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The Influence of Hexamethylenetetramine and Formaldehyde on the Rheological Behavior of Casein Base Coating Colors

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THE INFLUENCE OF HEXAMETHYLENETETRAMINE AND FORMALDEHYDE ON THE RHEOLOGICAL BEHAVIOR OF CASEIN BASE COATING COLORS

BY

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SUMMARY

The experimental work presented in this thesis shows the effect of formaldehyde and hexamethylenetetramine on the flow characteristics of coating colors formulated with casein as an adhesive. All experiments were performed at room temperature.

In general, the pH had marked effect upon viscosity of the coating colors: the higher the pH value, the more viscous the coating color. Furthermore, formaldehyde reacted faster with proteinaceous coating colors than hexamine.

Specifically, coating colors containing four per cent hexamine showed little change in viscosity and flow behavior while coating colors at the neutral pH value of seven containing eight per cent hexamine showed significant changes in viscosity and rheological behavior in storage over a period of several weeks. The coating colors at alkaline pH values in the eight per cent hexamine series showed little change in viscosity and flow behavior after six weeks.

Finally, coating colors containing formaldehyde were very reactive showing viscosity increases for all pH values. After a period of two weeks, the flow behavior changed from practically Newtonian to thixotropic-pseudoplastic at pH values of seven and eight while coating colors at pH value of nine were initially thixotropic-pseudoplastic and became increasingly thixotropic in storage. The colors at pH value of ten were initially thixotropic-plastic and became increasingly thixotropic in storage.

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THE INFLUENCE OF FORMALDEHYDE AND HEXAMETHYLENETETRAMINE ON THE RHEOLOGICAL BEHAVIOR OF CASEIN BASE COATING COLORS

Introduction

This thesis is designed to study the effect of formaldehyde and hexamethylenetetramine on the flow characteristics of coating colors formulated with casein as an adhesive.

Coating Color

A coating color, as used in the paper industry, consists of varying ratios of pigment and adhesive dispersed in a water. This color must meet several requirements. It must penetrate and bond satisfactorily to the paper surface. It must flow in such a manner to permit the required degree of spreading at machine speed and must have the property of leveling and settling when applied to the paper surface. When dried, it should give a smooth surface that can be calendered if necessary to produce gloss at reasonably low pressures. These properties are influenced mainly by the adhesive although the pigment chosen does have related effects (1).

Casein

Casein is a product prepared from the skim milk of cows. It is a phosphoprotein (2) which is amphoteric; i.e., it reacts with both acids and bases to form salts (3). Casein is used for many purposes, among them as a plastic and as an adhesive. In both cases, formaldehyde and its related compounds are used to harden the casein and to impart resistance to water.

Formaldehyde

Formaldehyde is an organic gas at standard conditions and belongs to the group of aldehydes. It is sold in aqueous solution of about 37% by weight with 10-15% methanol added to prevent polymerization. Its commercial name is Formalin 40% which means it contains 40 grams of the active chemical in 100 milliliters of the solution and is equivalent to 37 per cent by weight (4).

Hexamethylenetetramine

Hexamethylenetetramine is the reaction product of six moles of formaldehyde and four moles of ammonia. It is made commercially by combining equal volumes of 26^{o} Be' ammonia and Formalin 40%. Hexamethylenetetramine is an odorless crystalline compound and is available as granules or powder. It sublimes around 263^{o}C. without melting and with partial decomposition. It is somewhat volatile at lower temperatures and burns with a smokeless flame when subjected to fire (4, 5). This compound is also known commercially as Formin, Cystamin, Cystogen, Quinoform, and Urotropin. Its chemical formula is $C_6H_{12}N_4$. (4)

Reactions of Formaldehyde and Hexamethylenetetramine

The interaction of formaldehyde or hexamethylenetetramine with a casein bound coating mixture produces a chemical reaction which is obscure, but it is believed that the hardening depends upon the formation of cross linkages as a result of the coupling of amino groups by methylene bridges (6) or the production of triformals (7). Formaldehyde must be diluted consider-

ably to avoid thickening of a coating mixture. Factors influencing thickening of the coating color are the type of alkali used in solubilizing the casein, the amount of formaldehyde, the temperature, and the rate of addition (3). Ammonia is recommended to cut the casein (8) because it results in greater fluidity although there is a slight loss in adhesive strength (9). Since the order of addition of the ingredients of the coating mixture is important, the casein should be cut with an alkali; thereupon, it should be mixed with the pigment, and finally the formaldehyde should be added. It is recommended that if a 40% solution is used, 3.5 per cent of this solution based on the casein be added to the mixture (8). The pH of the coating color should be neutral or slightly acidic (9). Room temperature is suitable for mixing; the formaldehyde should be added very slowly with good agitation (10).

Hexamethylenetetramine, though not as effective as formaldehyde, may be used in greater proportions with less precautions (3). It is soluble in water and reacts slowly with casein solutions at room temperature. When the solution is heated to about 150^{o}F., hexamethylenetetramine reacts quickly and will thicken the coating color (10). The order of mixing the ingredients is the same as that used with formaldehyde.

Since formaldehyde and hexamethylenetetramine have profound influence on flow characteristics of casein base coating colors, knowledge of the theory of flow is necessary.

Rheology

Rheology is the science of the flow of matter. In order to cause flow of matter, a force must be applied and a means of measuring the results of the

force must be used. There are several terms used synonymously in describing this force among them ~~which~~ are shearing stress and shearing force. Likewise, the actual flow itself is used synonymously with the rate of shear, rate of flow, fluidity, or reciprocal of viscosity.

There are four types of flow which require consideration. For Newtonian flow, as shown in figure 1, characteristic of such fluids as water and mineral oil, the rate of shear is directly proportional to the shearing stress and its representative curve is linear (11).

Plastic or Bingham flow, as shown in figure 2, is that type of flow which is characteristic of pastes, printing inks, and clay-water suspensions. It is the only type of flow which has a yield value. The yield value is the minimum shearing force which is necessary to start continuous smooth flow. These types of material have yield value because they have a flocculated structure when at rest. Flocculation is believed to be due to an interaction of the particles to each other or to the vehicle in which they are suspended. A shearing force is necessary to separate the flocculated particles until it becomes a dispersed system; i.e., the interaction of the particles is no longer present and the particles act individually (11). Slippage or plug flow occurs with plastic materials. (A solid plug made by particles which are held together by the force of flocculation is lubricated by a thin layer of the vehicle and when a force is applied, the plug moves as a single piece) (12).

Pseudoplastic flow, as shown in figure 3, is that type of flow which is characteristic of solutions of nitrocellulose, vinyls, and rubbers. At

rest, these materials have a random orientation of molecules. When a shearing force is applied, these molecules have a tendency to align themselves and as the force increases, the degree of alignment also increases and the viscosity decreases (11).

Dilatant flow, as shown in figure 4, is that type of flow which is characteristic of fluids such as some closely packed pigment dispersions at high solids content. Quicksand is a good example of dilantancy. The resistance to flow increases at a greater rate than the increase in the rate of shear. As the system is disturbed, the voids between the particles are dilated resulting in insufficient liquid to fill them and causing the system to appear dry.

Thixotropy is a flow behavior often found in materials which exhibit plastic, dilatant, or pseudoplastic flow. A hysteresis loop always indicates the presence of thixotropy. The "up" curve shows decreasing viscosity with increasing shearing stress while the "down" curve shows constant viscosity with decreasing shearing stress. It is because the oriented pattern does not have time to "build up" that the "down" curve is linear.

It should be noted that plastic, pseudoplastic, and dilatant materials if submitted to extreme dilution, will eventually exhibit Newtonian flow (11).

FIG. 1

NEWTONIAN FLOW

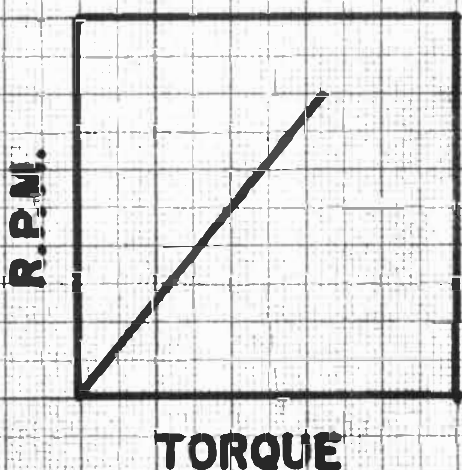


FIG. 2

PLASTIC FLOW

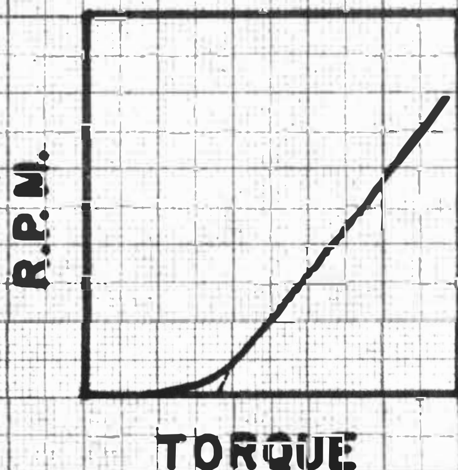


FIG. 3

PSEUDOPLASTIC FLOW

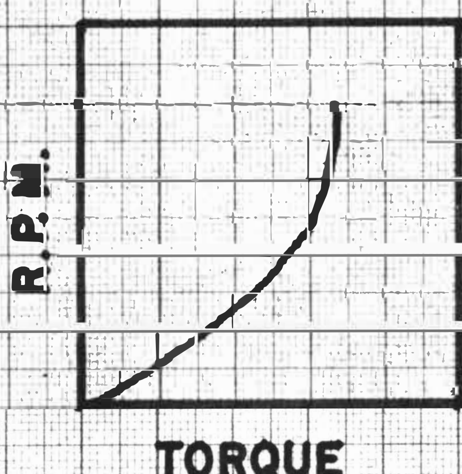
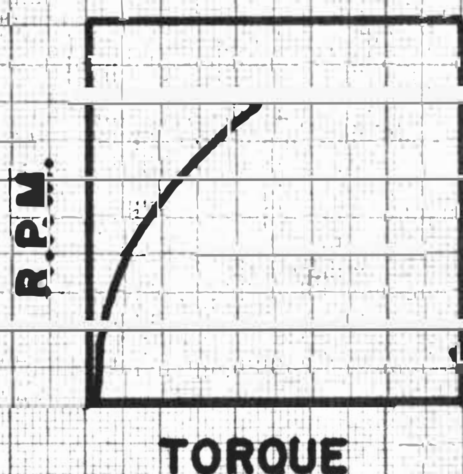


FIG. 4

DILATANT FLOW



EXPERIMENTAL DESIGN

It will be the purpose of the experimentation to reveal what influence hexamethylenetetramine and formaldehyde have on the rheological behavior of casein bound coating colors. The following set of conditions will be used for the experiment:

1. The Hercules High Shear Viscometer will be used to study the rheological behavior of the coating colors and to establish the data required for calculation of apparent viscosity at high shear.
2. The Brookfield Viscometer will be used to determine values of coating colors at low rate of shear.
3. The coating colors will be prepared at total solids that will provide for rheograms with significant patterns as a result of changing conditions of shear.
4. The coating colors will be adjusted to specific pH values and measured at regular intervals over a period up to six weeks.
5. The casein used in preparing the coating colors will be caustic cut to avoid chemical interference with the additives, hexamethylenetetramine and formaldehyde.
6. All experiments will be performed at room temperature.

The results of the experiments will be interpreted and conclusions will be drawn.

COATING COLORS

Materials Used

For the coating colors applied in the experiments the following raw materials were included:

Only clay was used as pigment. H. T. predispersed clay (Minerals & Chemicals Corporation of America) was chosen because it has a relatively low average particle size in the 78-82 per cent range below two microns in equivalent spherical diameter.

Casein was used as adhesive. A good grade of Argentine casein was selected.

Dowicide "G" was employed as preservative to prevent or retard spoilage of casein and the coating color.

All coating colors were prepared with distilled water.

Commercial grades of formaldehyde (40%) and hexamethylenetetramine were added to the clay-casein mixtures whenever required.

Preparation

For one batch of coating color, 320 grams of casein were soaked under agitation in 1110 grams of water for 15 minutes. Four per cent caustic soda as a ten per cent solution; i.e., 12.8 grams of caustic soda dissolved in 115.2 grams of water were added. The temperature of the mixture was raised to 140 F. and

maintained at that level for 20 minutes. The colloidal solution was permitted to cool. Thereupon 10.0 grams of Dowicide "G" dissolved in 40.0 grams of water were added to the adhesive.

A Day mixer with sigma blades was charged with 2000 grams of clay. A quantity of 1600 grams of casein solution was added slowly. The amount of dilution water added to adjust the coating color to 50 per cent solids was 1005 grams. Enough water was added to promote good shearing action and allowed to mix for 15 minutes. The remainder of the dilution water was then added slowly over a time interval of 30 minutes. Just prior to discharging the mix, the coating formulation was protected with 11.6 grams of Dowicide "G" dissolved in 48.0 grams of water. The discharged mix was stored in sterilized jars at room temperature.

Application of Additives and Adjustments for pH Values and Solids Content

To produce coating colors for the control series, i.e. without additive, three 800 gram portions were taken from the master batch at 50 per cent solids. In order to adjust these portions to 45 per cent solids and to pH values of 7.0, 8.0 and 9.0, 88.8 grams of dilution water were added to each of these 800 gram portions. Small amounts of the dilution water were replaced with acetic acid or ammonium hydroxide to adjust these 800 gram portions to pH values of 7.0, 8.0, and 9.0.

To produce coating colors for the four per cent hexamine series, i.e. four per cent based on the weight of the casein, one 800 gram portion was taken from the master batch at 50 per cent solids. In order to adjust this portion to 45 per cent solids and pH value of eight, 22.0 grams of a 10 per cent solution of commercial hexamine plus 66.7 grams of dilution water were added to this 800 gram portion. A small amount of the dilution water was replaced with a dilute solution of acetic acid to adjust the pH value of the color to 8.0

To produce coating colors for the eight per cent hexamine series, i.e. eight per cent hexamine based on the weight of casein, three 800 gram portions were taken from the master batch at 50 per cent solids. In order to adjust these portions to 45 per cent solids and pH values of 7.0, 8.0, and 9.0, 44 grams of a 10 per cent solution of commercial hexamine plus 44.6 grams of dilution water were added to each of these 800 gram portions. Small amounts of the dilution water were replaced with dilute solutions of acetic acid or ammonium hydroxide to adjust the individual 800 gram portions to pH values of 7.0, 8.0, and 9.0 respectively.

To produce coating colors for the five per cent formaldehyde series, i.e. five per cent of (40%) formaldehyde solution based on the weight of casein, four 800 gram portions were taken from the master batch at 50 per cent solids. In order to adjust these portions to 35 per cent solids and pH values of 7.0, 8.0, 9.0 and 10.0, 1.78

grams of (40%) commercial formaldehyde solution plus 343 grams of dilution water were added to each of these 800 gram portions. Small amounts of the dilution water were replaced with dilute solutions of acetic acid or sodium hydroxide to adjust the individual 800 gram portions to pH values of 7.0, 8.0, 9.0 and 10.0 respectively.

METHODS OF MEASUREMENT

Hercules High Shear Viscometer

The instrument used to produce all the rheograms shown in this report was the Hercules High Shear Viscometer. A 100,000 dyne-centimeter spring with the "B" bob was employed to draw the rheograms. While time required for the up-curve to a maximum of 1050 r.p.m. was from 25 to 30 seconds, the down curve to 0 r.p.m. required 10 seconds only. In order to record smooth curves it was necessary to centrifuge the coating colors for a maximum period of ten minutes to reduce foam and entrapped air.

The formula used for calculation of the apparent viscosity from the rheograms was that developed by Margules (13). This formula relates torque and angular velocity to the viscosity of Newtonian liquids.

The Brookfield Viscometer

The Brookfield Viscometer was employed as a means of checking the apparent viscosities of the coating colors obtained at 50 r.p.m. against those calculated from the rheograms at 1050 r.p.m. The numerical results were different because the shearing force of the Hercules High Shear Viscometer was much greater than that of the Brookfield instrument. However, the values obtained by both methods of measurement are related and their difference is significant. Spindles were chosen to obtain accurate viscosity readings.

PRESENTATION OF DATA

The data obtained on the rheological properties of casein bound coatings utilizing hexamine and formaldehyde as additives are found in Tables I and II, and Figures 1 through 29.

DISCUSSION OF RESULTS

The experimental results in this work are divided into four parts: Control Series, Four Per Cent Hexamine Series, Eight Per Cent Hexamine Series, and Five Per Cent Formaldehyde Series. It was found that colors prepared at 45 per cent solids would provide rheograms with significant patterns for the control and two hexamine series as a result of changing conditions of shear. To produce significant rheograms for the formaldehyde series, it was necessary to reduce the solids to 35 per cent.

The Control Series

This series was made from coating colors containing casein, clay, and preservative only. The control coatings were slightly thixotropic-pseudoplastic as shown in Curve Numbers 1, 2, and 3. Tables I and II illustrate that as the pH values increase from seven to nine, the apparent and Brookfield viscosities of these colors increase significantly.

The Four Per Cent Hexamine Series

This series was made from clay-casein coating colors containing four per cent hexamine based on the weight of the casein. Curves

Number 4, 5, 6, and 7 reveal these coatings to be likewise slightly thixotropic-pseudoplastic. Tables I and II show that the apparent and Brookfield viscosities of these colors did not change significantly over a period of two weeks.

