The Thermal Dehydration of Magnesium Sulfite Hexahydrate ($MgSO_3.6H_2O$) and Magnesium Sulfite Trihydrate ($MgSO_3.3H_2O$);

A mechanistic Study using Thermo-analytical Techniques and the Development of an Analytical Method for Quantitating Mixtures of the Hydrates

BY

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ABSTRACT

The thermal dehydration of $MgSO_3.3H_2O$ and $MgSO_3.6H_2O$ have been studied by differential thermal analysis, differential scanning calorimetry and thermal gravimetric analysis.

Similar studies by other groups led to contradictory conclusions. In this investigation, these results were reconciled and it was concluded that $MgSO_3.6H_2O$, under equilibrium conditions, dehydrates in two steps through the intermediate formation of $MgSO_3.3H_2O$.

One consequence of this work is the development of a simple analytical procedure, using TGA, for the quantitative determination of both hydrates in mixtures and in the presence of thermally inactive material.

APPROVAL OF THESIS

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Hexahydrate ($MgSO_3.6H_2O$) and Magnesium Sulfite
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Method for Quantitating Mixtures of the Hydrates.

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FOR

DEPARTMENT OF CHEMISTRY

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMITTEE

APPROVED: ______________________

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INTRODUCTION

The thermal dehydration of the two known stable hydrates of magnesium sulfite, namely, magnesium sulfite hexahydrate ($MgSO_3 \cdot 6H_2O$) and magnesium sulfite trihydrate ($MgSO_3 . 3H_2O$) have been studied. On the one hand, this work is of practical importance because in the Magnesia Scrubbing Regeneration Process (CHEMICO)(8, the thermal dehydration of the magnesium sulfite hydrates is a significant step. On the other hand, this study is of scientific interest because the mechanism of the dehydration has been the subject of controversy.

In the Magnesia Scrubbing Regeneration Process (CHEMICO), sulfur dioxide in the flue gas is removed by scrubbing with a magnesia (MgO) base slurry. Hydrates of $MgSO_3$ are formed; also $MgSO_4$ is formed by oxidation. A portion of the slurry is withdrawn and centrifuged. The solid is separated from the liquid, which is recycled. The solids are then dehydrated in a dryer and, afterwards, calcined at 1400°F-1600°F with coke added to the solids. Heating is sufficient to effect the thermal decomposition of $MgSO_3$; the coke reduces $MgSO_4$ to $MgSO_3$. The useful products of calcination are MgO, which is recycled back to the slurry, and SO_2, which is converted to sulfuric acid.

Turning to the scientific relevance of this study, thermal dehydration studies have been reported by three groups and the results were apparently contradictory. Okabe and

Hori(5)used three different techniques to study the dehydration: Differential Thermal Analysis (DTA), X-ray and Infrared (IR). From the DTA and X-ray results, they concluded that $MgSO_3.6H_2O$ loses three water molecules between 60°C and 100°C to form $MgSO_3.3H_2O$. The latter at 200°C completely dehydrates to yield amorphus anhydrous $MgSO_3$. But in the infrared investigation, they reported that the spectra does not change when the trihydrate goes to the anhydrous state at 200°C. It does not seem plausible that the transformation suggested could have occurred without any change in the infrared spectra. The band in the 3500 cm^{-1} region is obviously an O-H stretching band, therefore, if the salt is dehydrated it would be expected that this band would disappear.

Two other investigations using DTA were carried out by groups at the Tennessee Valley Authority (TVA). These studies were not published, but are presented, in part, in an EPA-sponsored critical analysis of the Magnesia Process prepared by TVA(6). In the above cited report, Jordan's work based upon DTA leads to the conclusion that the thermal dehydration of $MgSO_3.6H_2O$ takes place in one step starting at 100°C and that $MgSO_3.3H_2O$ dehydrates in one step, starting at 160°C.

In the other study, Hatfield and co-workers reported that $MgSO_3.6H_2O$ loses nearly all its water when heated in a stream of argon or air at 104°C for 16 hrs. This, too, supports the inference that the thermal dehydration of the hexahydrate occurs in one step. It is also reported that

$MgSO_3.3H_2O$ is partially dehydrated when heated in air for 16 hrs. at 160°C.

In the above-cited EPA report, it is suggested that the apparently contradictory results may be due to differences in experimental conditions. It was speculated that the samples were heated in sealed tubes in the work of Okabe and Hori, although such information was not provided in that paper. Without presenting a critical analysis of the effects of having the samples open or closed to the atmosphere, it is concluded in the TVA report that the results of the TVA groups, in which the samples are open to the atmosphere, are valid and that $MgSO_3.6H_2O$ dehydrates in one step to $MgSO_3$ at 100°C.

The purpose of this study is to reconcile the contradictory results. Thermoanalytical techniques are used exclusively: Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). Other groups in this laboratory have studied the thermal dehydration using Mass Spectroscopy and Infrared Spectroscopy. These results will be reported separately.

EXPERIMENTAL

$MgSO_3.3H_2O$ (97.9%) and $MgSO_3.6H_2O$ (99.0%) used in this study were laboratory prepared samples. Each hydrate was studied individually; also synthetic mixtures of both hydrates were studied.

The DuPont thermal analyzer was employed in this investigation. This included the DuPont 900 differential thermal analyzer (DTA) equipped with both the standard DTA cell and the differential calorimetric cell (DSC). The DuPont 950 TGA unit,which is an attachment to the DuPont 900,was also used.

DTA(9) is a thermal technique in which the heat effects, associated with chemical or physical changes, are recorded as a function of temperature or time as the substance is heated at a uniform rate. Enthalpic changes, either endothermic or exothermic, are recorded. The sample temperature is continuously compared with a reference material temperature; the difference in temperature is recorded as a function of furnace temperature or time. DTA is reported to have been first used by LeChatelier(4) in 1887 for studying clay. Since that date many developments have been introduced and the literature has grown exponentially. DTA has been used for the study of the thermal dehydration of hydrates. For example, the reader is referred to the work of Wendlant and Hoiberg(10).

In contrast to DTA, in which the temperature difference between the sample and the reference is measured, in DSC it is the heat necessary to equalize the temperature between the sample and the reference which is measured. This technique thus can be used to measure enthalpic changes quantitatively.

TGA is a technique in which a sample is continuously weighed as it is heated at a linear rate. The resulting thermogram gives information concerning the thermal stability of the substance under investigation. TGA was first described by Honda (2) in 1915. Griffith (1) has applied TGA to the study of mixtures of hydrates and anhydrous salts.

Thermal methods of analysis are uniquely applicable for study of dehydration processes. Dehydration can be observed as endothermic changes in DTA, heats of dehydration in DSC, and as weight losses in TGA.

RESULTS AND DISCUSSION

First, the DTA results will be considered. A typical thermogram for the dehydration of $MgSO_3.3H_2O$ is shown in Figure 1. Only one endothermic transition is observed, starting at 190°C. On the other hand, in the thermogram of $MgSO_3.6H_2O$ shown in Figure 2, two endothermic transitions are observed. One starts at 90°C and the other coinciding with the endotherm observed for the trihydrate, starts at 190°C. The inference to be drawn from this data is that the hexahydrate does degrade in two steps and that the two steps involve a transition from the hexaform to the triform.

