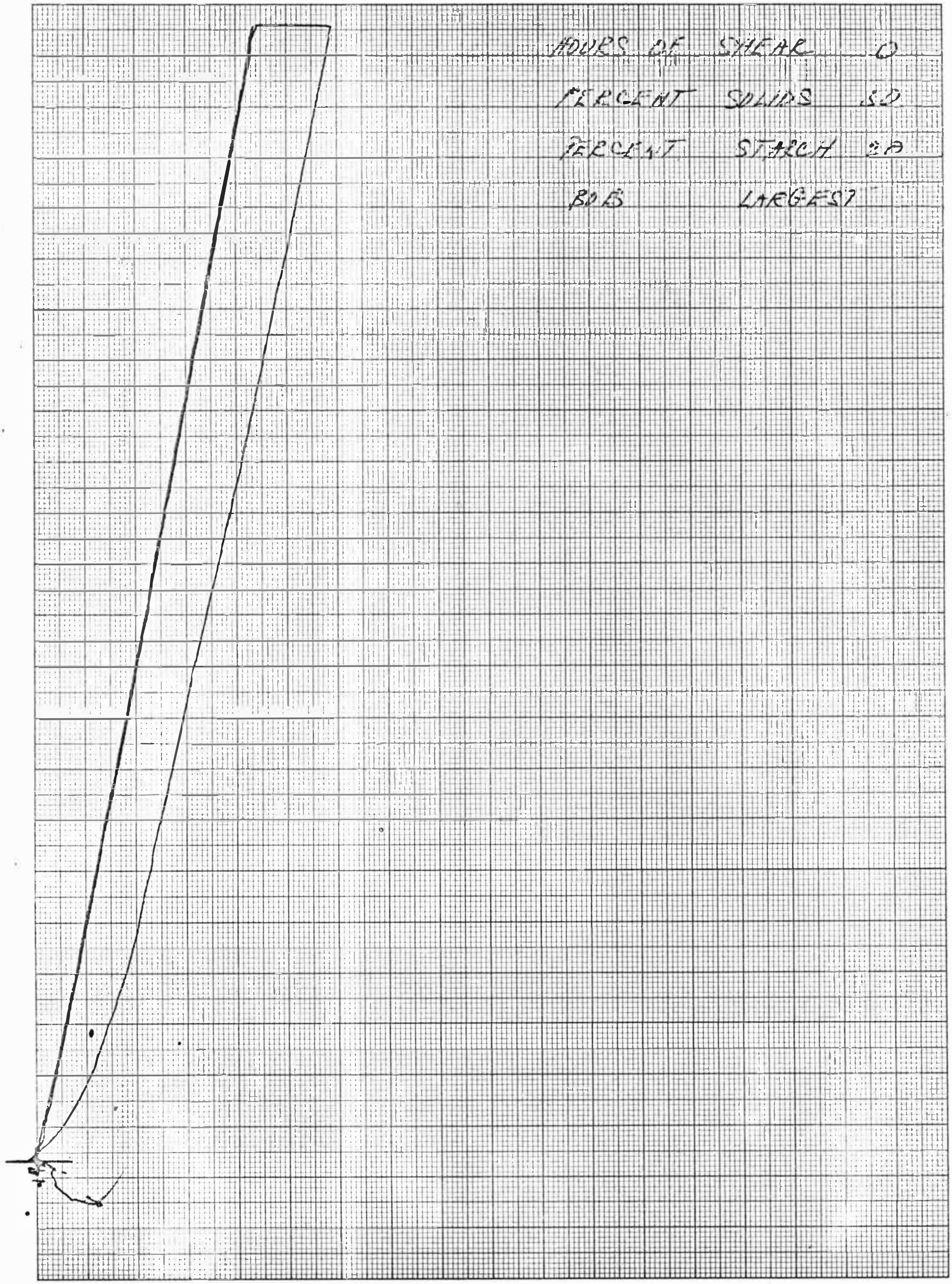
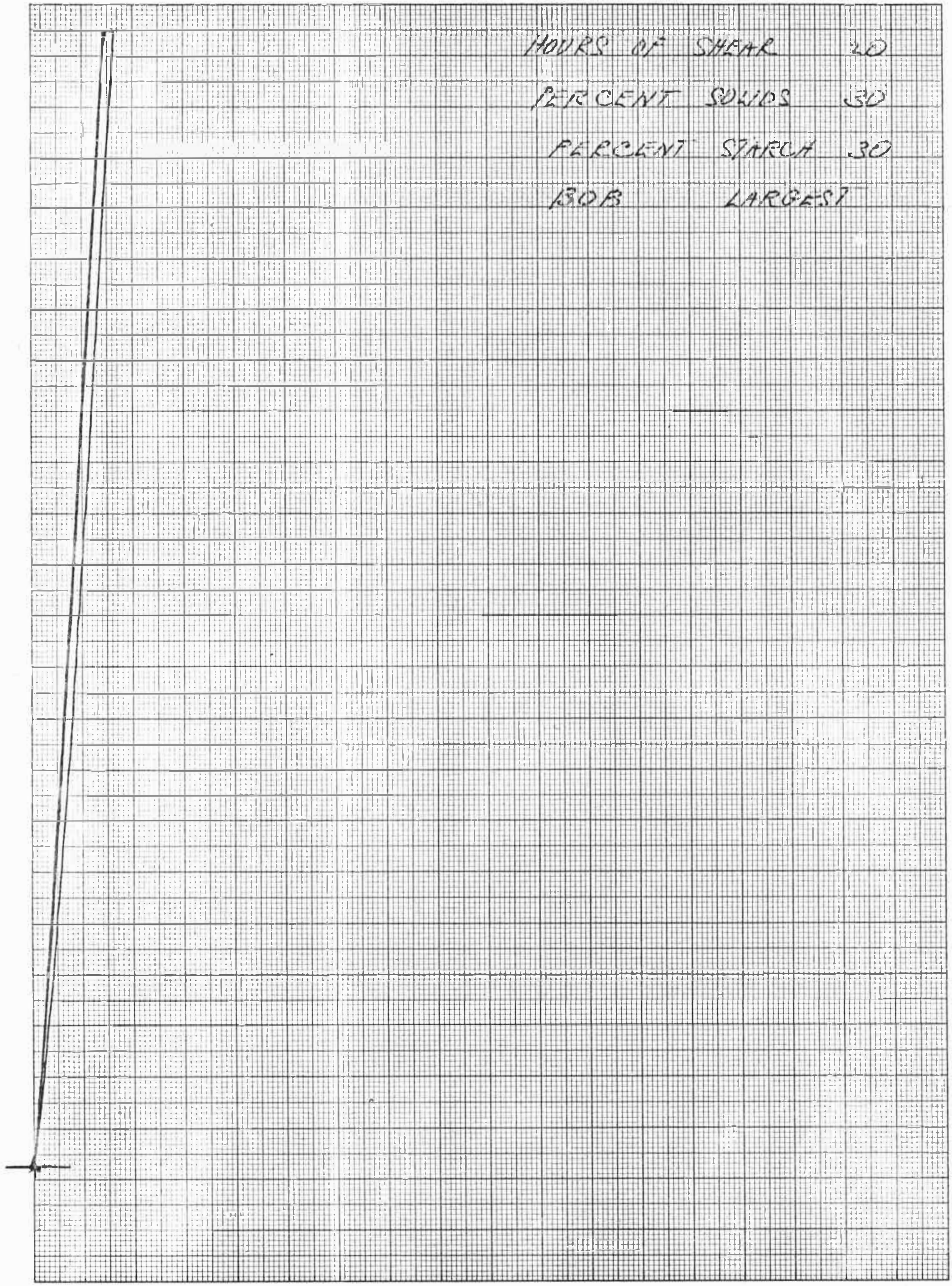
PERCENT SOLIDS 50
PERCENT STARCH 10
BOB LARGEST