The Eight Per Cent Hexamine Series

This series was made from clay-casein coating colors containing eight per cent hexamine based on the weight of casein. Curves Number 8, 9, 10, and 11 show the effect of time on the flow properties of this color at the pH value of seven. This coating changes from practically Newtonian to thixotropic-pseudoplastic after a period of six weeks. The apparent and Brookfield viscosities as shown in Tables I and II for this pH value show significant increases over the above mentioned period of time.

Curves Number 12, 13, and 14 show the rheological behavior to be thixotropic-pseudoplastic at pH value of eight. The apparent and Brookfield viscosities show no significant changes after six weeks (See Tables I and II).

Curves Number 15, 16, and 17 illustrate the flow properties to be thixotropic-pseudoplastic at pH value of nine. The apparent and Brookfield viscosities show no significant changes after six weeks (See Tables I and II). In this series there is a trend toward increasing viscosities as the pH values become larger.

The Five Per Cent Formaldehyde Series

This series was made from clay-casein coating colors containing five per cent formaldehyde (40%) based on the weight of casein. Curves Number 18, 19, and 20 at pH value of seven and Curves Number 21, 22, and 23 at pH value of eight show the flow behavior and Tables I and II point out the viscosity changes of these colors after a period of two weeks. The flow properties change from practically Newtonian to thixotropic-pseudoplastic and the apparent and Brookfield viscosities show corresponding significant increases after this two week interval.

Curves Number 24, 25, and 26 indicate the rheological behavior and Tables I and II reveal the apparent and Brookfield viscosities when the color has the pH value of nine. Measurements of this color were taken over a time interval of one week. These colors are thixotropic-pseudoplastic and the amount of thixotropy increases as does the apparent and Brookfield viscosities after one week.

Curves Number 27, 28, and 29 show the rheological behavior and Tables I and II indicate the apparent and Brookfield viscosities when this color has the pH value of 10. Measurements of this color after one week reveal this color to be thixotropic-plastic and the amount of thixotropy increasing with time.

A comparison of results obtained at pH values of 7, 8, 9, and 10 in this series indicates increasing viscosity with increasing pH.

CONCLUSIONS

The following conclusions were drawn from the results of the experimental work:

General Conclusions

1. The pH had marked effect upon viscosity of the coating colors: the higher the pH value, the more viscous the coating color.
2. At room temperature formaldehyde reacted faster with proteinaceous coating colors than hexamine.

Specific Conclusions for Hexamine Containing Colors

3. The measurements taken for the four per cent hexamine series showed no significant change in viscosity or rheological behavior over a period of two weeks. The rheograms indicated these colors to be thixotropic-pseudoplastic.
4. The measurements taken for the colors at the neutral pH value of seven in the eight per cent hexamine series revealed a tenfold increase in viscosity after six weeks. The rheograms for this series indicated that the rheological behavior changed from practically Newtonian to thixotropic-pseudoplastic at the end of six weeks.

5. The measurements taken for the alkaline pH values of eight and nine in the eight per cent hexamine series showed practically no change in viscosity and flow properties over a time interval of six weeks. The rheograms indicated these colors to be thixotropic-pseudoplastic.

Specific Conclusions for Formaldehyde Containing Colors

6. The measurements taken for the pH values of seven and eight in the five per cent formaldehyde series revealed a significant increase in viscosity and change in flow behavior from practically Newtonian to thixotropic-pseudoplastic after a period of two weeks.
7. The measurements taken for the pH values of nine in the five per cent formaldehyde series indicated after one week an accelerated substantial increase in viscosity and thixotropy. Again, this color was thixotropic-pseudoplastic.
8. The measurements taken for the pH value of ten in the five per cent formaldehyde series showed after one week substantial increases in viscosity and thixotropy. This color was thixotropic-plastic.

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TABLE I - RHEOLOGICAL PROPERTIES OF COATING COLORS*

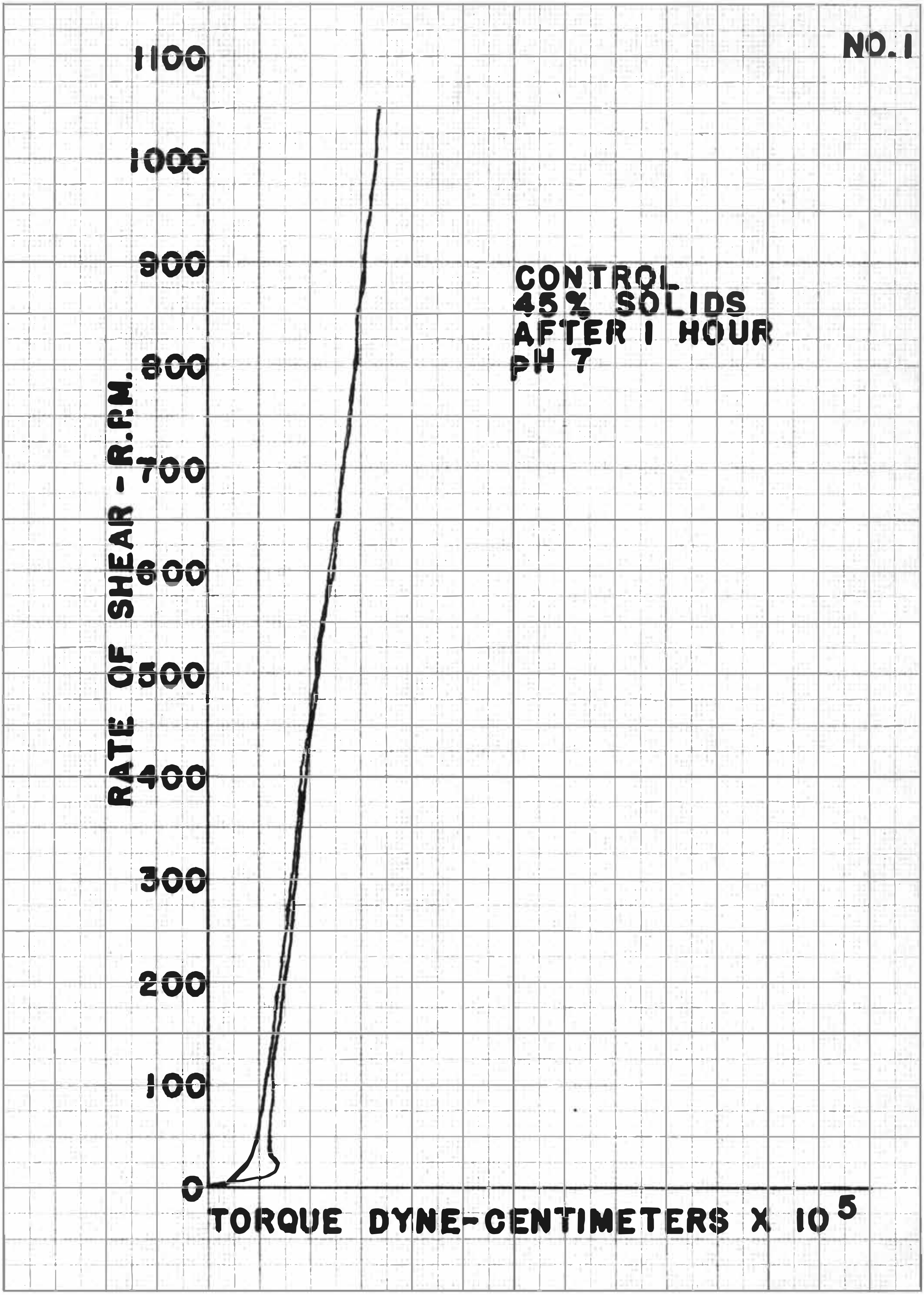
Curve No.	Storage Time	% Additive Based on Casein Solids Hexa.	Form.	pH	Total Solids of Color %	Apparent Viscosity 1050 r.p.m.	Brookfield Viscosity 50 r.p.m.	Type of Rheogram
1	1 hr.	----	----	7	45	4.54	105.6	T-PSPL**
2	1 hr.	----	----	8	45	4.80	120.8	T-PSPL
3	1 hr.	----	----	9	45	6.80	152.0	T-PSPL
4	4 hrs.	4%	----	8	45	6.40	115.6	T-PSPL
5	1 day	4%	----	8	45	6.80	120.0	T-PSPL
6	7 days	4%	----	8	45	7.20	122.0	T-PSPL
7	14 days	4%	----	8	45	6.14	124.0	T-PSPL
8	4 hrs.	8%	----	7	45	1.60	16.0	P-N***
9	1 day	8%	----	7	45	1.60	16.0	P-N
10	2 days	8%	----	7	45	1.40	24.0	P-N
11	6 weeks	8%	----	7	45	5.46	168.0	T-PSPL
12	4 hrs.	8%	----	8	45	3.72	80.0	T-PSPL
13	1 day	8%	----	8	45	3.48	80.0	T-PSPL
14	2 days	8%	----	8	45	3.80	80.0	T-PSPL
15	4 hrs.	8%	----	9	45	5.99	99.2	T-PSPL
16	1 day	8%	----	9	45	6.39	101.6	T-PSPL
17	2 days	8%	----	9	45	5.54	96.0	T-PSPL
18	1 hr.	----	5%	7	35	0.40	2.68	P-N
19	24 hrs.	----	5%	7	35	1.07	9.08	P-N
20	2 weeks	----	5%	7	35	1.60	28.2	T-PSPL
21	1 hr.	----	5%	8	35	1.33	8.60	P-N
22	24 hrs.	----	5%	8	35	1.86	10.6	P-N
23	2 weeks	----	5%	8	35	2.80	28.2	T-PSPL
24	1 hr.	----	5%	9	35	2.12	38.4	T-PSPL
25	24 hrs.	----	5%	9	35	2.51	44.8	T-PSPL
26	1 week	----	5%	9	35	4.00	78.4	T-PSPL
27	1 hr.	----	5%	10	35	7.32	144.0	T-PL****
28	24 hrs.	----	5%	10	35	7.75	128.0	T-PL
29	1 week	----	5%	10	35	7.20	160.0	T-PL

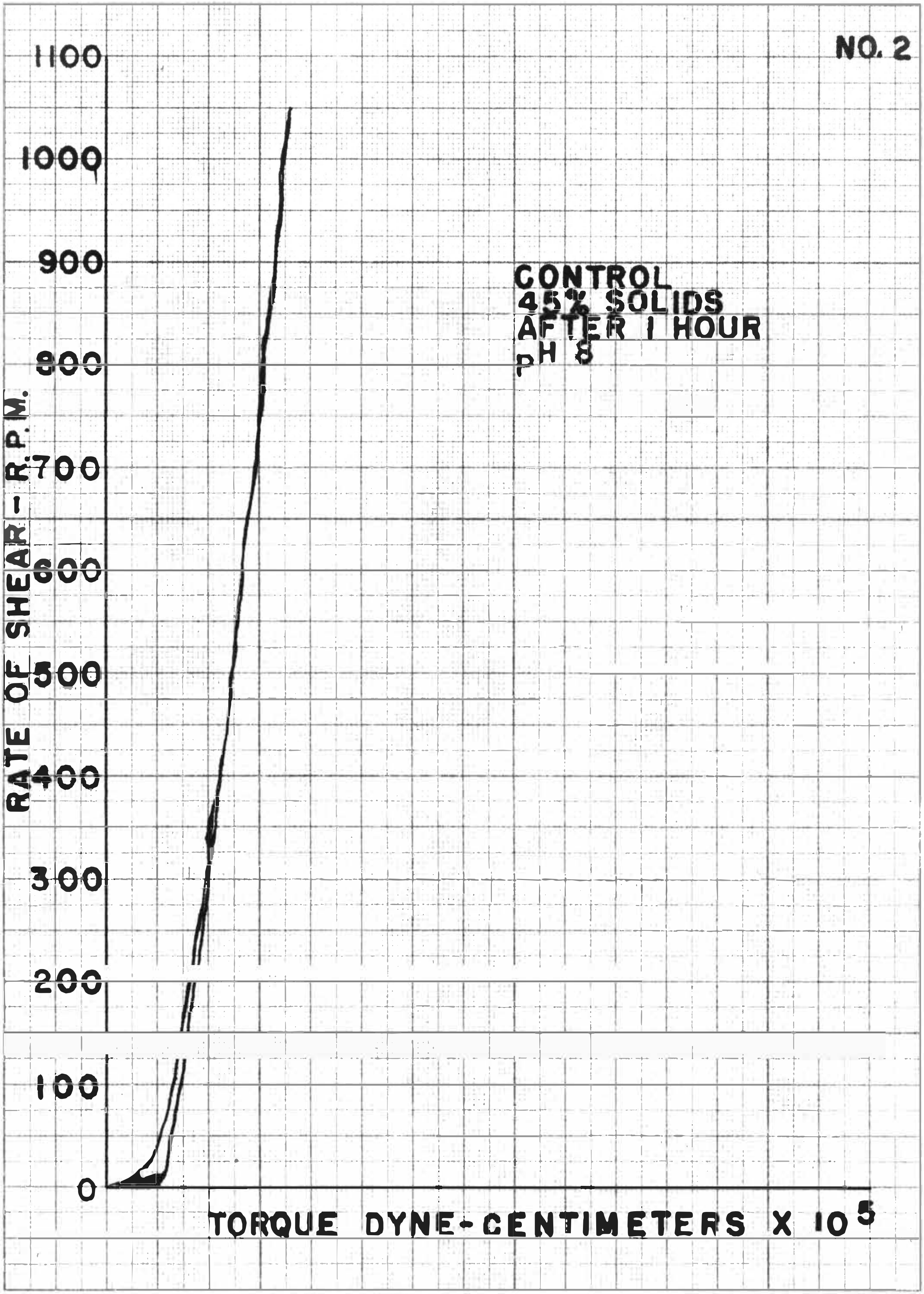
Note: * All coating colors prepared with 16 parts of casein for 100 parts of clay.
** T-PSPL - Thixotropic Pseudoplastic
*** P-N - Practically Newtonian
**** T-PL - Thixotropic Plastic

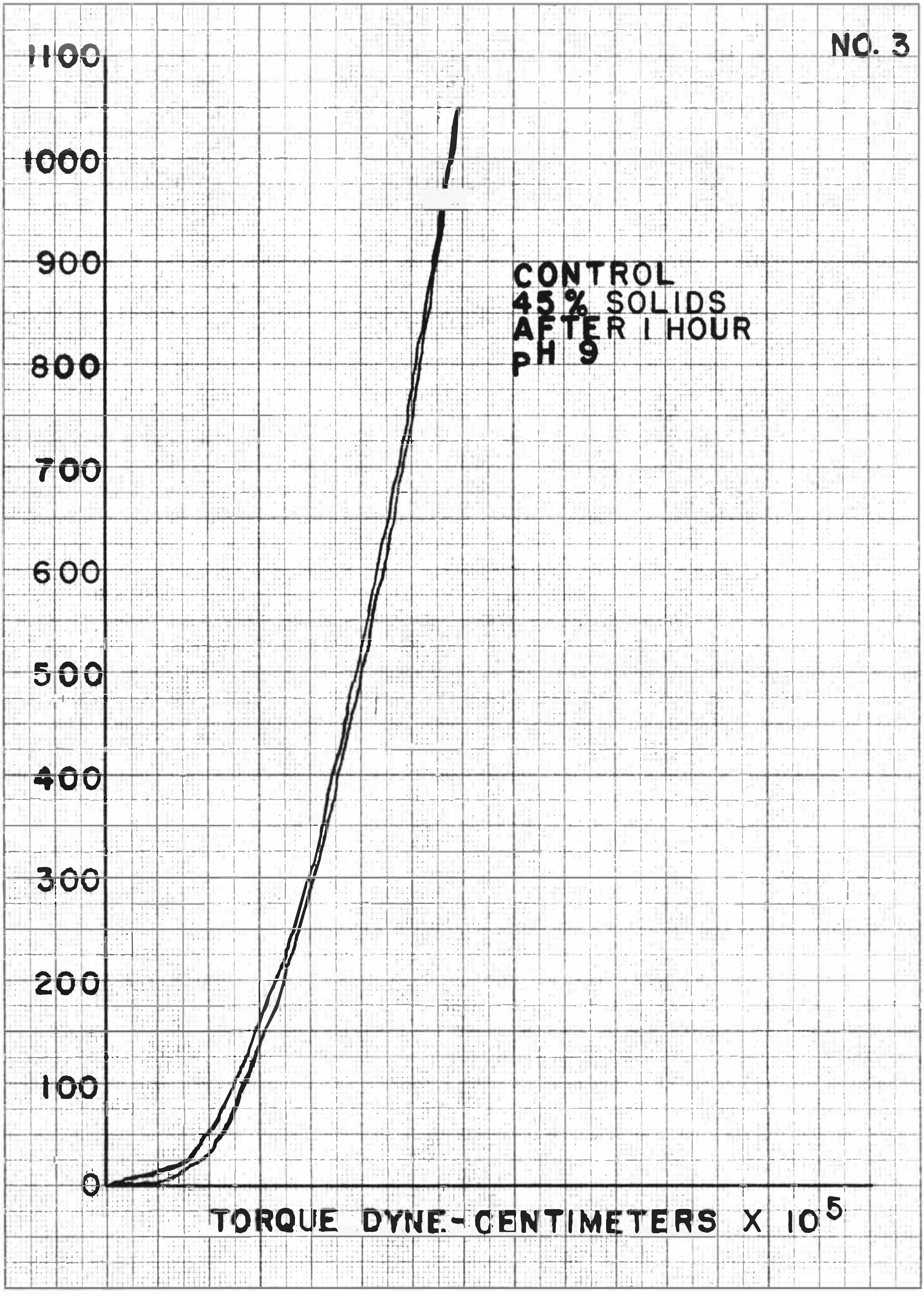
Table II - Brookfield Viscosities at 50 R.P.M.