Next, studies were carried out using DSC. In this case, it is the heat input rather than the temperature which is measured. The DSC thermogram of $MgSO_3.3H_2O$ is shown in Figure 3. Only one endothermic transition was observed starting at 100°C with a peak maximum at 160°C. Both DTA and DSC analyses indicate that the thermal dehydration of $MgSO_3.3H_2O$ is a one step process. From DSC data, it appears that the dehydration of $MgSO_3.3H_2O$ starts at a low temperature, 100°C, in contrast to the DTA data from which it is inferred that 190°C is the starting temperature.

The DSC thermogram of $MgSO_3.6H_2O$ is shown in Figure 4. It is significant to note that only one endothermic transition was observed starting at 45°C with a peak maximum at 90°C. DSC results suggest that the thermal dehydration of $MgSO_3.6H_2O$

takes place in one step starting at 45°C, in contrast to the two step mechanism starting at 90°C to be drawn from the DTA results.

Since the phenomena measured by DTA and DSC is the same, it was expected that the results would be consistent. Surprisingly, this was not the case. From the DSC data, it appears that the dehydration of both hydrates starts at a lower temperature and the hexaform dehydrates in one step and not in two steps as was inferred from the DTA results.

The apparent contradiction between the DTA and the DSC results can be rationalized by considering the relationship between the dehydration reaction and the sample environmental conditions. In any dehydration reaction water is liberated; if the latter is continuously removed from the reaction atmosphere two consequences are observed. First, the dehydration starts at a lower temperature, and, secondly, equilibrium is not attained.

On the one hand in the DSC studies, the sample is placed in an open dish and is heated under a sweeping stream of nitrogen. Under these conditions the liberated water is continuously removed from the reaction environment. On the other hand, in the DTA studies, the sample is heated in a self-generated atmosphere because it is placed in a capillary tube. Under the open conditions encountered in DSC, thermal dehydration starts at a lower temperature, 45°C versus 90°C and only one endothermic transition is observed for the hexaform, whereas in the DTA studies two were observed.

To confirm the above rationalization of the differences between the DTA and the DSC studies, the thermal dehydration was studied by another independent technique, TGA, in which it was possible to heat the samples either in an open condition or in a self-generated atmosphere. TGA thermograms, under open conditions, were obtained by the conventional procedure in which the sample is placed in an open platinum dish under a sweeping blanket of nitrogen. TGA, under self-generated atmosphere, was achieved by placing the sample in a capillary tube with a thermocouple inside. Then, the whole tube was placed in the platinum dish.

In Figure 5, the TGA of $MgSO_3.3H_2O$, under open conditions is shown. Thermal dehydration starts at 100°C and takes place in one step. The weight loss of the sample is 34.0%, which corresponds to the loss of 3 moles of water. The effect of operating under open conditions is shown in Figure 6 for $MgSO_3.6H_2O$. Thermal dehydration of the hexaform starts at 70°C and takes place in one step. The weight loss of the sample is 51%, which corresponds to the loss of 6 moles of water.

The thermograms for the trihydrate and the hexahydrate, respectively, under the conditions of a self-generated atmosphere are shown in Figures 7 and 8. $MgSO_3.3H_2O$, as shown in Figure 7, loses 34.5% of its weight in one step. This is in a very good agreement with TGA under open conditions, but thermal dehydration starts at 220°C, i.e., at a higher temperature, because of the self-generated atmosphere conditions. The weight loss for the hexahydrate under a self-generated atmosphere, as shown in Figure 8, is 51%, which corresponds to the loss of 6 moles of water. It is significant to note that the thermal dehydration of the hexaform starts at a higher temperature and takes place in two steps, with a weight loss of 25.5% in each step. In other words, $MgSO_3.6H_2O$ loses 3 moles of water in each dehydration step.

Thus, when the TGA study of the hexaform is carried out under a non-equilibrium condition, because of heating the sample under a sweeping blanket of nitrogen, equilibrium is not attained due to the continuous removal of the liberated water. As a result, thermal dehydration starts at a lower temperature and takes place in one step. On the other hand, if equilibrium is attained, because of heating the sample in a self-generated atmosphere, the TGA results showed that thermal dehydration starts at a higher temperature and takes place in two steps. First, dehydration leads to the formation of $MgSO_3.3H_2O$, then, to the anhydrous $MgSO_3$. These TGA observations are consistent with the explanation of the differences observed in the DTA and the DSC studies. The results are summarized in Table 1 for $MgSO_3.3H_2O$ and in

Table 2 for $MgSO_3.6H_2O$. The onset of the endotherms as a function of the method are compared.

APPLICATION

The observations made in the TGA studies were used as bases for developing a new analytical method for quantitating mixtures of the tri- and hexahydrates. It had been observed that although the second weight loss for the hexahydrate overlapped that of the trihydrate, nevertheless, from a knowledge of the first weight loss of the hexahydrate, the contribution of the hexahydrate to the second weight loss could be calculated.

The accuracy of the method was investigated by analyzing the thermograms of synthetic mixtures of the hexahydrate and the trihydrate ranging from 10% to 90%. The thermograms are shown in Figures 9-19.

From these thermograms, the water content and the magnesium sulfite content could be calculated. First, the water content calculations will be considered and compared to the theoretical values. The water content of each hydrate in a mixture can be obtained from the TGA thermogram, by taking into account the fact that the weight loss in the first dehydration step at 175°C represents the first three moles of water in $MgSO_3.6H_2O$, i.e., 50% of the water content of the hexaform. Thus the water content can be calculated, from the TGA thermogram, as follows:

$$\% \ H_2O \text{ in } MgSO_3.6H_2O \text{ in a mixture} = (\% \text{ weight loss in the first step at } 175°C)(2)$$

% H_2O in $MgSO_3.3H_2O$ in a mixture = (% weight loss in the second step at 400° C) - (% weight loss in the first step at 175° C)

The theoretical values of the water content are calculated as follows:

% H_2O in $MgSO_3.6H_2O$ in a mixture = % $MgSO_3.6H_2O$ in the mixture

$$X \frac{6H_2O}{MgSO_3.6H_2O} X\ 100$$

$$= \%\ MgSO_3.6H_2O \text{ in the mixture } X \frac{108}{212.3} X\ 100$$

$$= \%\ MgSO_3.6H_2O \text{ in the mixture } X\ 50.9$$

% H_2O in $MgSO_3.3H_2O$ in a mixture = % $MgSO_3.3H_2O$ in the mixture

$$X \frac{3\ H_2O}{MgSO_3.3H_2O} X\ 100$$

$$= \%\ MgSO_3.3H_2O \text{ in the mixture } X \frac{54}{158.3} X\ 100$$

$$= \%\ MgSO_3.3H_2O \text{ in the mixture } X\ 34.1$$

Both theoretical and observed values of the water content are shown in Table 3. The percent water (observed values) is plotted versus magnesium sulfite content in Figure 21 for $MgSO_3.3H_2O$ and in Figure 22 for $MgSO_3.6H_2O$.

The magnesium sulfite content can be calculated from the TGA thermograms by considering the same aspects mentioned in the water content calculations, and, taking into account that 6 moles of water represent 50.9% by weight of $MgSO_3.6H_2O$, and that 3 moles of water represent 34.1% by weight of $MgSO_3.3H_2O$. Thus the percent of each hydrate in a mixture is calculated as follows:

$$\%\ MgSO_3.6H_2O \text{ in a mixture} = \%\text{ weight loss at } 175^\circ C \times 2 \times \frac{100}{50.9}$$

$$\%\ MgSO_3.3H_2O \text{ in a mixture} = (\%\text{ weight loss between } 175^\circ \text{ and } 400^\circ C - \%\text{ weight loss at } 175^\circ C) \times \frac{100}{34.1}$$

The data obtained is compared versus the theoretical values in Table 4 for the triform and in Table 5 for the hexaform. The accuracy of the method, as shown in Tables 4 and 5, was found to be ± 3% if no calibration curve is used. A value of less than 1% is to be expected if a calibration curve is used.