188

(20.)



Millimeters to the Centimeter T-20


HOURS OF SHEAR 20
PERCENT SOLIDS 30
PERCENT STARCH 30
BOB LARGEST

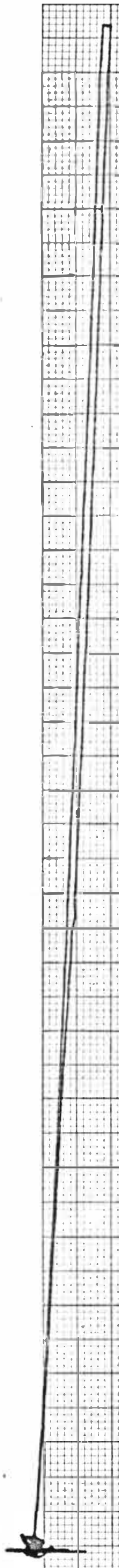
30-30-20

HOURS OF SHEAR 20

PERCENT SOLIDS 40

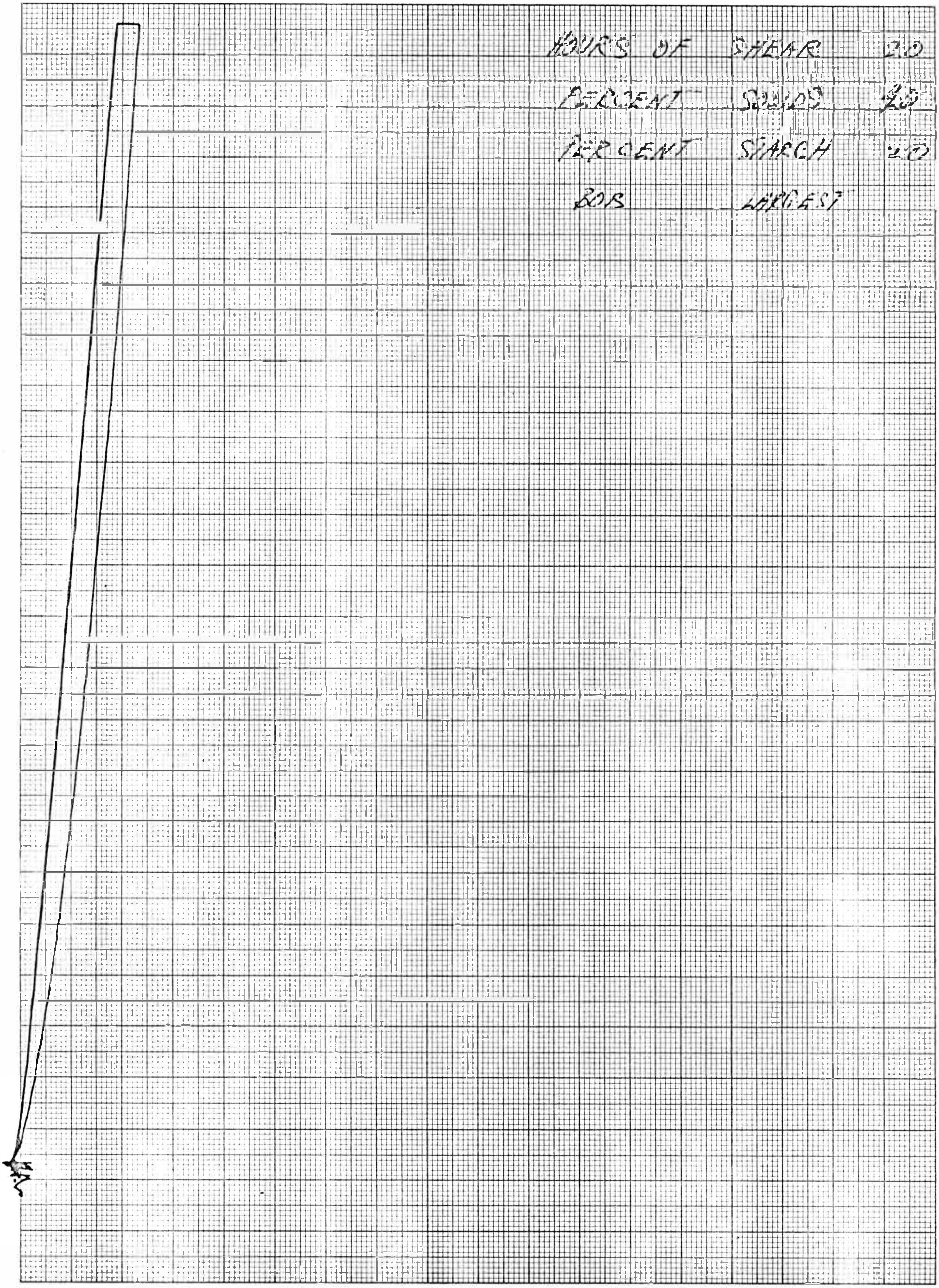
PERCENT STARCH 10

BOB LARGEST



illimeters to the Centimeter

40-10-20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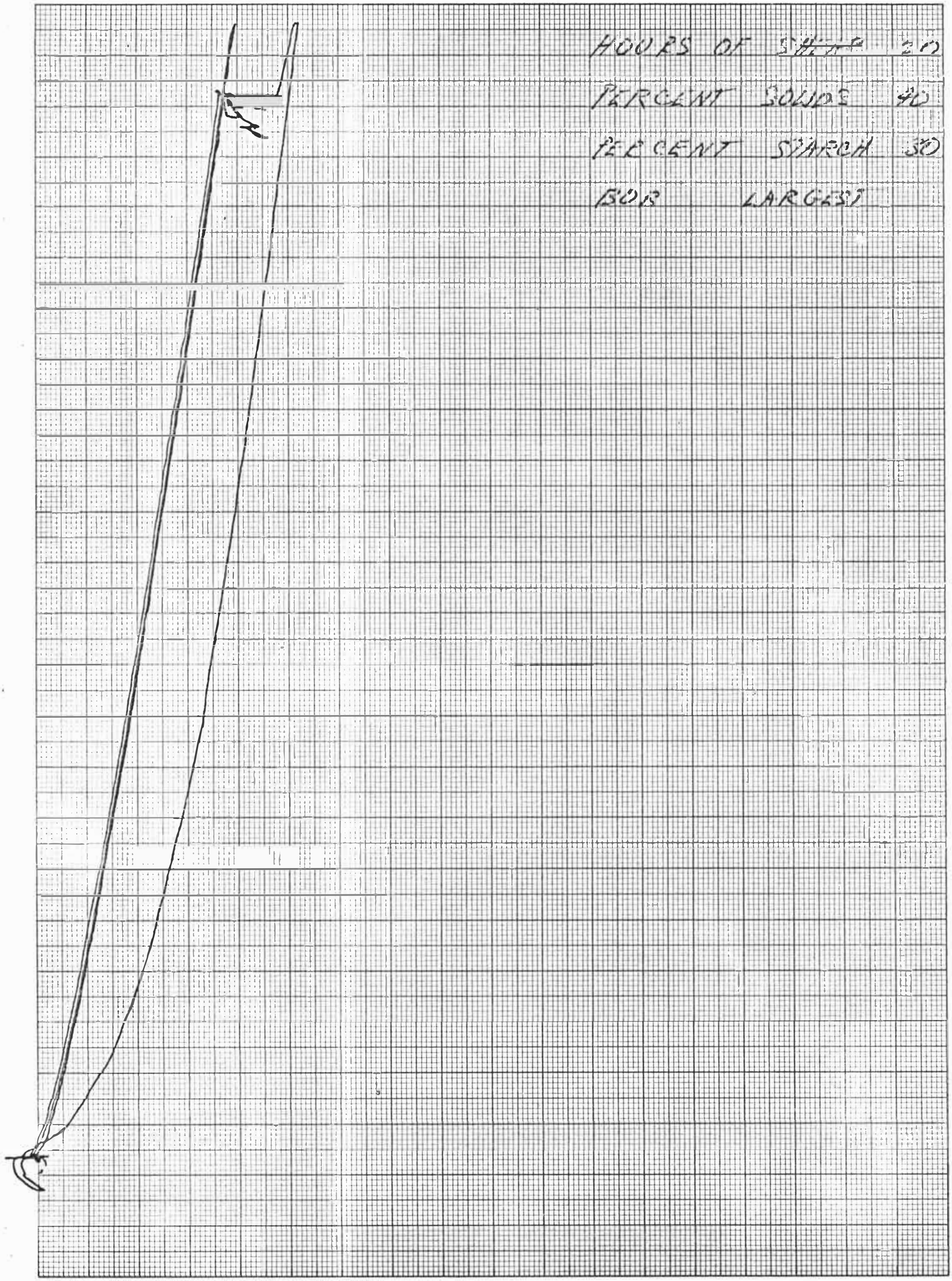
40-20-20