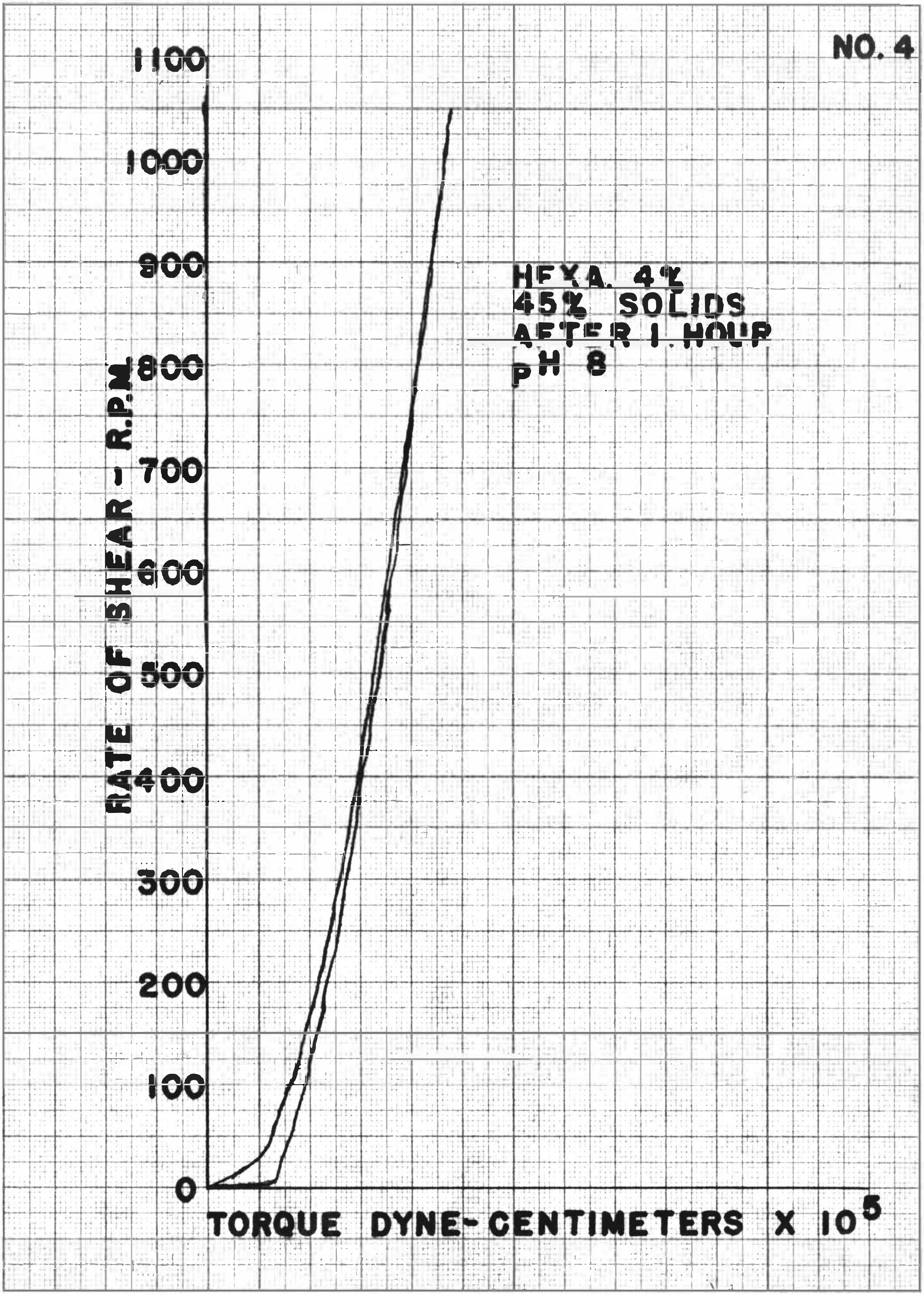
Additive Used*	Total Solids Per Cent	pH Value	After 1 hr.	After 4 hrs.	After 24 hrs.	After 48 hrs.	After 7 days	After 14 days	After 42 day
None	45	7	105.6	----	----	----	----	----	----
None	45	8	120.8	----	----	----	----	----	----
None	45	9	152.0	----	----	----	----	----	----
None	35	7	1.04	----	----	----	----	----	----
None	35	8	0.96	----	----	----	----	----	----
None	35	9	1.52	----	----	----	----	----	----
Hexa 4%	45	8	----	115.6	120.0	----	122.0	124.0	----
Hexa 8%	45	7	----	16.0	16.0	24.0	32.0	----	168.0
Hexa 8%	45	8	----	80.0	80.0	80.0	82.4	----	80.0
Hexa 8%	45	9	----	99.2	101.6	96.0	98.4	----	88.0
Form.5% **	35	7	2.68	----	9.08	----	26.9	28.2	----
Form.5%	35	8	8.60	----	10.6	----	28.2	32.1	----
Form.5%	35	9	38.4	----	44.8	----	78.4	----	----
Form.5%	35		144.0	----	128.0	----	160.0	----	----

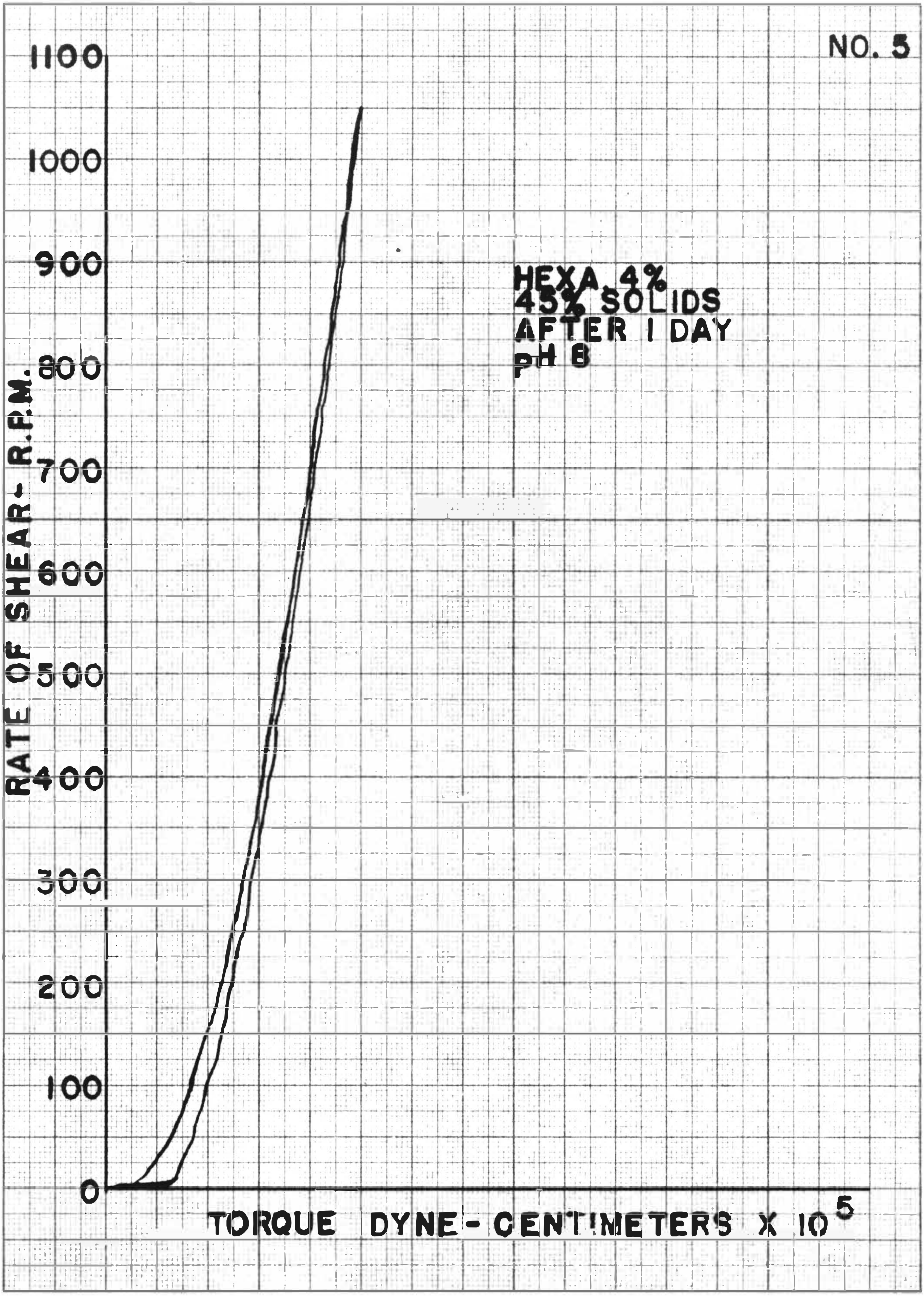
Notes: * In per cent based on weight of casein.
** In per cent of Formaldehyde Solution (40%) based on weight of casein.


NO. I
1100
1000
900
800
700
600
500
400
300
200
100
0
RATE OF SHEAR - R.P.M.
CONTROL
45% SOLIDS
AFTER I HOUR
PH 7
TORQUE DYNE-CENTIMETERS X 10 5

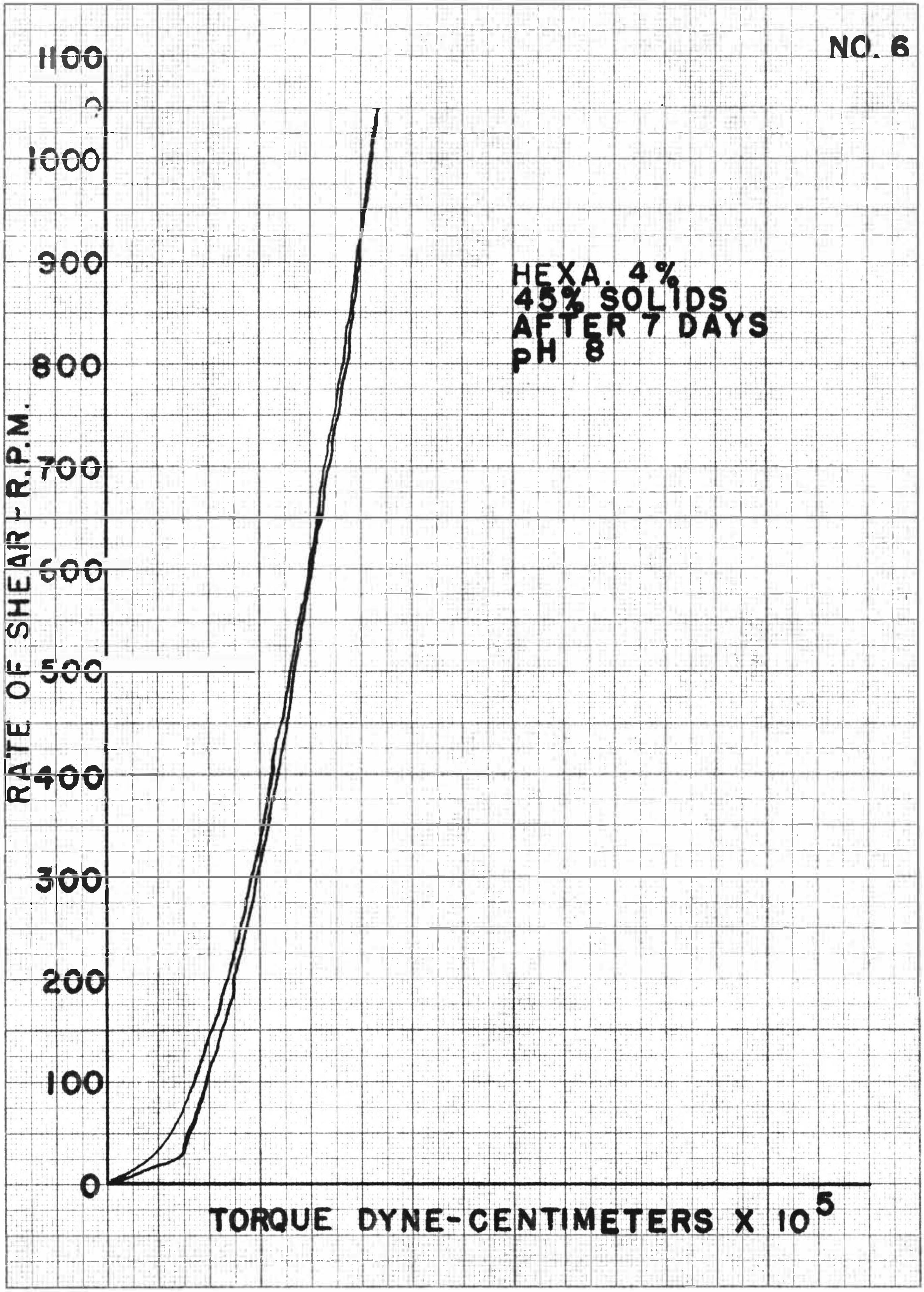

NO. 2
CONTROL
45% SOLIDS
AFTER 1 HOUR
pH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

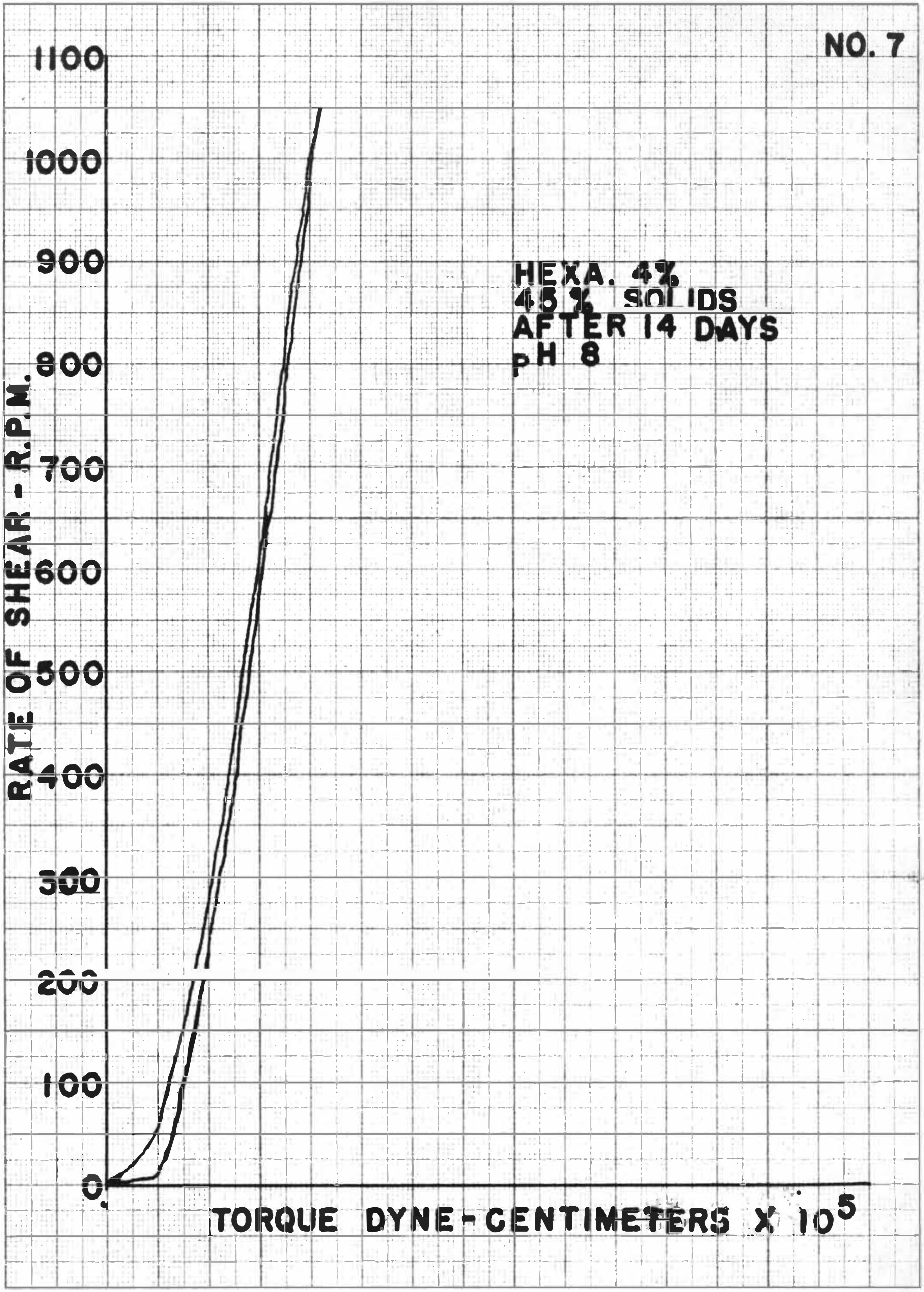

NO. 3
1100
1000
900
800
700
600
500
400
300
200
100
0
CONTROL
45% SOLIDS
AFTER 1 HOUR
pH 9
TORQUE DYNE-CENTIMETERS X 10^5