Furthermore, the TGA method was tested in the presence of TGA inactive material. This was achieved by analyzing a mixture of $MgSO_3.3H_2O$, $MgSO_3.6H_2O$ and glass beads. The mixture was subjected to the same experimental conditions of a self-generated atmosphere. The TGA thermogram is shown in Figure 20. From the results summarized in Table 6, it is concluded that this method does not suffer any interferences due to the presence of thermally inactive materials.

Relevant to the nature of the materials obtained in the Magnesia Process, the quantitative analysis of mixtures of $MgSO_3.3H_2O$ and $MgSO_3.6H_2O$ has to be considered in the light of the following contexts: one, only these two hydrates are present; two, in the presence of MgO, three, in the presence of another hydrate, $MgSO_4.7H_2O$. The latter is a common product in the Magnesia Process.

When only the two hydrates are present, methods available include total sulfite by iodine titration(3), X-ray analysis(5), and a wet chemical method developed by Dr. Ray which will be referred to as Ray's Method(7).

In the presence of MgO and/or $MgSO_4.7H_2O$ the measurement of the sulfite content cannot be used to determine the ratio of the hydrates. From the available literature which is limited to the one paper previously cited(5), it is not clear as to whether or not quantitative analysis is possible using the X-ray method in the presence of MgO and/or $MgSO_4.7H_2O$. Ray's method is applicable in the presence of these materials.

The TGA method is simpler than Ray's method but it is not applicable in the presence of $MgSO_4.7H_2O$. On the other hand, Dr. Ray(7) has developed a simple procedure for quantitatively stripping $MgSO_4.7H_2O$ from mixtures of $MgSO_3.3H_2O$, $MgSO_3.6H_2O$ and MgO. Therefore it appears that the TGA technique in conjunction with Ray's stripping procedure is the optimum method.

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Table 1

Starting Temperature of Thermal Dehydration of $MgSO_3 . 3H_2O$

Technique	Experimental Conditions	Onset of the Endotherm
DTA	self-generated	190°C
DSC	open conditions	100°C
TGA	open conditions	100°C
TGA	self-generated	200°C

Table 2

Starting Temperature of

Thermal Dehydration of $MgSO_3.6H_2O$

Technique	Experimental Condition	First Endotherm	Second Endotherm
DTA	self-generated	90°C	190°C
DSC	open conditions	45°C	not observed
TGA	open conditions	70°C	not observed
TGA	self-generated	125°C	220°C

Table 3

Calculated and Observed Values of Water Content in Synthetic Mixtures

	Composition		Calculated H_2O content in			Observed H_2O content in		
Std#	%$MgSO_3.3H_2O$	%$MgSO_3 6H_2O$	Triform	Hexaform	Total	Triform	Hexaform	Total
1	0.0%	100%	0%	50.9%	50.9%	0%	52%	52%
2	10.29%	84.71%	3.5%	45.56%	49.06%	3.4%	44.4%	47.8%
3	18.96%	81.04%	6.46%	41.19%	47.65%	6.6%	39.4%	46%
4	29.37%	70.63%	10%	35.9%	45.9%	9.0%	35.0%	44%
5	38.24%	61.76%	13.03%	31.39%	44.42%	12%	32%	44%
6	50%	50%	17.04%	25.42%	42.46%	16.4%	26%	42.4%
7	59.84%	40.16%	20.39%	20.41%	40.8%	19.8%	20.4%	40.2%
8	70.19%	29.81%	23.91%	15.15%	39.06%	23%	16%	39%
9	79.34%	20.66%	27.03%	10.5%	37.53%	26.4%	10.6%	37%
10	90.18	9.82%	30.72%	4.99%	35.71%	30.2%	5%	35.2%
11	100%	0%	34.1%	0%	34.1%	34.8%	0%	34.8%

Table 4

$MgSO_3.3H_2O$ Content from TGA

Std#	Theoretical Value	Observed Value	Deviation
1	0%	0%	0%
2	10.29%	10.26%	-.03%
3	18.96%	19.35%	+.39%
4	29.37%	26.39%	-2.98%
5	38.24%	35.24%	-3.00%
6	50.0%	48.1%	-1.9%
7	59.84%	58.06%	-1.78%
8	70.19%	67.45%	-2.74%
9	79.34%	77.42%	-1.92%
10	90.18%	88.56%	-1.62%
11	100.00%	102.0%	+2.0%

Table 5

$MgSO_3 . 6H_2O$ Content

From TGA

Std#	Theoretical Value	Observed Value	Deviation
1	100%	102.2%	+2.2%
2	89.71%	87.3%	-2.41%
3	81.04%	78.45%	-2.54%
4	70.63%	68.8%	-1.83%
5	61.76%	62.9%	+1.14%
6	50%	51.11%	+1.11%
7	40.16%	40.1%	-.06%
8	29.81%	31.45%	+1.64%
9	20.66%	20.84%	+.18%
10	9.82%	9.83%	+.01%
11	0%	0%	0%

Table 6

TGA results of a synthetic mixture containing thermally inactive compound

	Theoretical Value	Observed Value
$MgSO_3.3H_2O$	44.3%	43.2%
$MgSO_3.6H_2O$	30.0%	29.3%
glass beads	25.7%	27.5%*

*This value was obtained by difference

DU PONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 3H_2O$

Fig. No. 1

ORIGIN:

SIZE 6 mg

REF. glass beads

PROG. MODE heat

RATE 10 °C/MIN, START 30 °C

ATM. self-generated MM

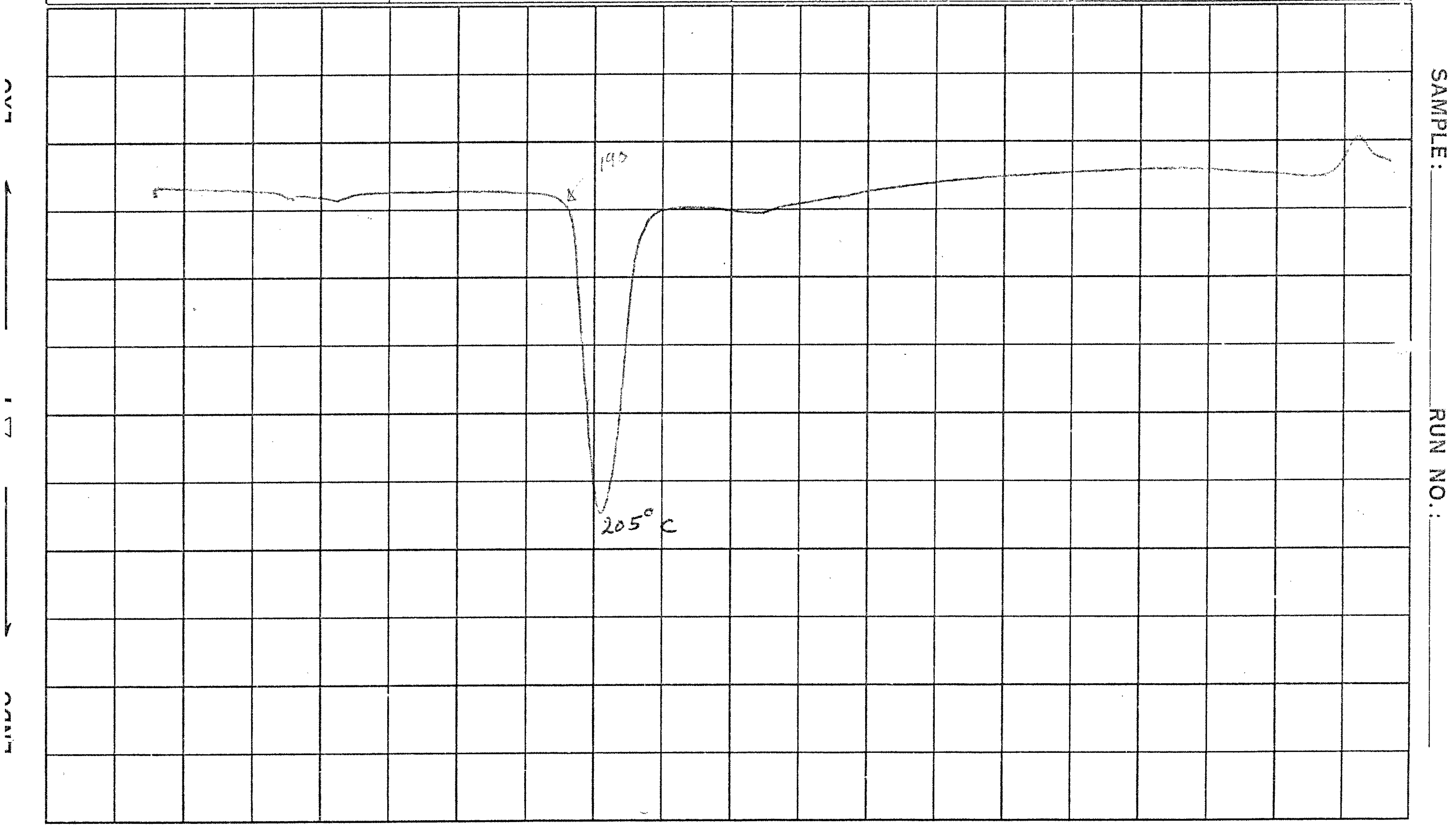
	T	ΔT
SCALE	50 °C/IN.	2 °C/IN.
SHIFT	0 IN.	0 IN.