188

40-30-



Millimeters to the Centimeter

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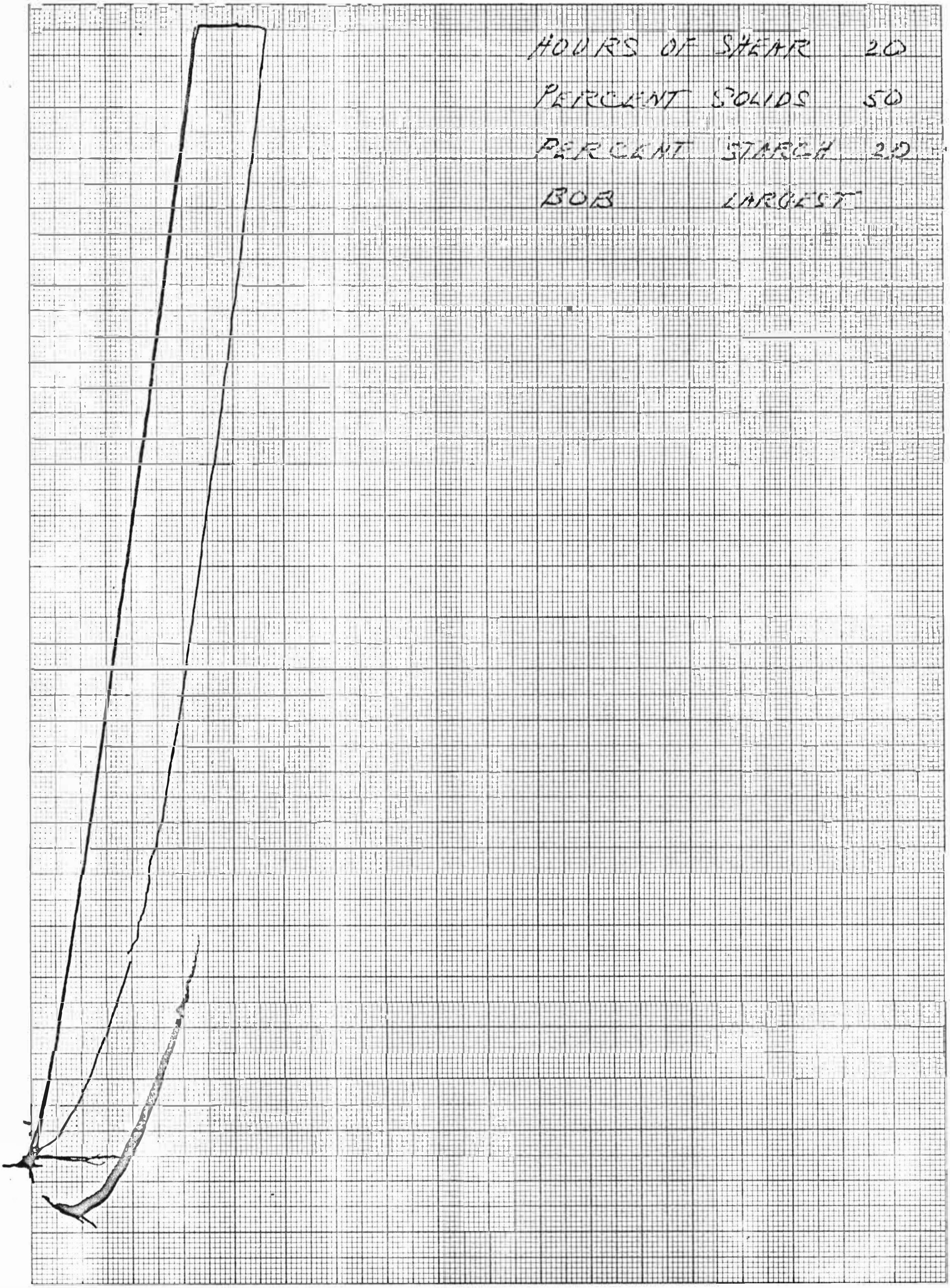
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PERCENT STARCH 20
BOB LARGEST

50-20-20