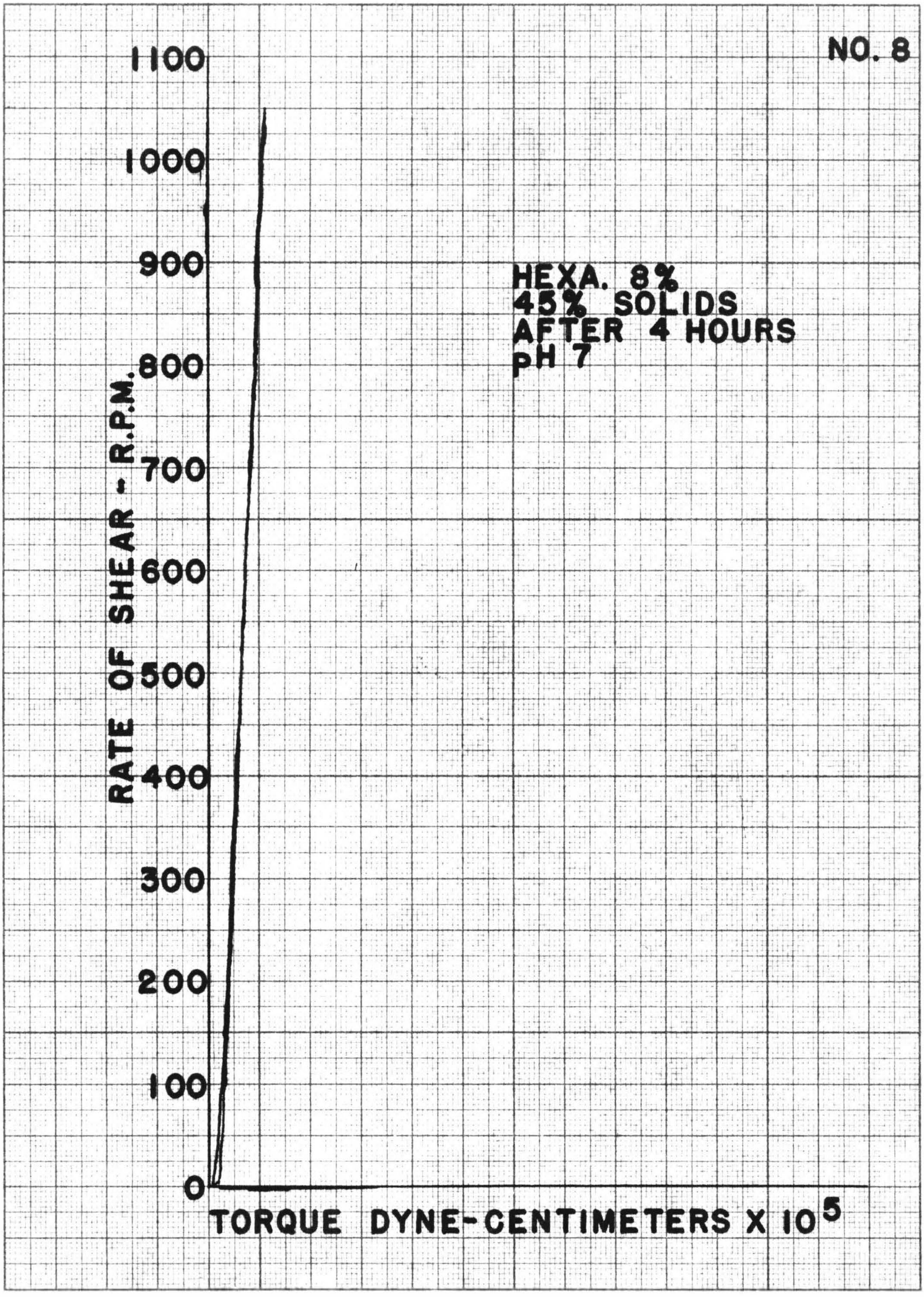

NO. 4
HEXA. 4%
45% SOLIDS
AFTER 1 HOUR
pH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

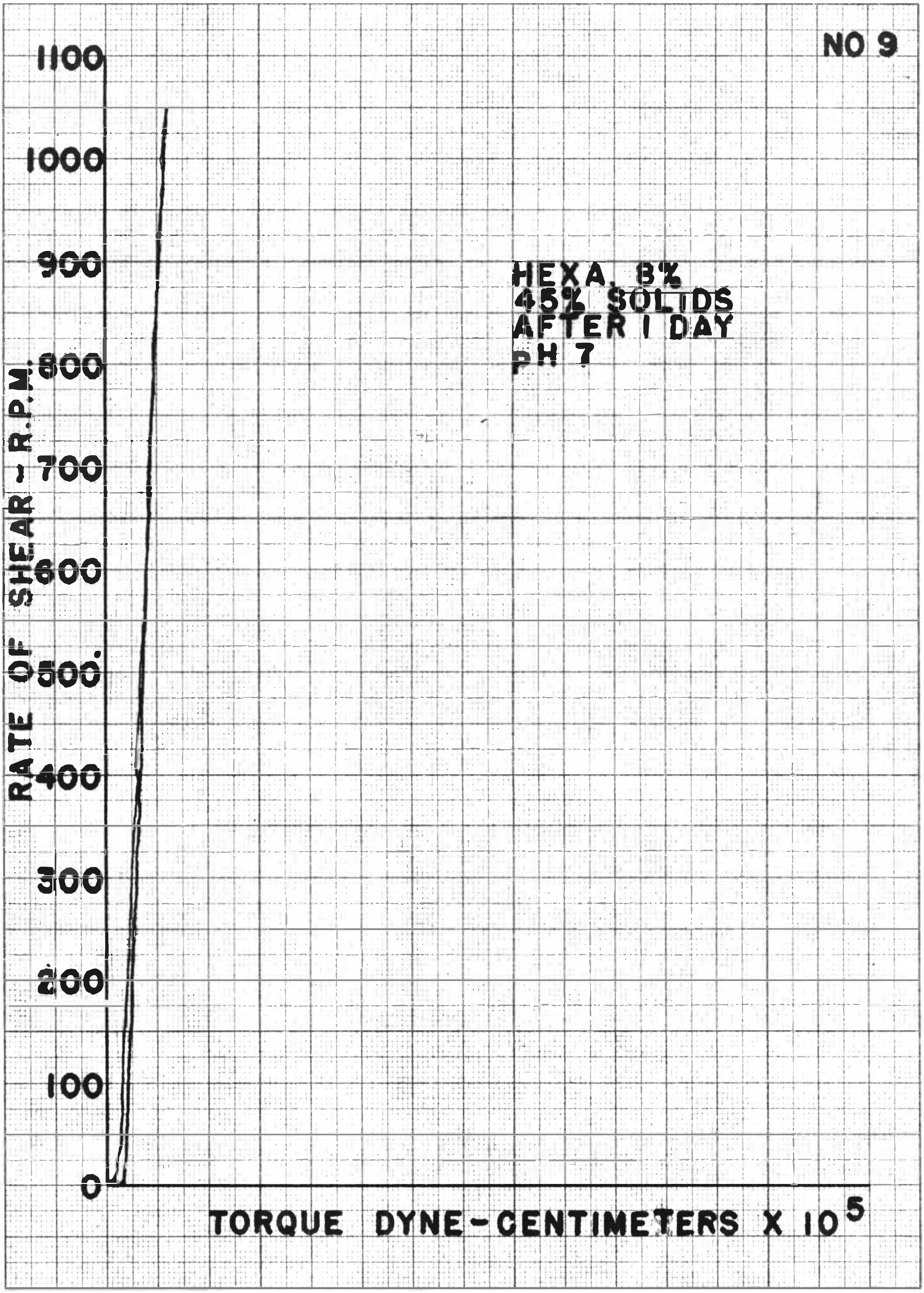


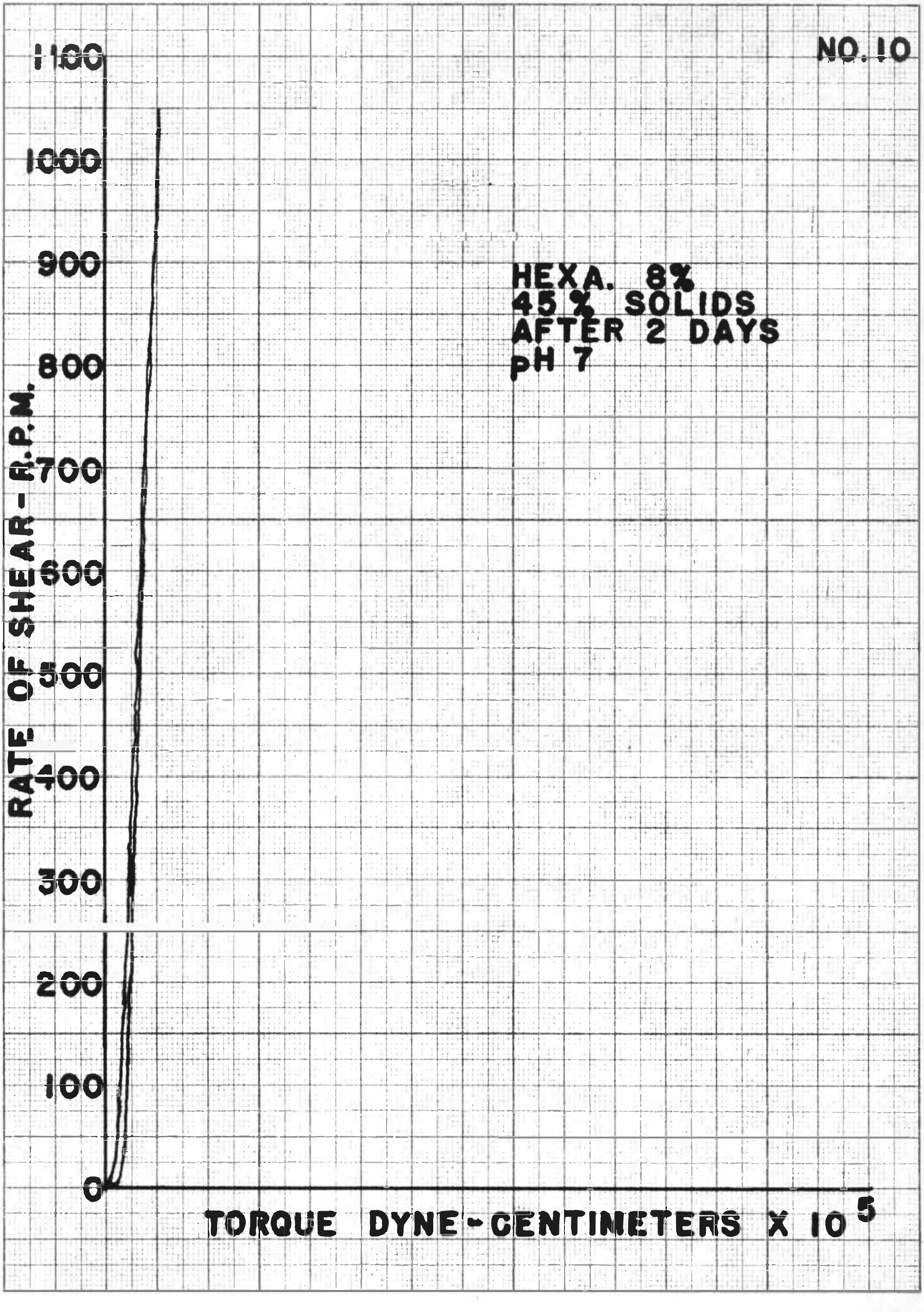
NO. 5
HEXA 4%
45% SOLIDS
AFTER 1 DAY
PH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE - CENTIMETERS X 10^5

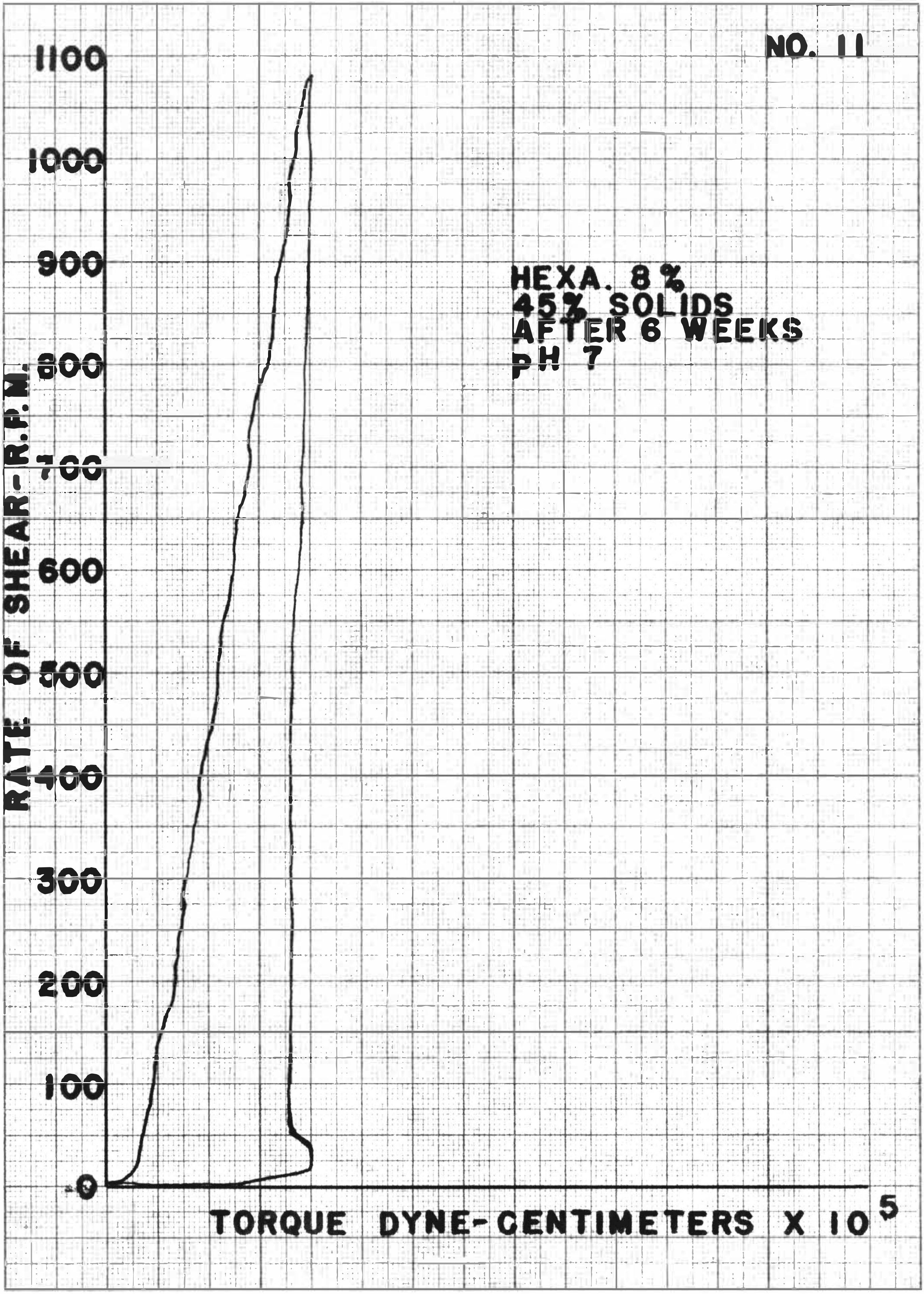

NO. 6
HEXA. 4%
45% SOLIDS
AFTER 7 DAYS
pH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5


NO. 7
HEXA. 4%
45% SOLIDS
AFTER 14 DAYS
pH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