RUN NO. 1

DATE 11/8/74

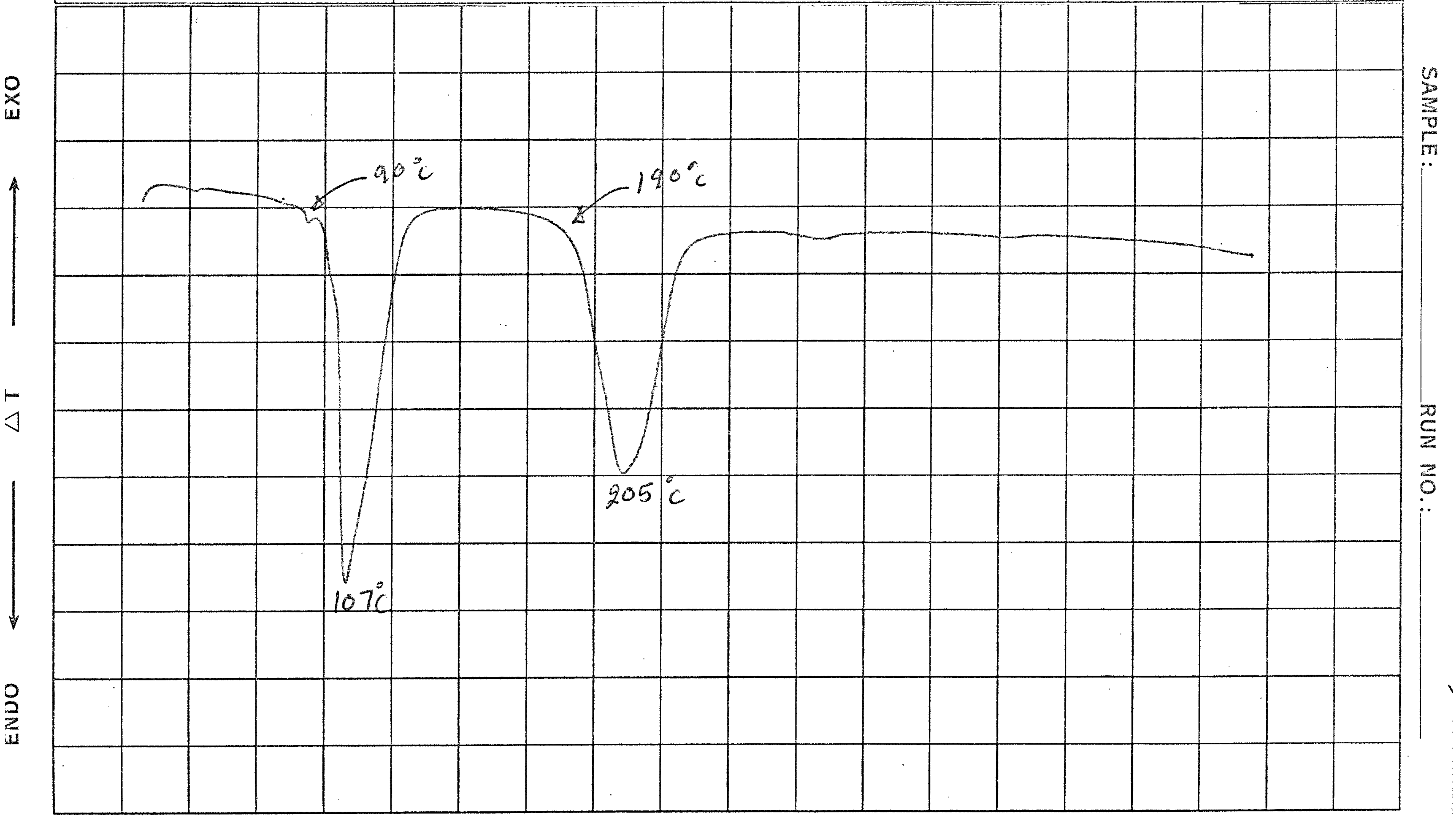
OPERATOR RM

BASE LINE SLOPE 0



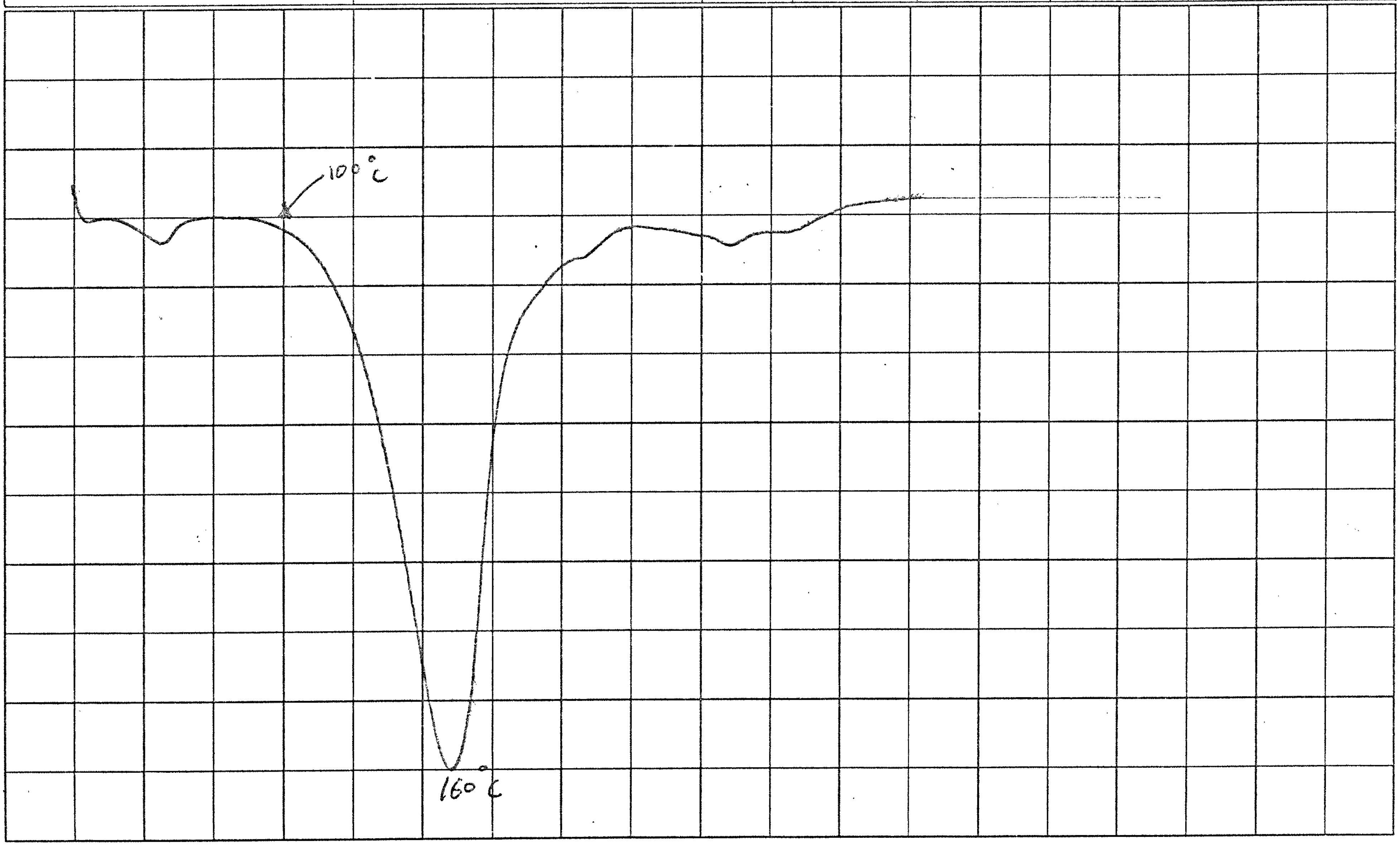
DU PONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 6H_2O$	**SIZE** 8 mg	**ATM.** self-generated **MM**	**RUN NO.** 1
Fig. No. 2	**REF.** glass beads	**T** / **△ T**	**DATE** 11/8/74
	PROG. MODE heat	**SCALE** 50 °C/IN. / 2 °C/IN.	**OPERATOR** RM
ORIGIN:	**RATE** 10 °C/MIN **,START** 30 **°C**	**SHIFT** 0 **IN.** / 0 **IN.**	**BASE LINE SLOPE** 0



DUPONT INSTRUMENTS

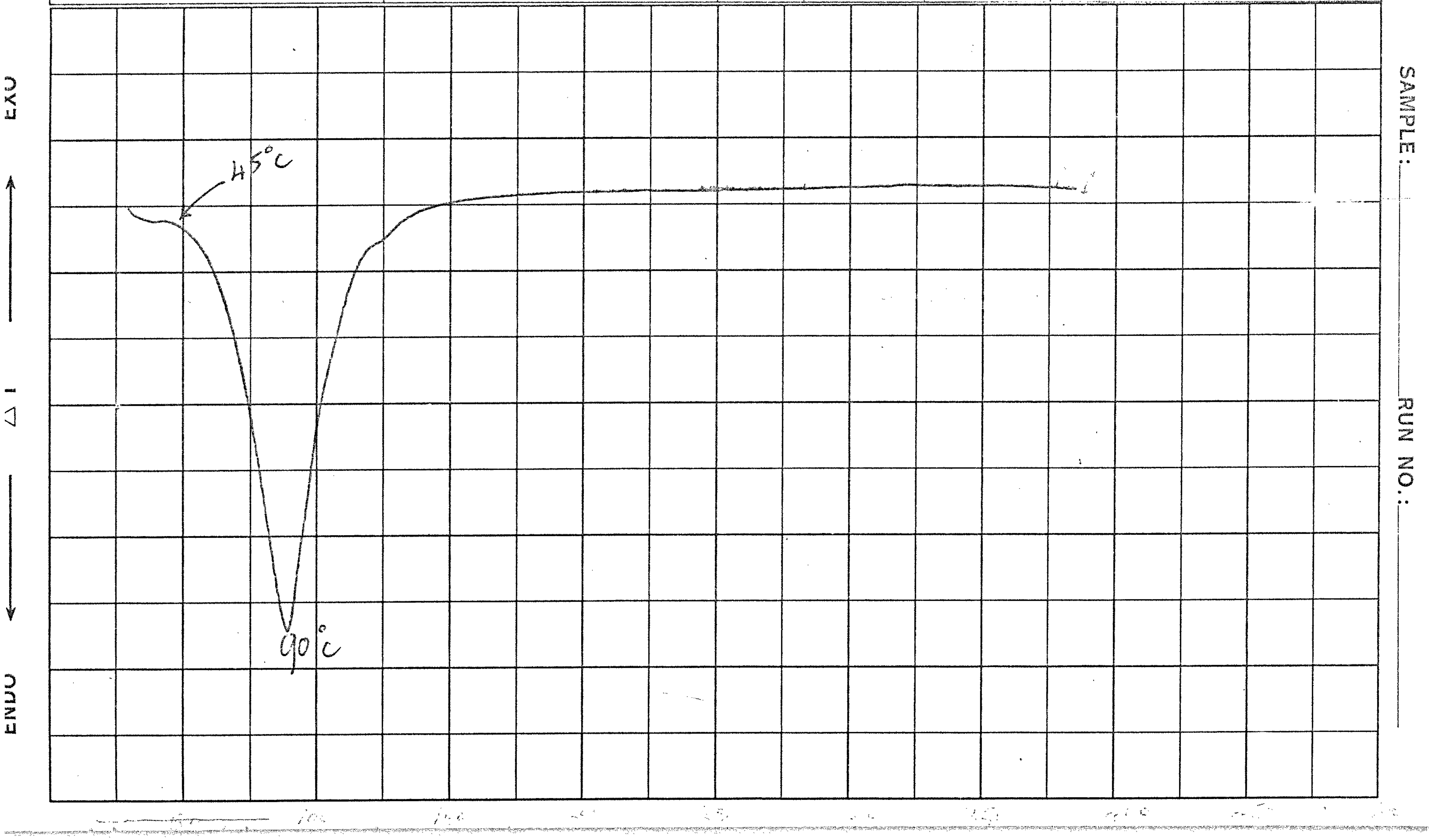
SAMPLE: $MgSO_3.3H_2O$	**SIZE** 12 mg	**ATM.** N_2 , 30 **MM**	**RUN NO.** 1
Fig. No. 3	**REF.** empty pan	T / △ T	**DATE** 11/9/74
	PROG. MODE heat	**SCALE** 50 °C/IN. / 1 °C/IN.	**OPERATOR** RM
ORIGIN:	**RATE** 10 °C/MIN **, START** 25 **°C**	**SHIFT** 0 **IN.** / 0 **IN.**	**BASE LINE SLOPE** 0



SAMPLE: ______ RUN NO.: ______

DU PONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 6H_2O$ Fig. No. 4	SIZE 5 mg	ATM. N_2 , 30 MM			RUN NO. 1
	REF. empty pan		T	ΔT	DATE 11/9/74
	PROG. MODE heat	SCALE	50 °C/IN.	1 °C/IN.	OPERATOR RM
ORIGIN:	RATE 10 °C/MIN, START 30 °C	SHIFT	0 IN.	0 IN.	BASE LINE SLOPE 0



DU PONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 3H_2O$

Fig. No. 5

SIZE 20 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 4 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

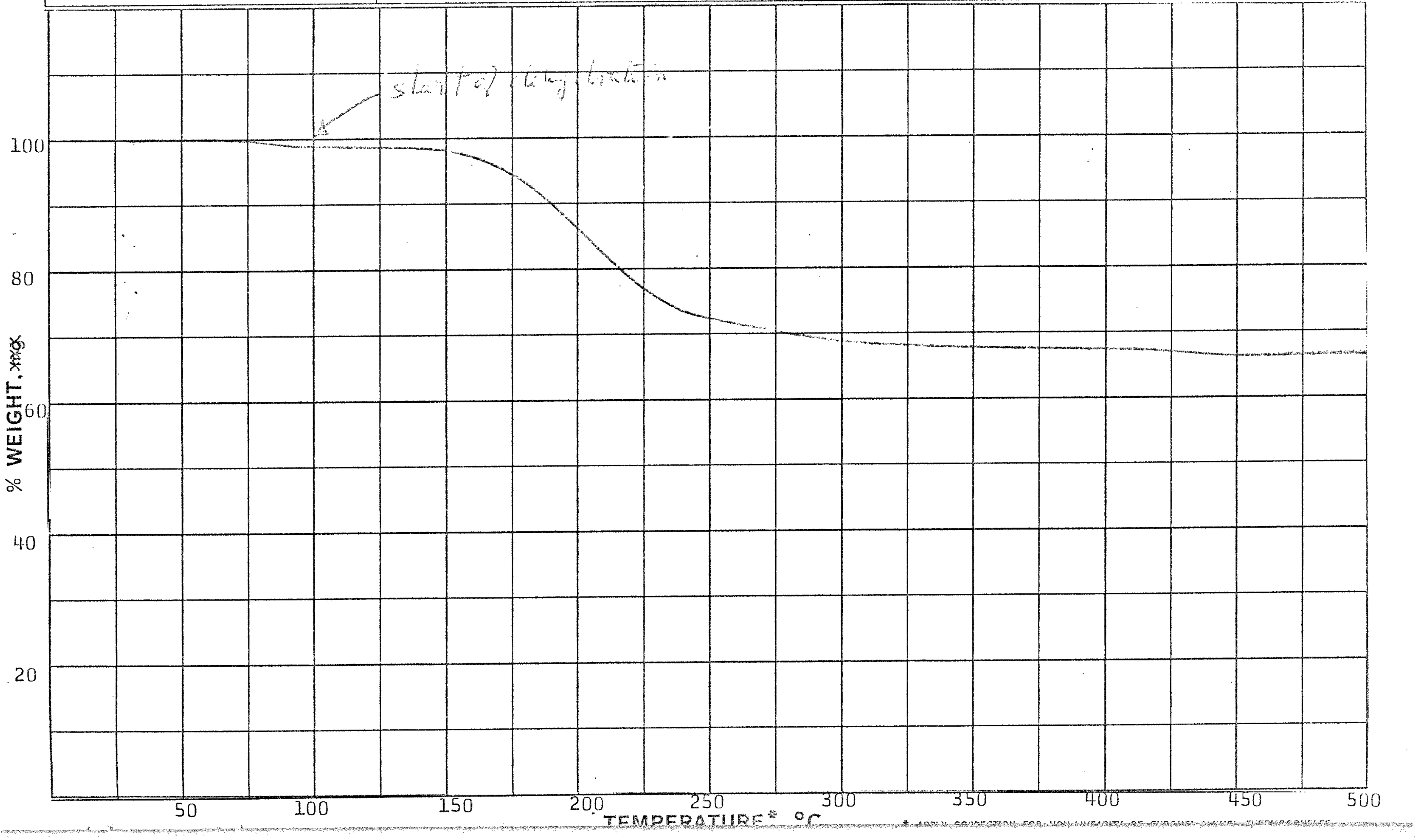
RUN NO. 1 DATE 11/12/74

OPERATOR RM

HEATING RATE 10 °C/min.

ATM. N_2, 30 ml/min.

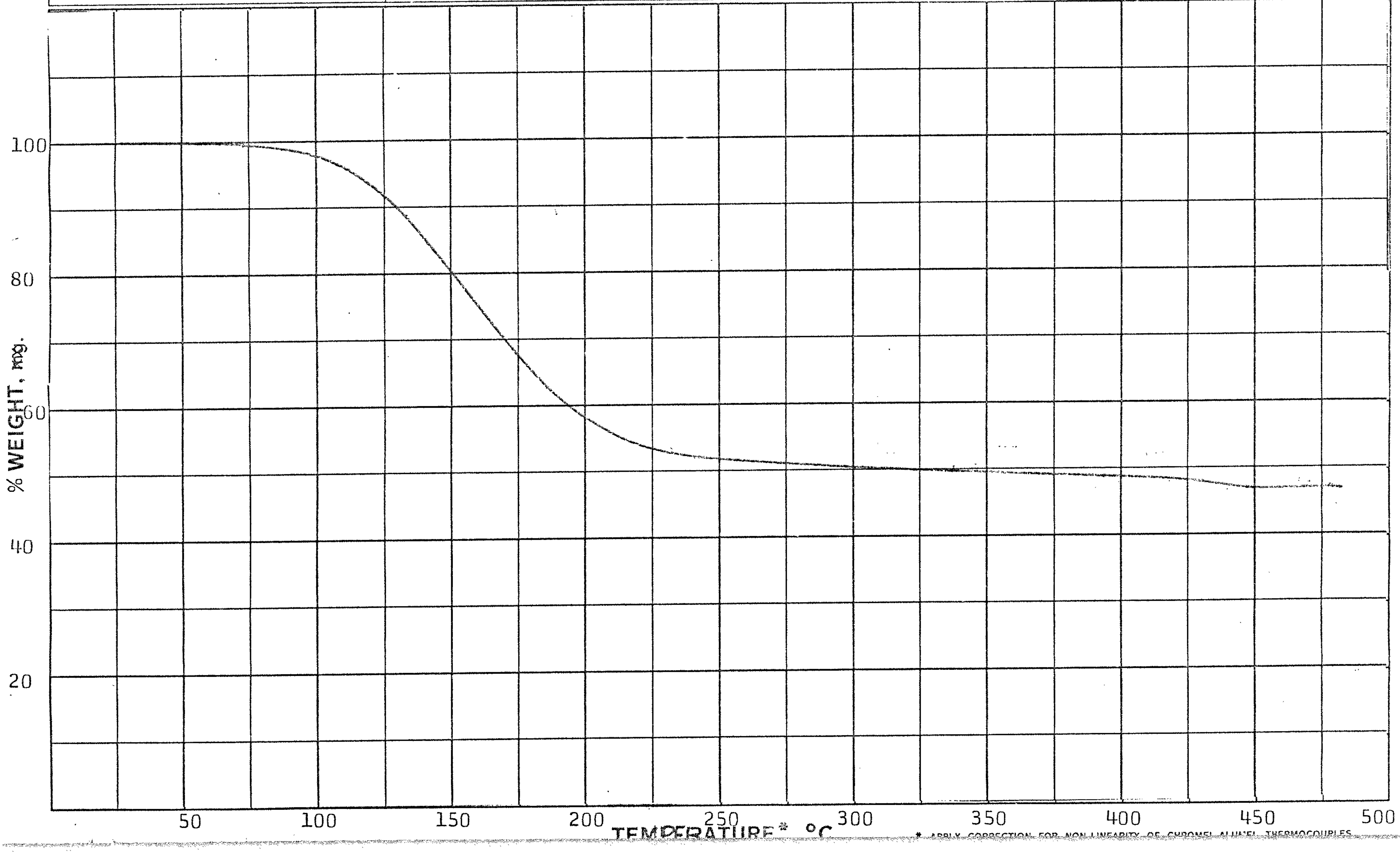
TIME CONSTANT 1 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DUPONT INSTRUMENTS