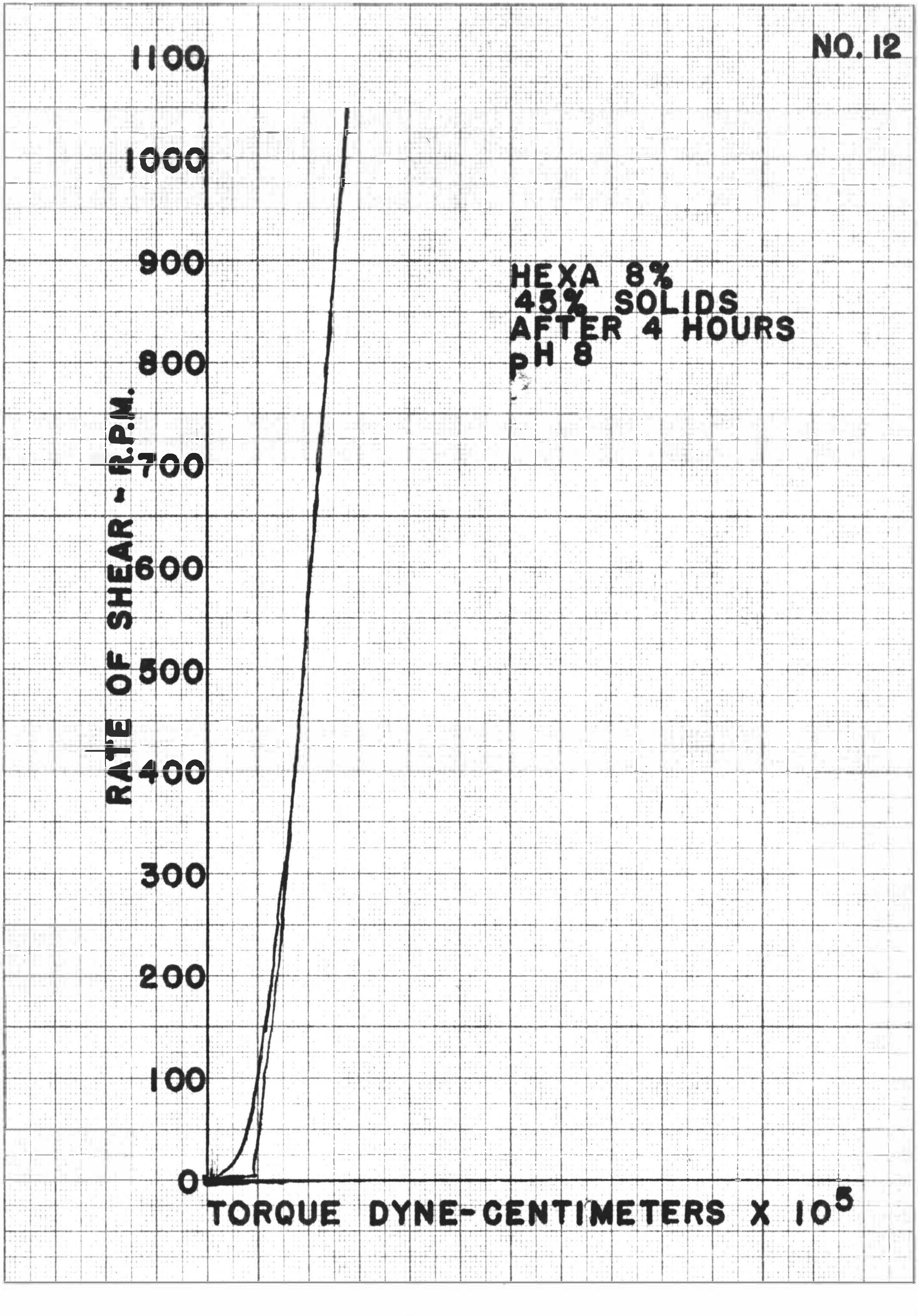

NO. 8
HEXA. 8%
45% SOLIDS
AFTER 4 HOURS
pH 7
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

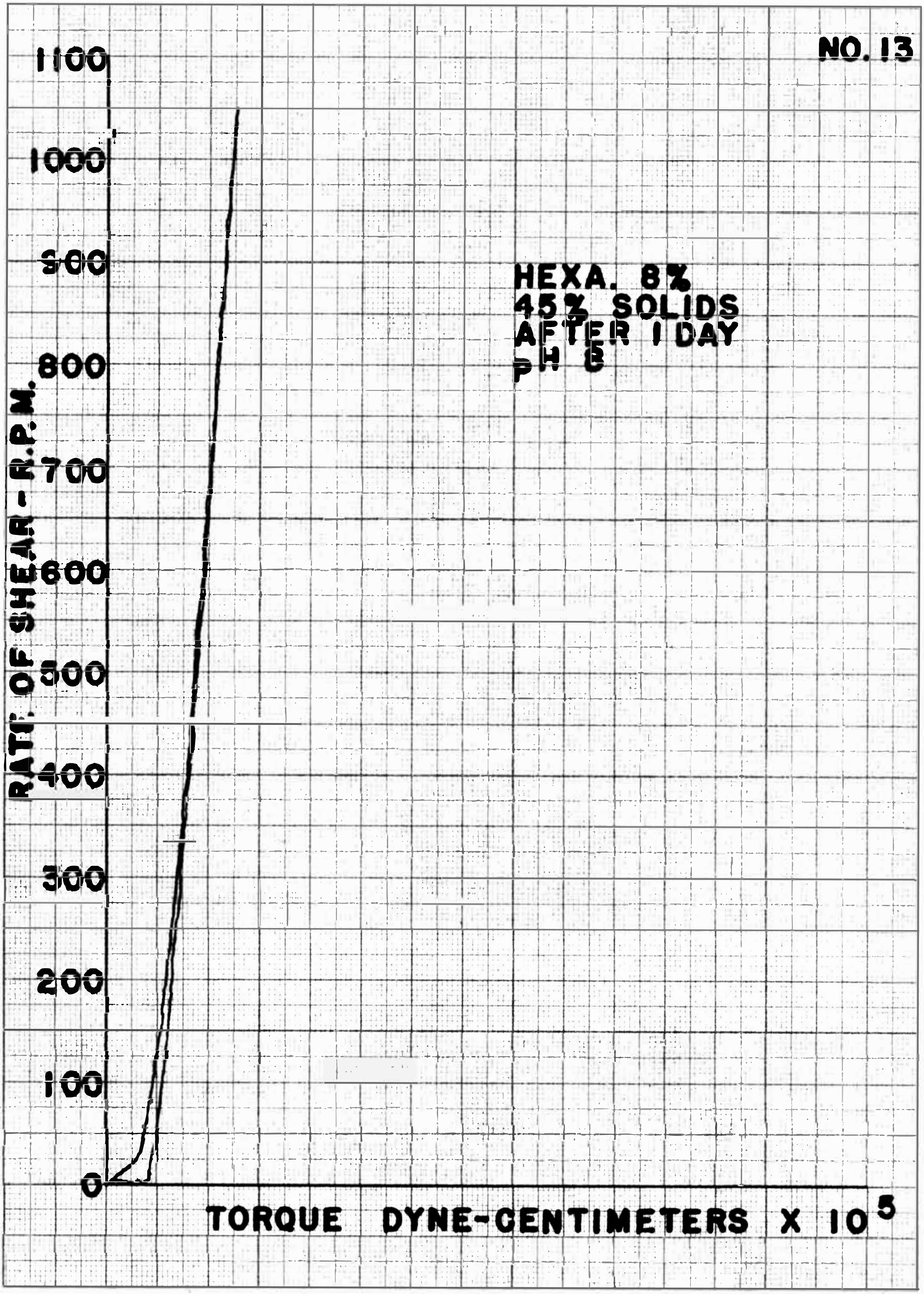

NO 9
HEXA. 8%
45% SOLIDS
AFTER 1 DAY
PH 7
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

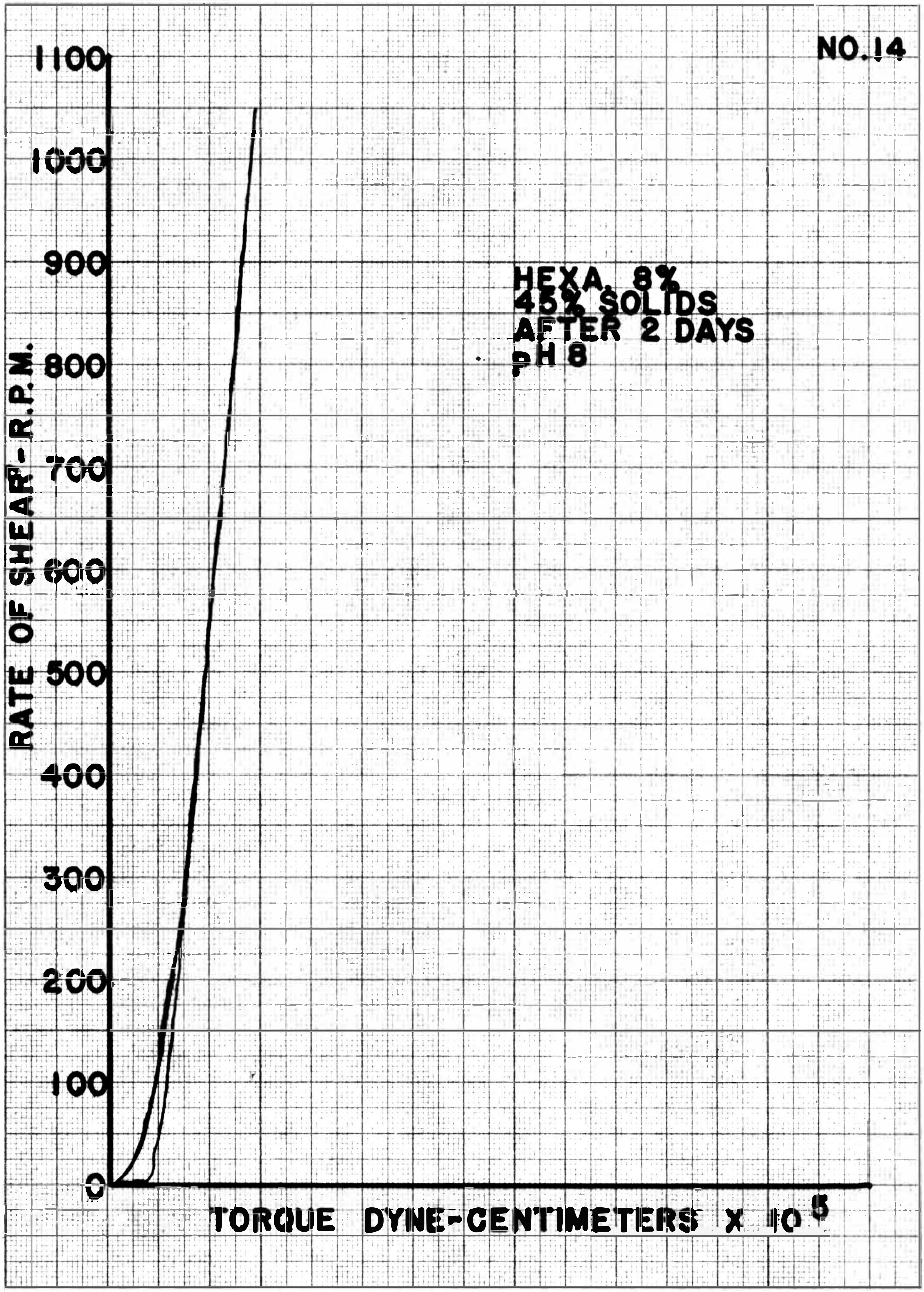

NO. 10
HEXA. 8%
45 % SOLIDS
AFTER 2 DAYS
pH 7
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE - CENTIMETERS X 10 5

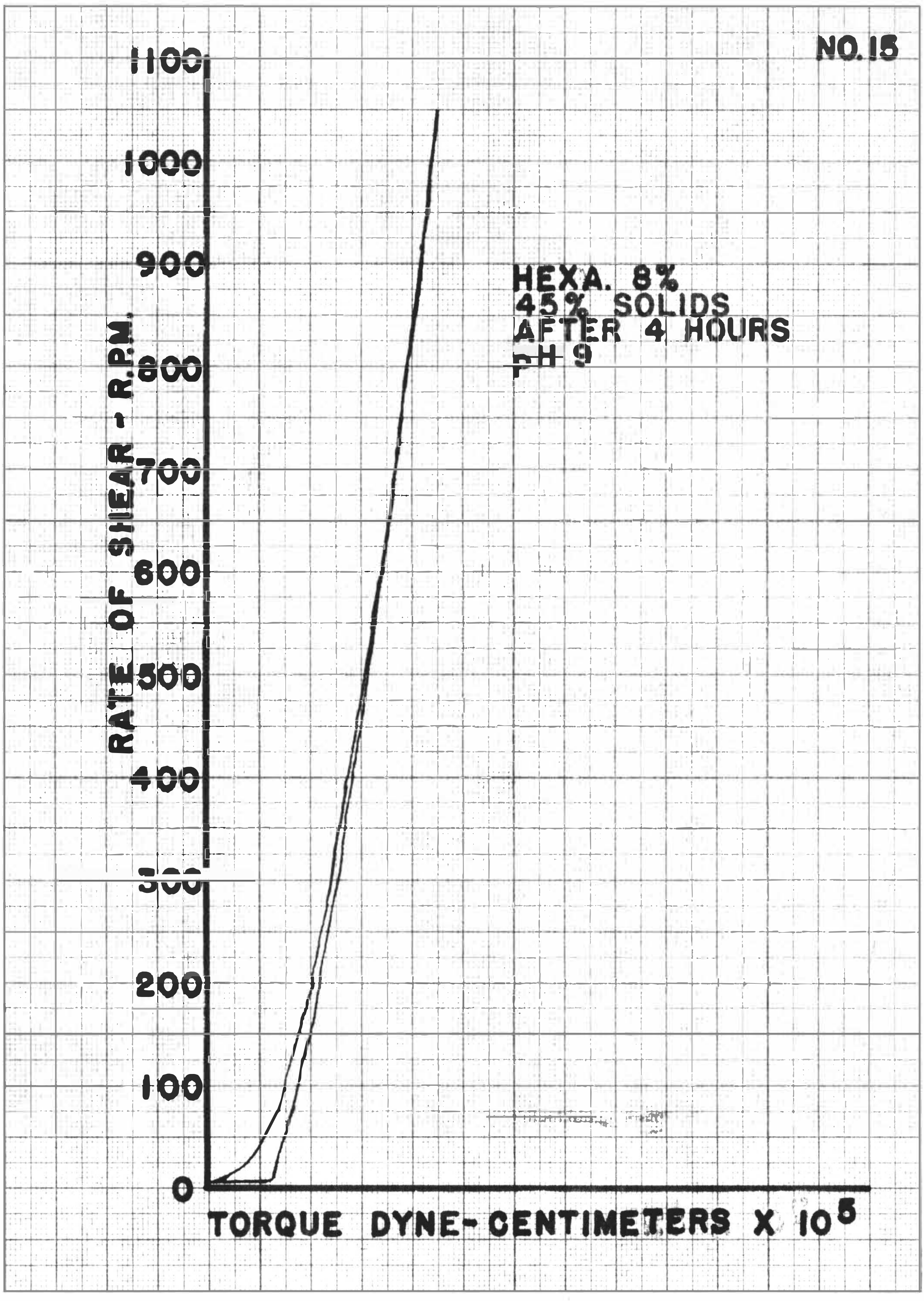


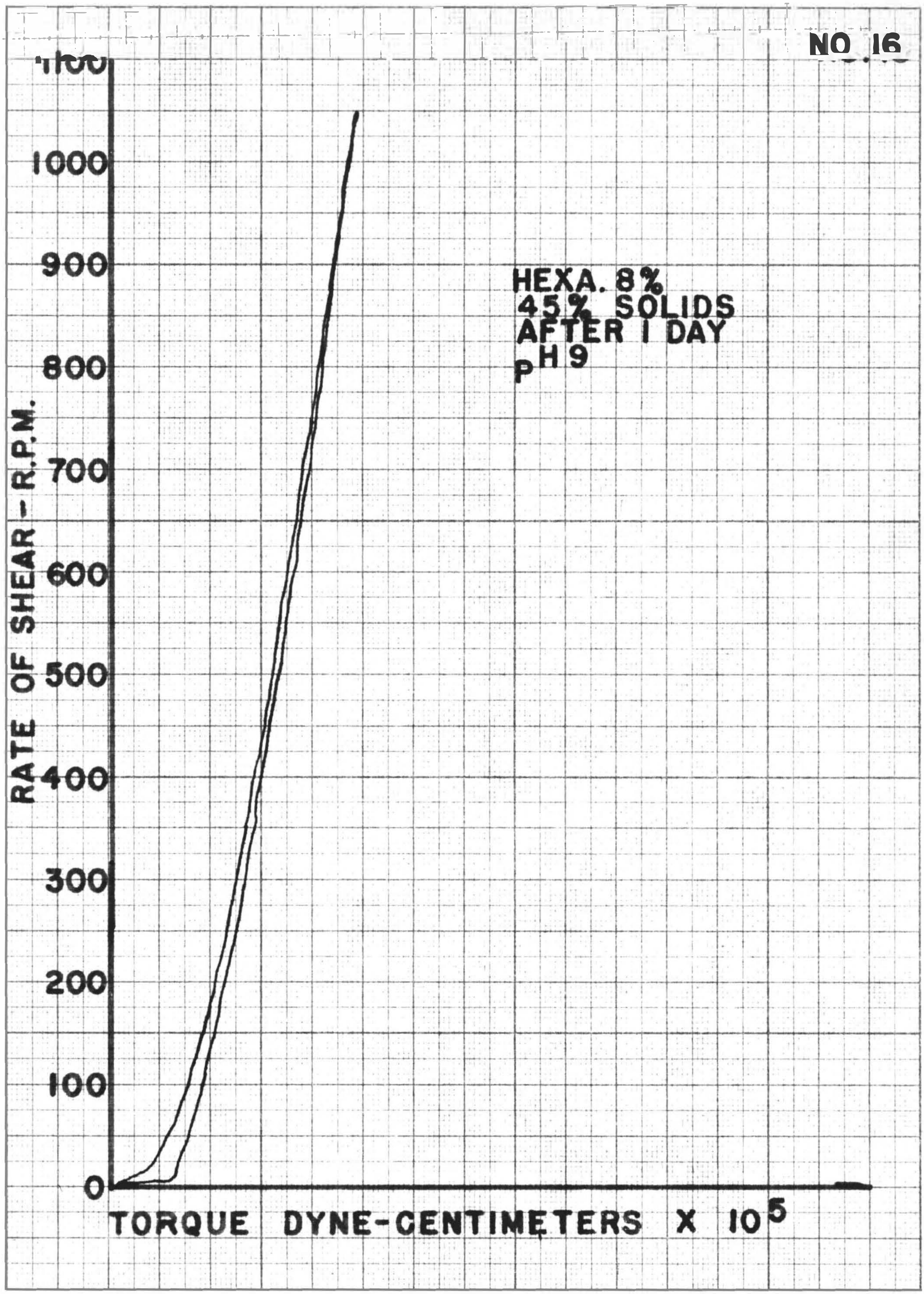
NO. 11
HEXA. 8 %
45% SOLIDS
AFTER 6 WEEKS
pH 7
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