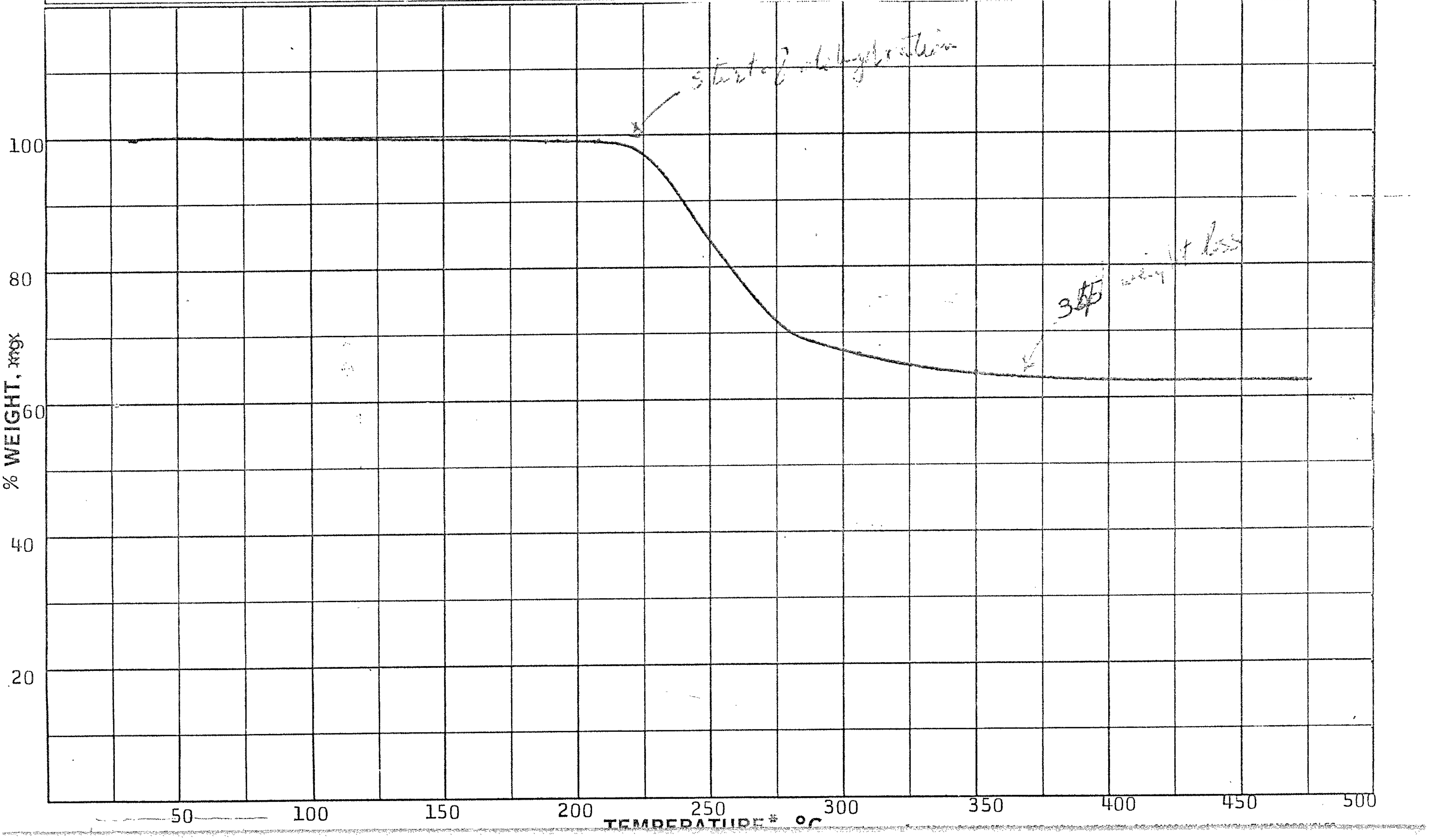
SAMPLE: $MgSO_3.6H_2O$ Fig. No. 6 **SIZE** 20 mg.	**X-AXIS** **TEMP. SCALE** 50 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)**	**Y-AXIS** **SCALE** 4 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 5 mg.	**RUN NO.** 1 **DATE** 11/12/74 **OPERATOR** RM **HEATING RATE** 10 °C/min. **ATM.** N_2, 30 ml/min. **TIME CONSTANT** 1 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

DUPONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 3H_2O$ Fig. No. 7 SIZE 5 mg.	X-AXIS TEMP. SCALE 50 °C/inch SHIFT 0 inch TIME SCALE (ALT.)	Y-AXIS SCALE 2 mg./inch (SCALE SETTING X 2) SUPPRESSION 60 mg.	RUN NO. 1 DATE 11/15/74 OPERATOR RM HEATING RATE 10 °C/min. ATM. self-generated TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 6H_2O$

Fig. No. 8

SIZE 5 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 1 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 60 mg.