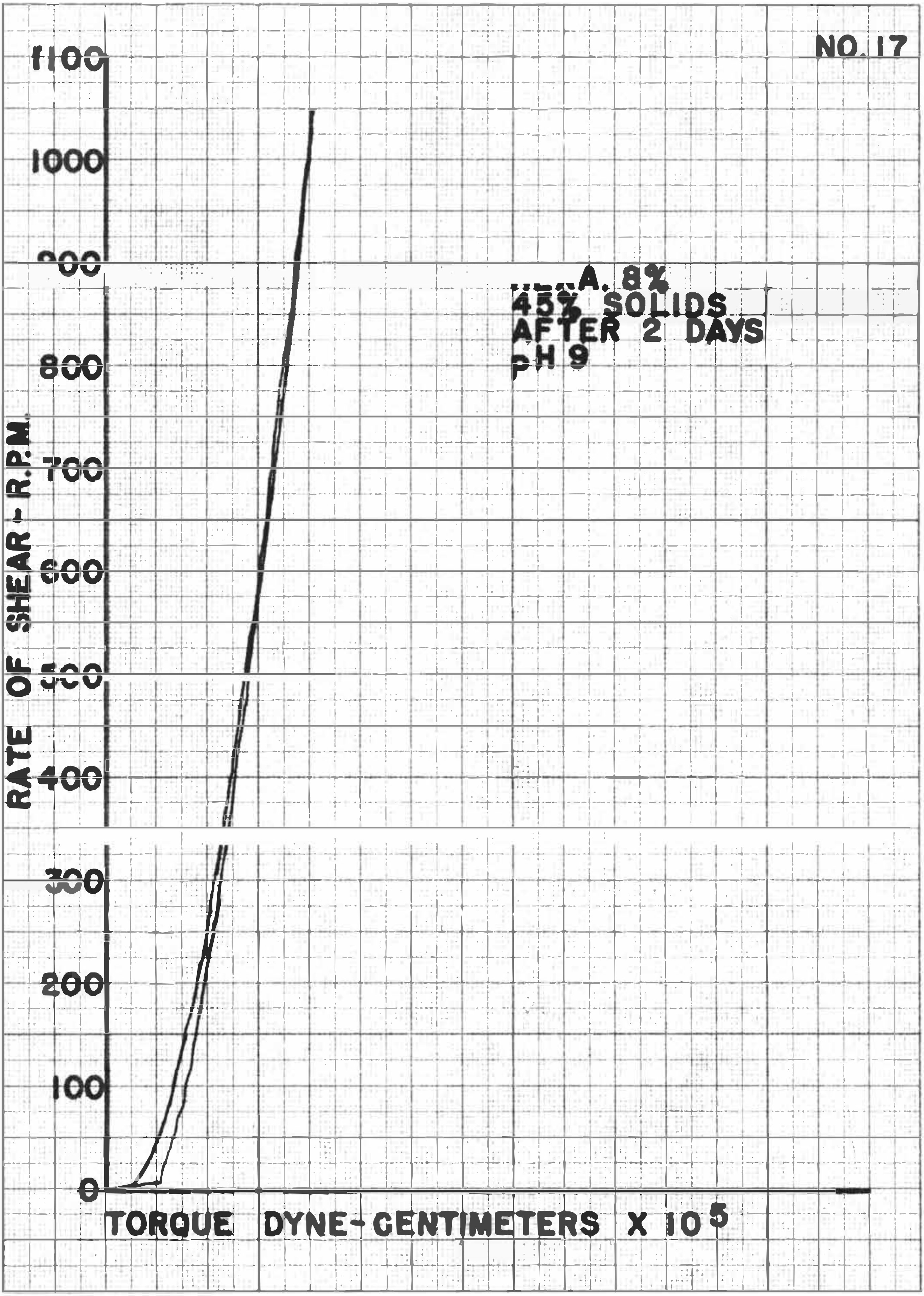

NO. 12
HEXA 8%
45% SOLIDS
AFTER 4 HOURS
pH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

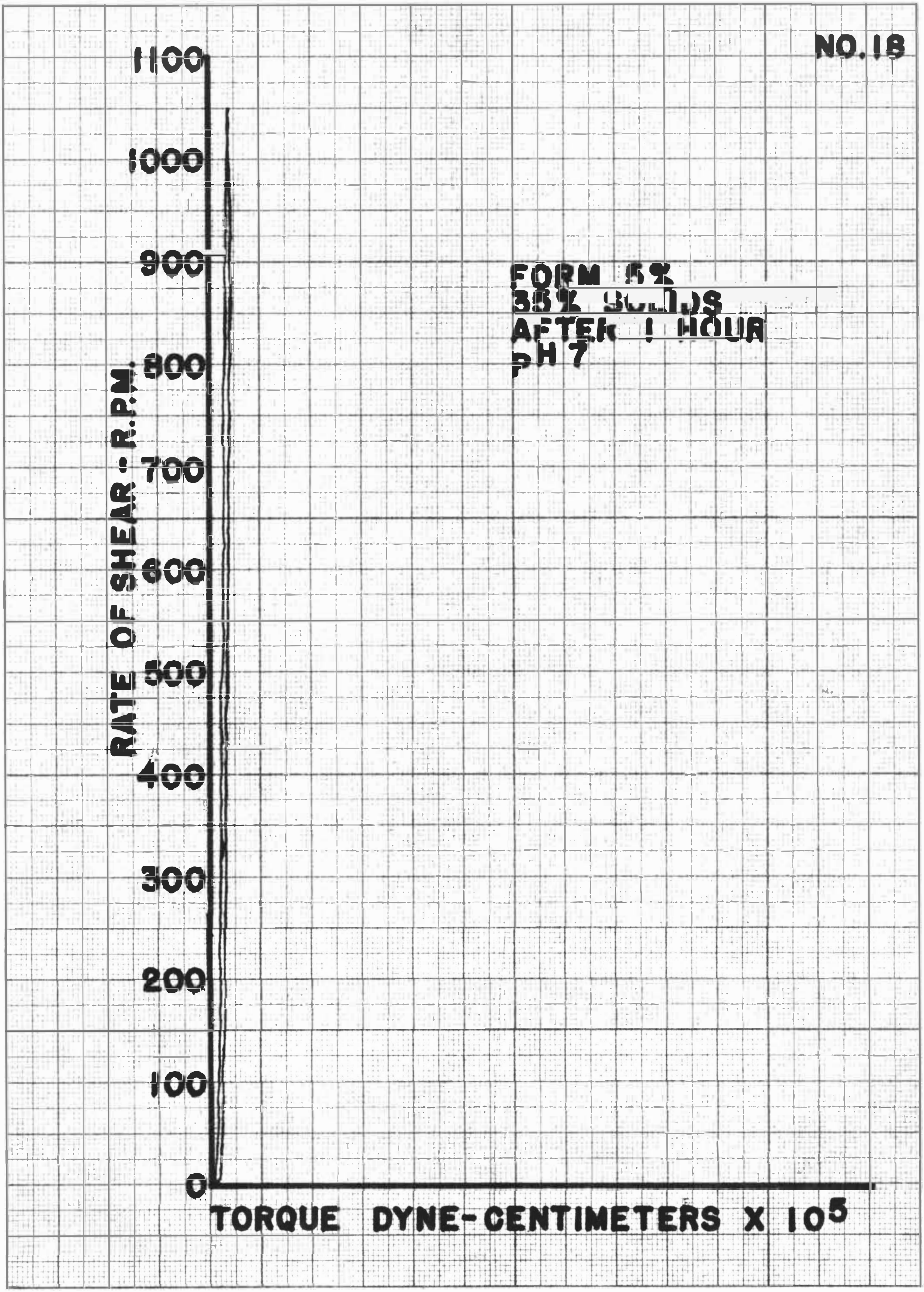

NO. 13
HEXA. 8%
45% SOLIDS
AFTER 1 DAY
PH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

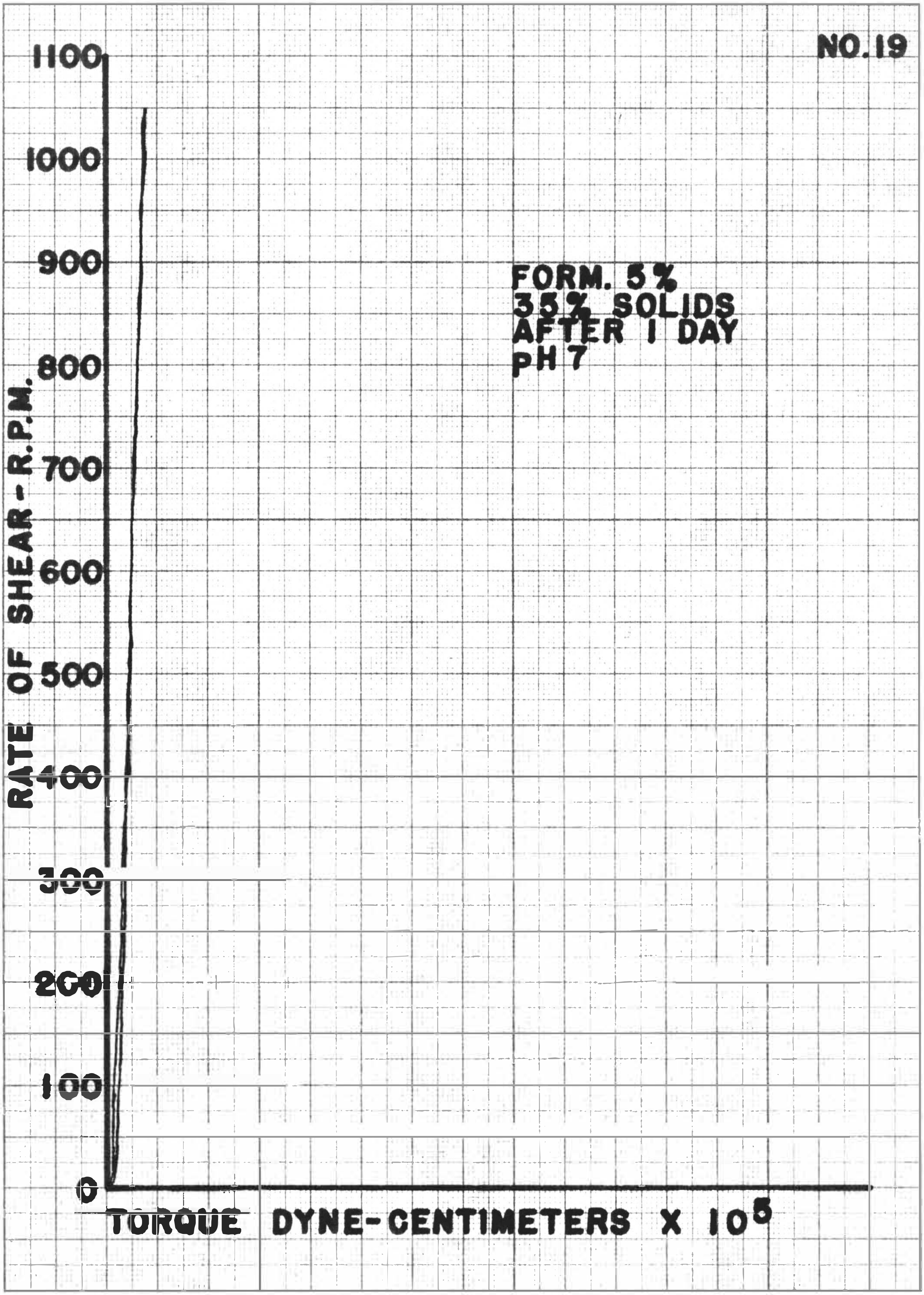

NO.14
1100
1000
900
800
700
600
500
400
300
200
100
0
RATE OF SHEAR - R.P.M.
HEXA. 8%
45% SOLIDS
AFTER 2 DAYS
pH 8
TORQUE DYNE-CENTIMETERS X 10^5

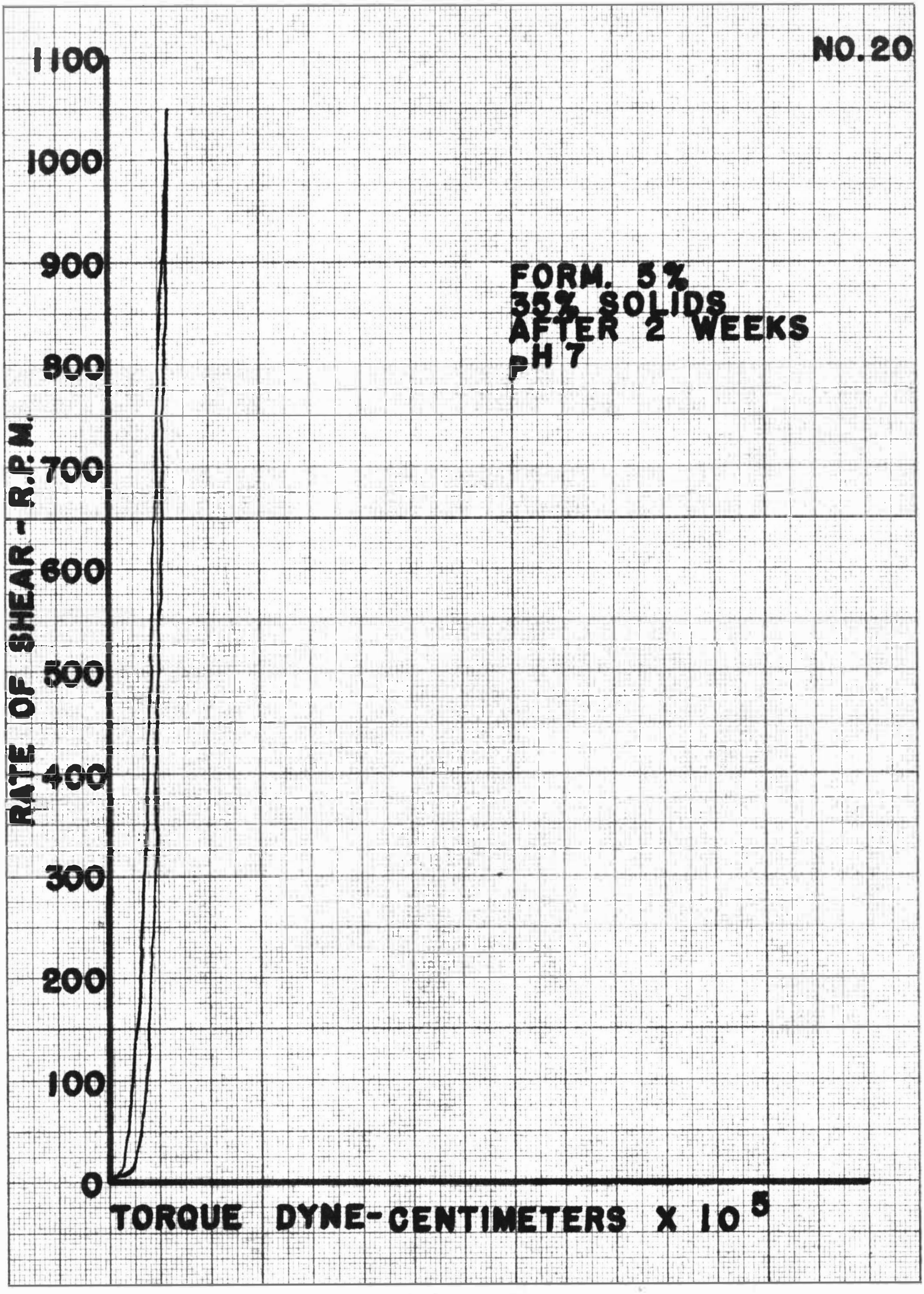

NO. 15
HEXA. 8%
45% SOLIDS
AFTER 4 HOURS
pH 9
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

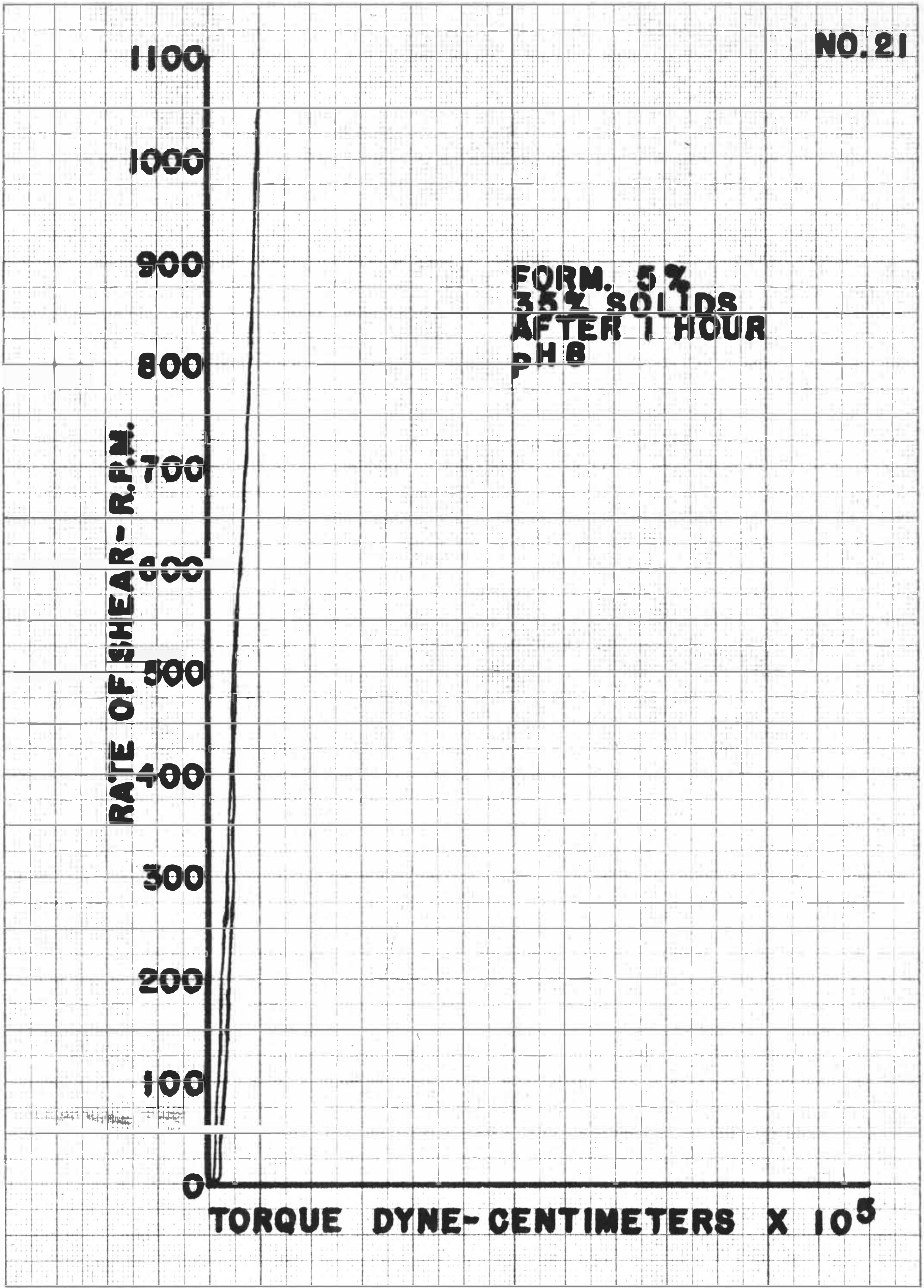

NO 16
1100
1000
900
800
700
600
500
400
300
200
100
0
RATE OF SHEAR - R.P.M.
TORQUE DYNE-CENTIMETERS X 10^5
HEXA. 8%
45% SOLIDS
AFTER 1 DAY
pH 9

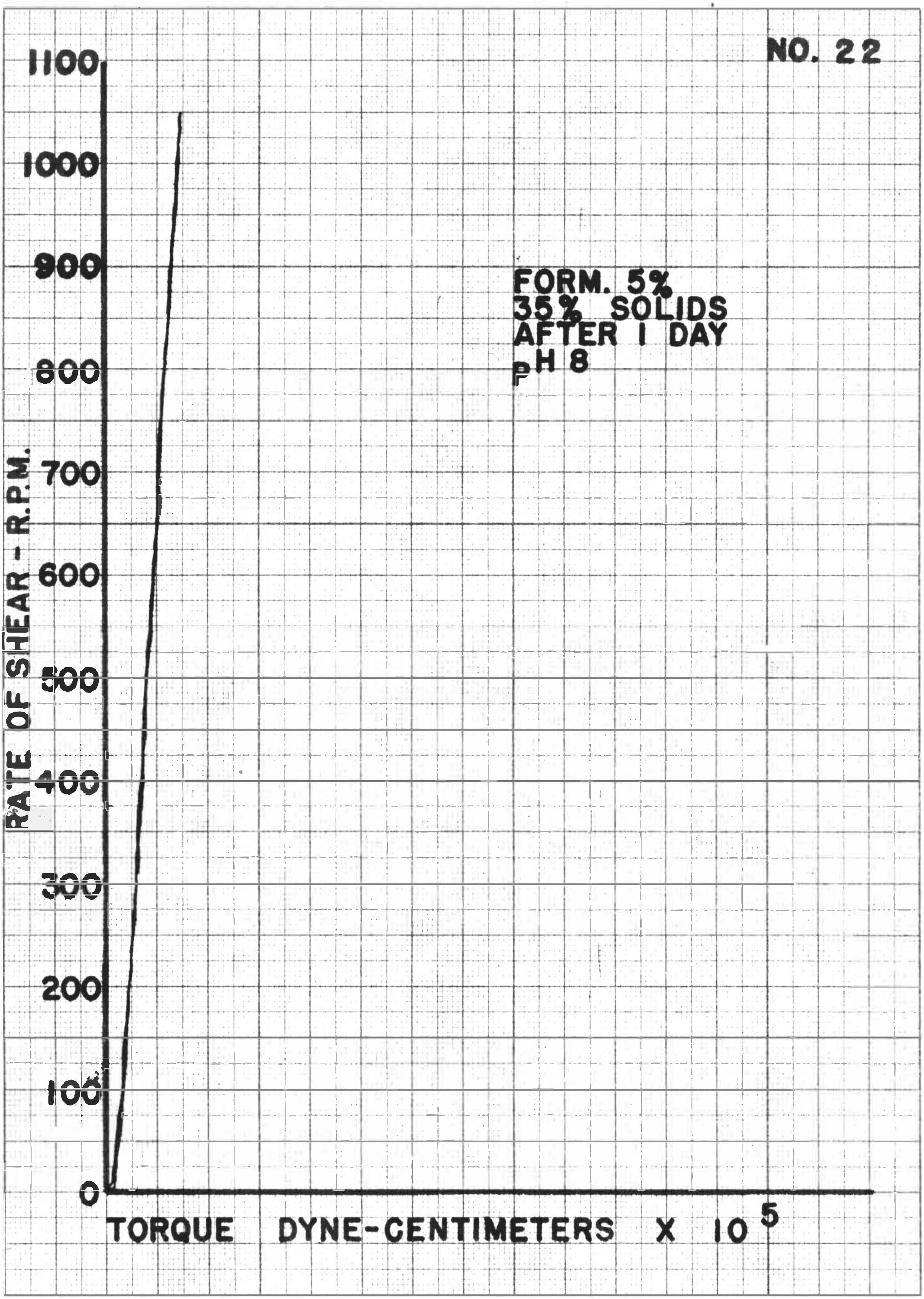

NO. 17
45% SOLIDS
AFTER 2 DAYS
pH 9
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

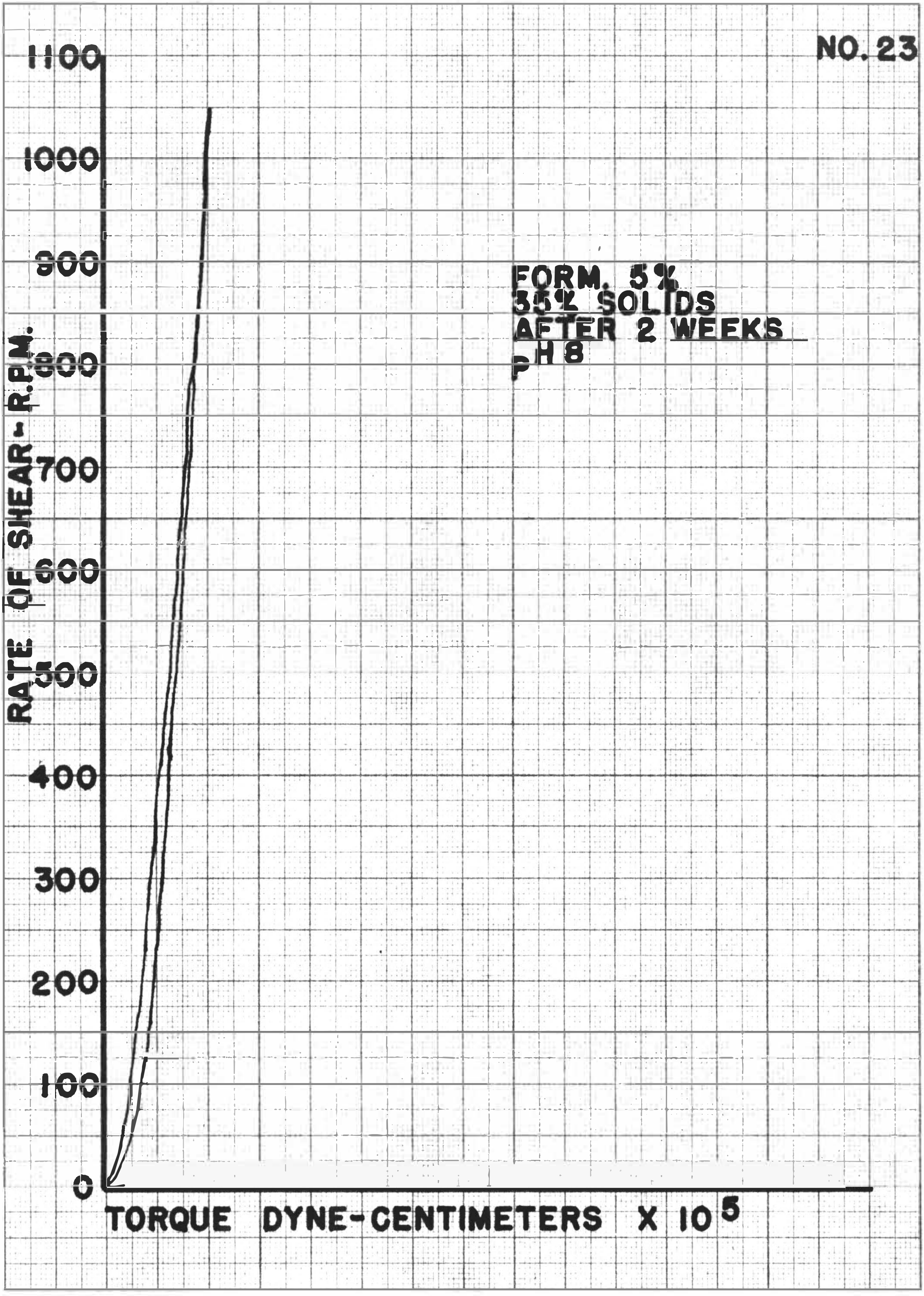

NO. 18
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
FORM 5%
35% SOLIDS
AFTER 1 HOUR
PH 7
TORQUE DYNE-CENTIMETERS X 10^5

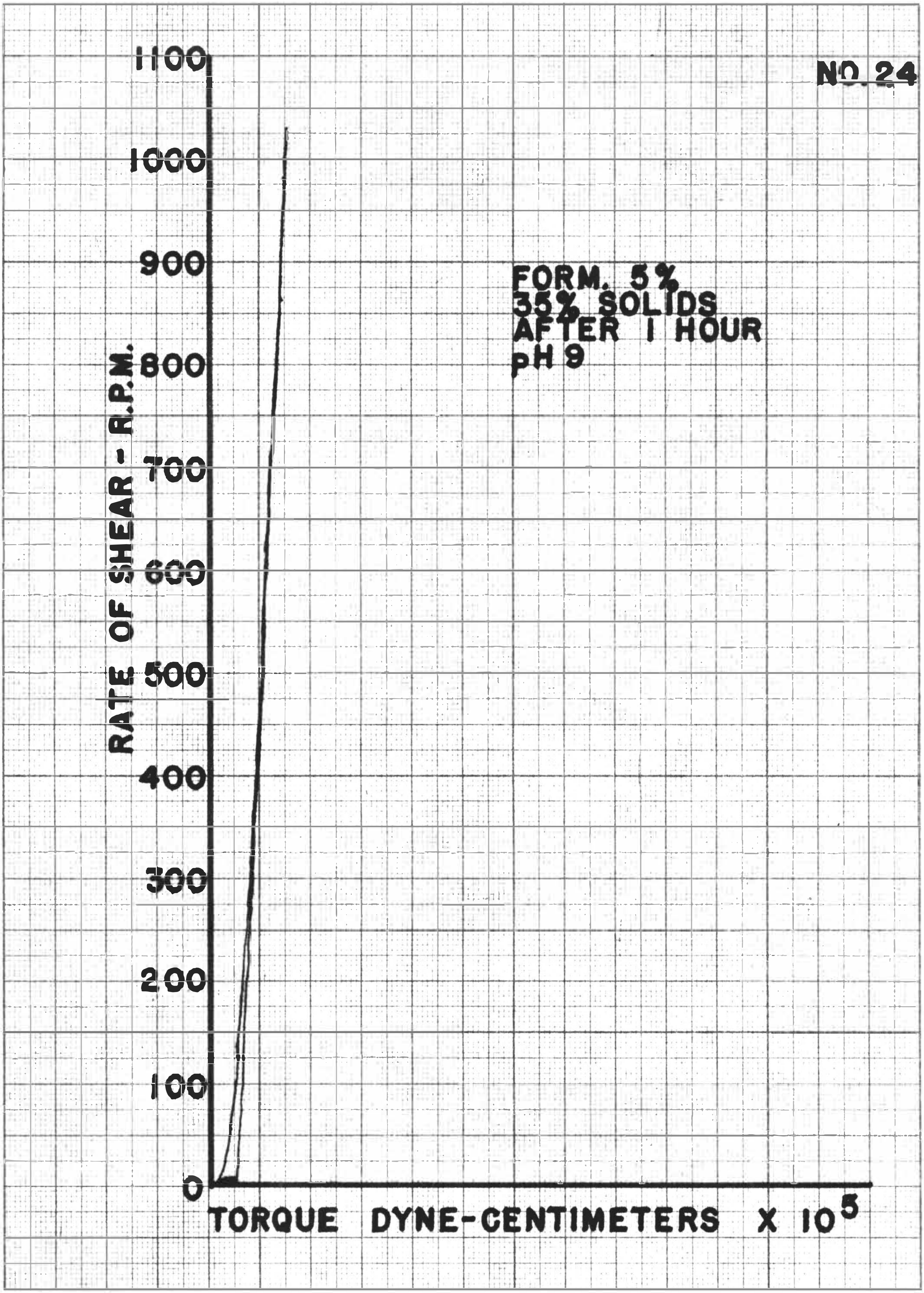

NO.19
FORM. 5%
35% SOLIDS
AFTER 1 DAY
PH 7
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

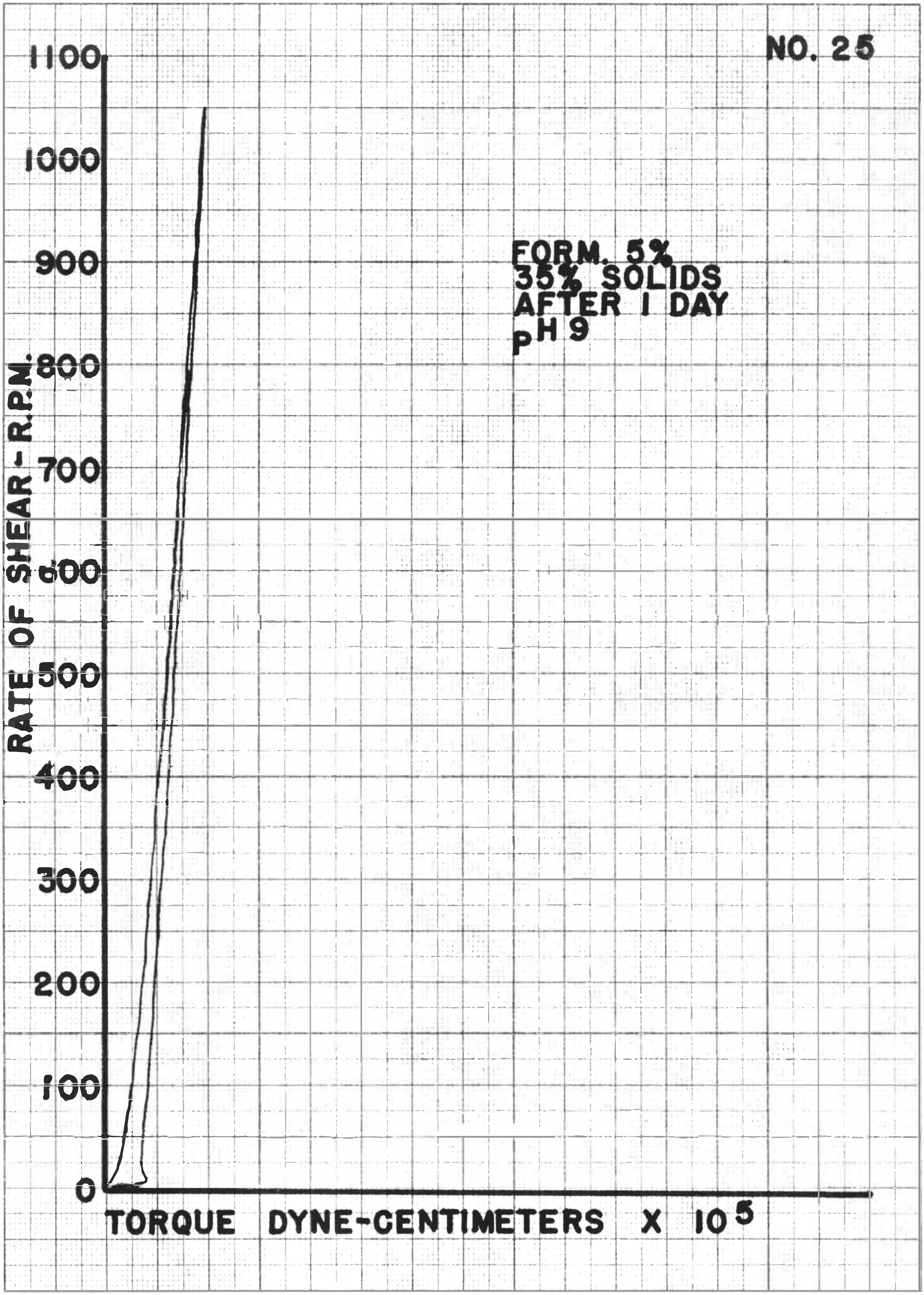

NO. 20
FORM. 5%
35% SOLIDS
AFTER 2 WEEKS
pH 7
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5


NO. 21
1100
1000
900
800
700
600
500
400
300
200
100
0
RATE OF SHEAR - R.P.M.
FORM. 5%
35% SOLIDS
AFTER 1 HOUR
pH 8
TORQUE DYNE-CENTIMETERS X 10^5

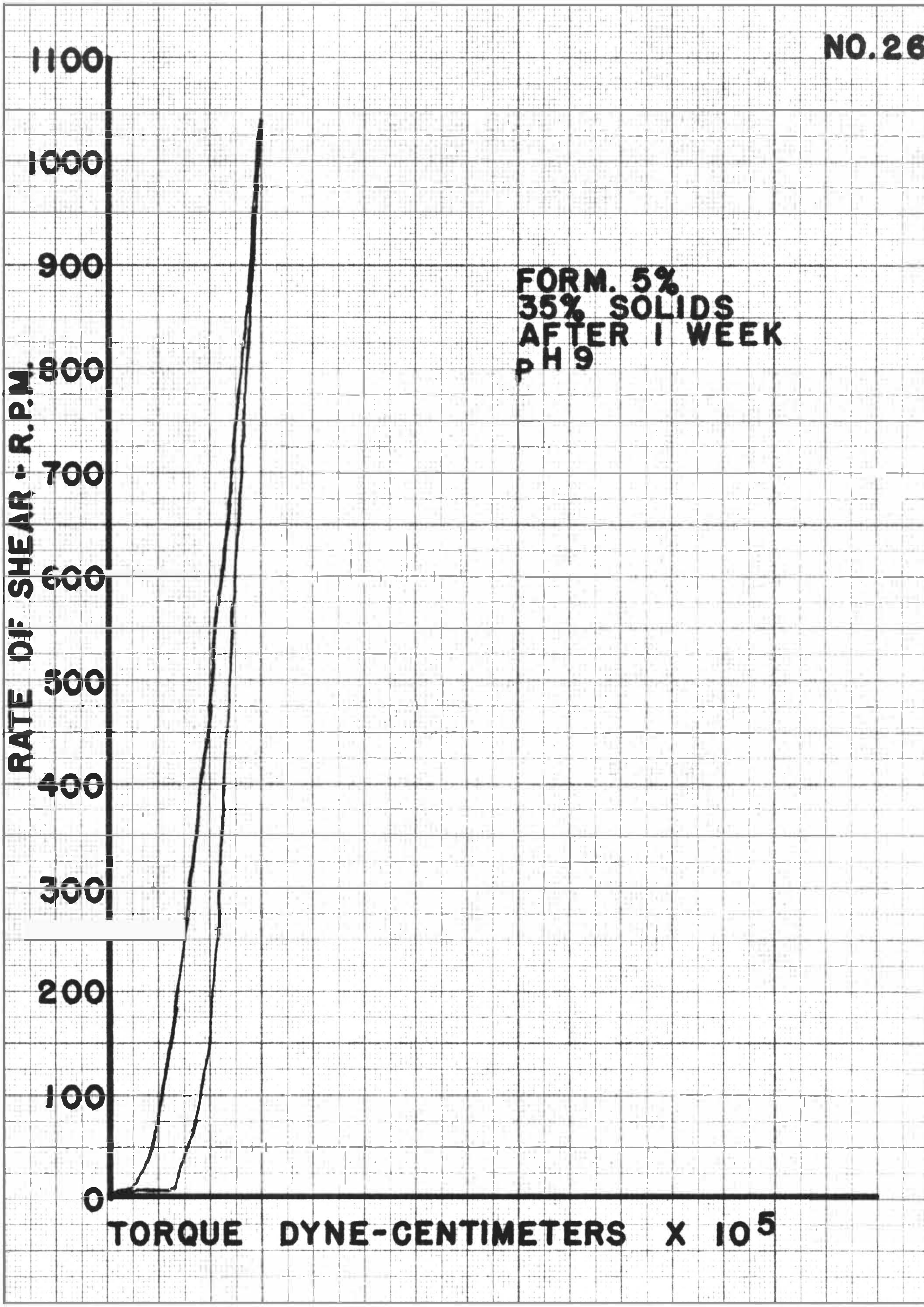

NO. 22
FORM. 5%
35% SOLIDS
AFTER 1 DAY
pH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10 5

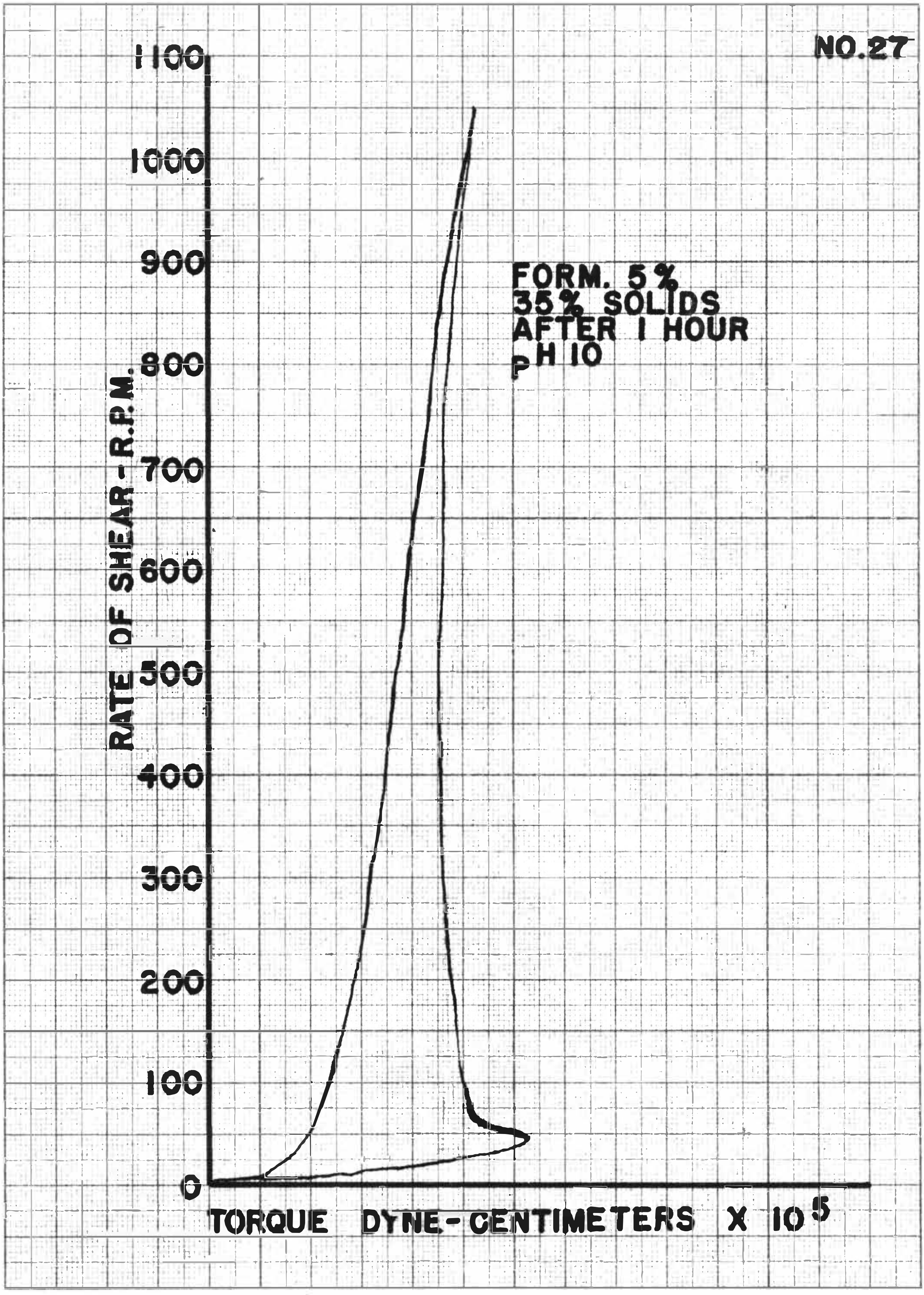

NO. 23
FORM. 5%
35% SOLIDS
AFTER 2 WEEKS
PH 8
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5


NO. 24
FORM. 5%
35% SOLIDS
AFTER 1 HOUR
pH 9
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5

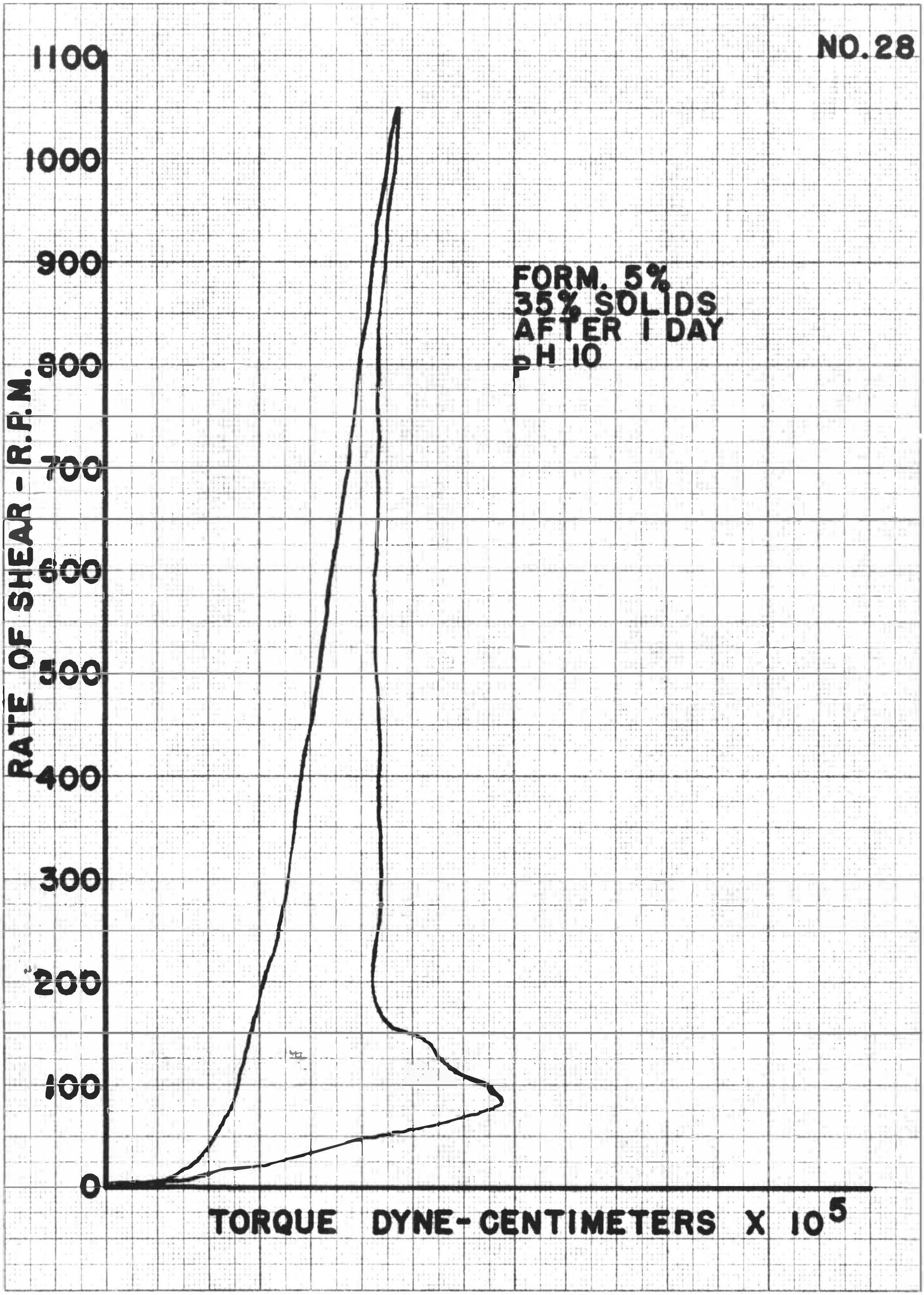


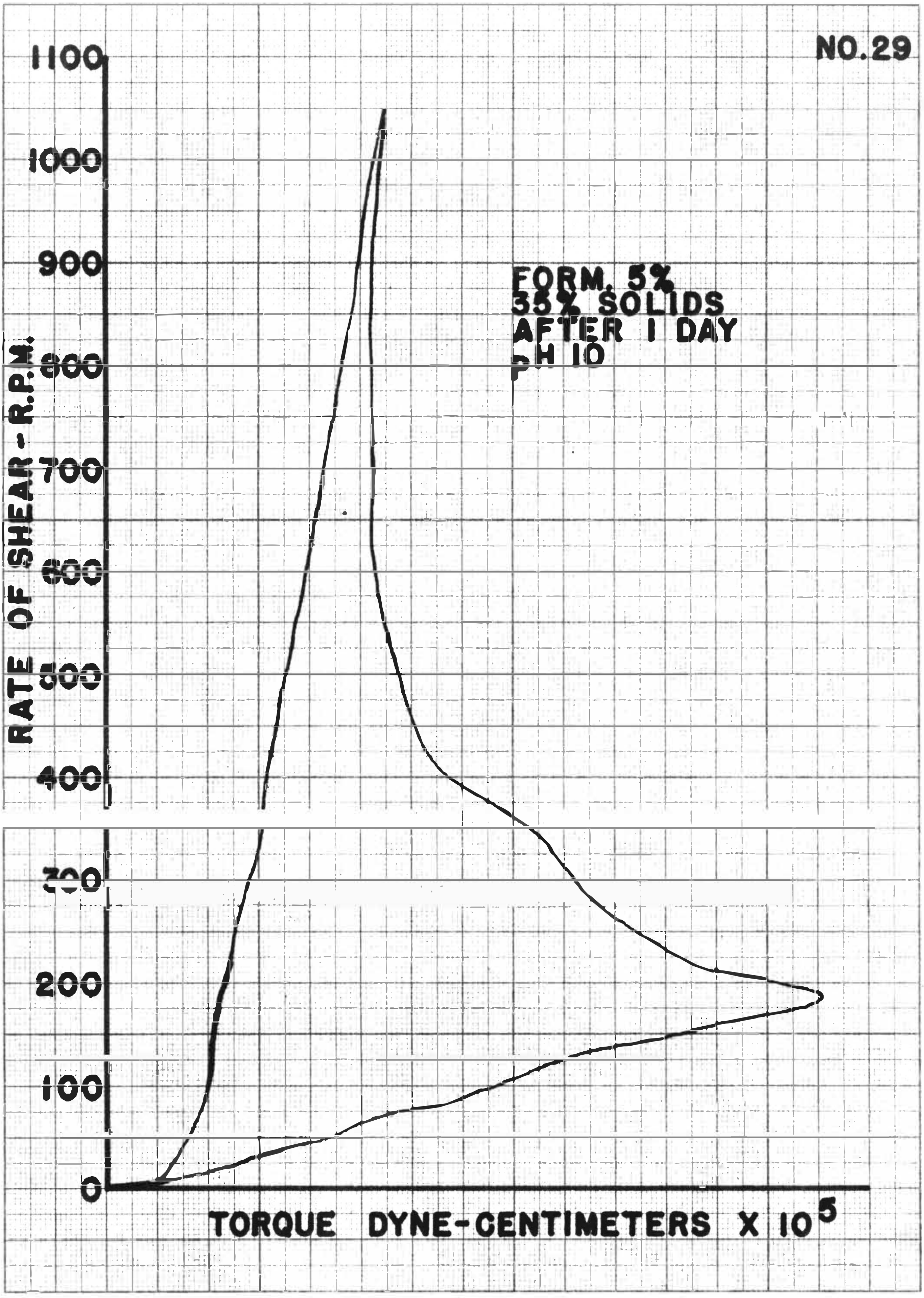
NO. 25
FORM. 5%
35% SOLIDS
AFTER 1 DAY
pH 9
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5


NO. 26
FORM. 5%
35% SOLIDS
AFTER 1 WEEK
pH 9
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5



NO.27
FORM. 5%
35% SOLIDS
AFTER 1 HOUR
pH 10
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5


NO. 28
FORM. 5%
35% SOLIDS
AFTER 1 DAY
pH 10
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5


NO. 29
FORM. 5%
35% SOLIDS
AFTER 1 DAY
pH 10
RATE OF SHEAR - R.P.M.
1100
1000
900
800
700
600
500
400
300
200
100
0
TORQUE DYNE-CENTIMETERS X 10^5