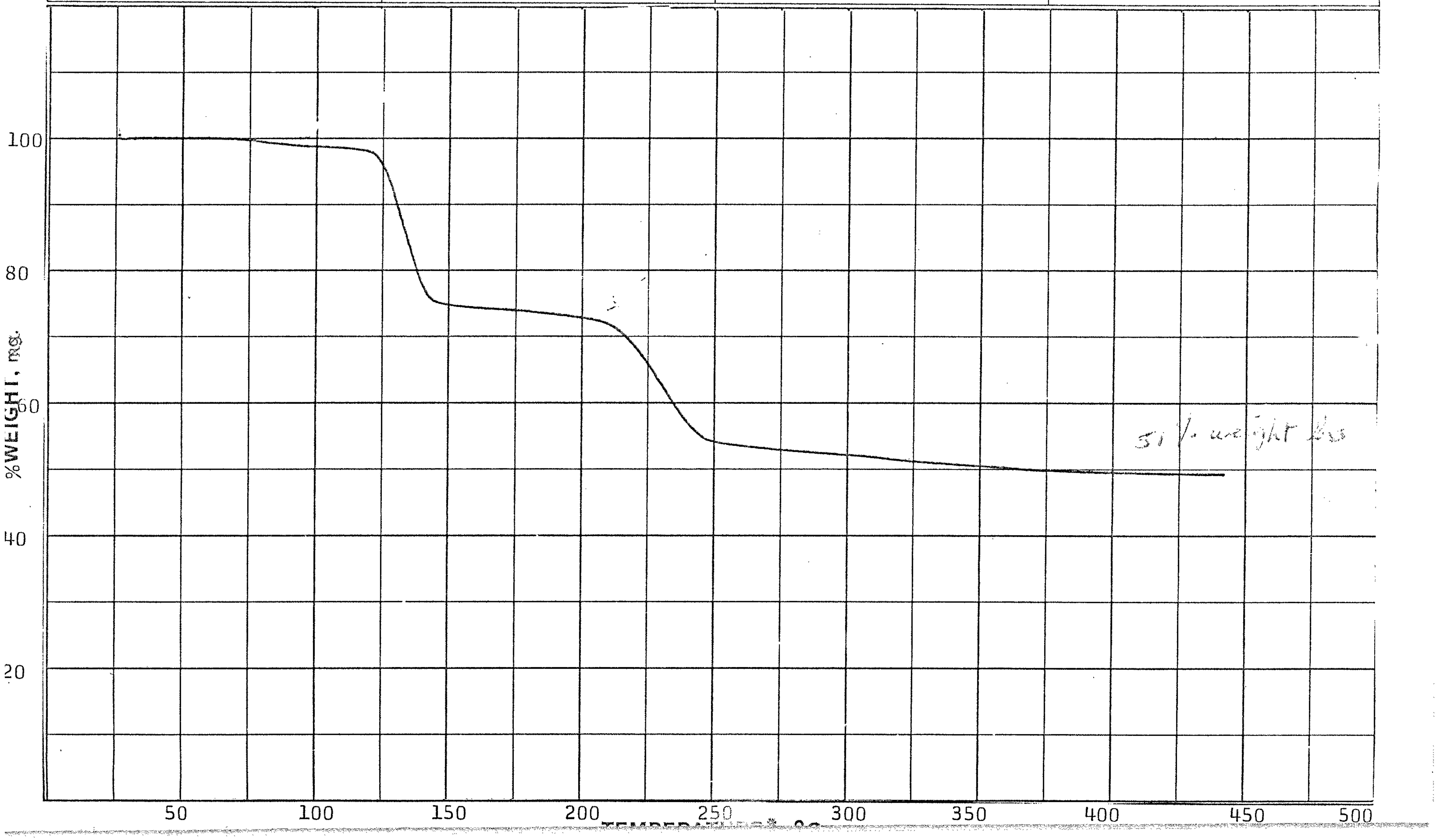
RUN NO. 1 **DATE** 11/16/74

OPERATOR RM

HEATING RATE 10 °C/min.

ATM. self-generated

TIME CONSTANT sec.



DU PONT INSTRUMENTS

SAMPLE: Std #1
100% $MgSO_3 \cdot 6H_2O$

Fig. No. 9

SIZE 12 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)

SUPPRESSION 50 mg.

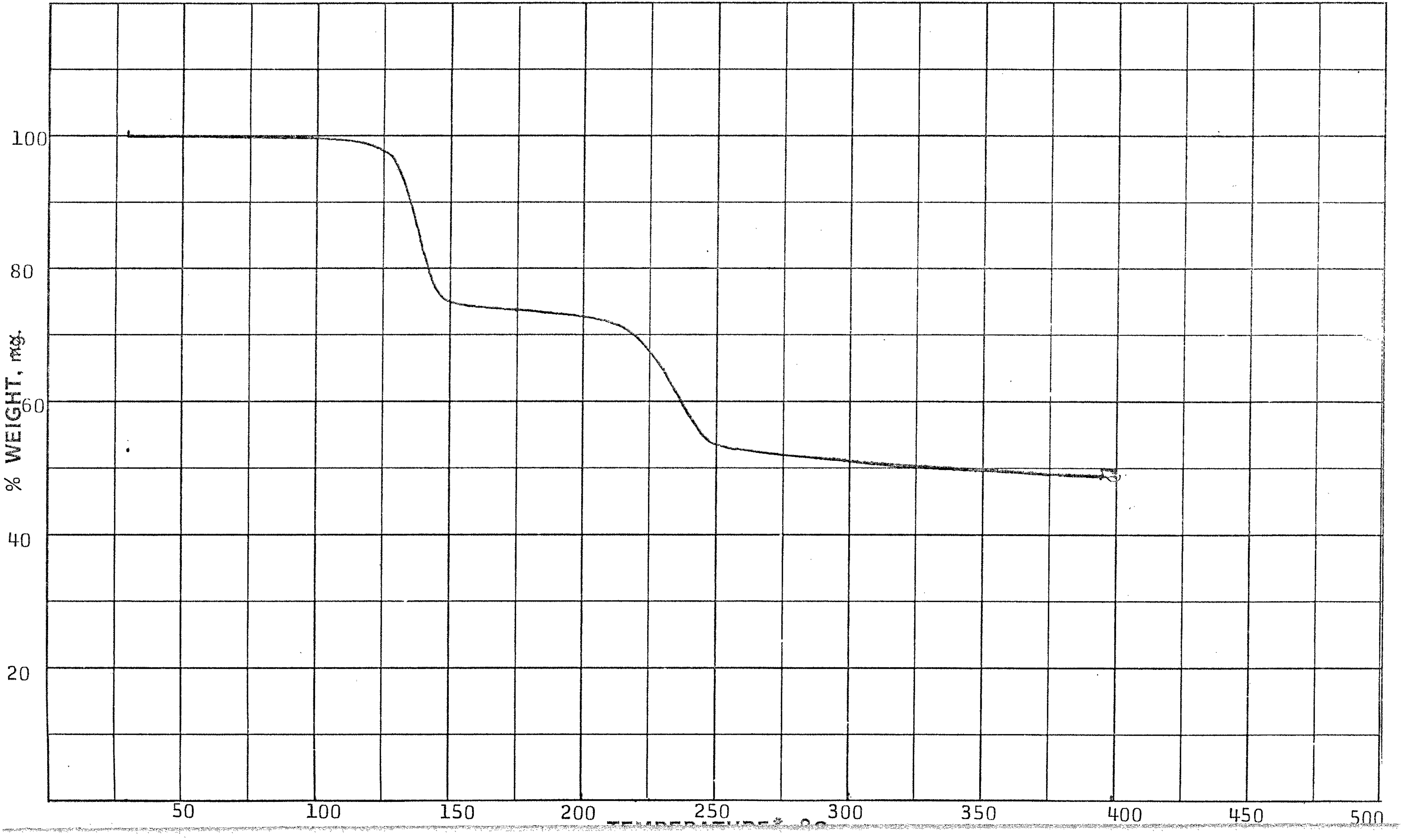
RUN NO. 1 **DATE** 11/17/74

OPERATOR RM

HEATING RATE 10 °C/min.

ATM. self-generated

TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

SAMPLE: Std #2
10.29% $MgSO_3 . 3H_2O$
89.71% $MgSO_3 . 6H_2O$

Fig. No. 10

SIZE 10 mg.

X-AXIS

TEMP. SCALE 100 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

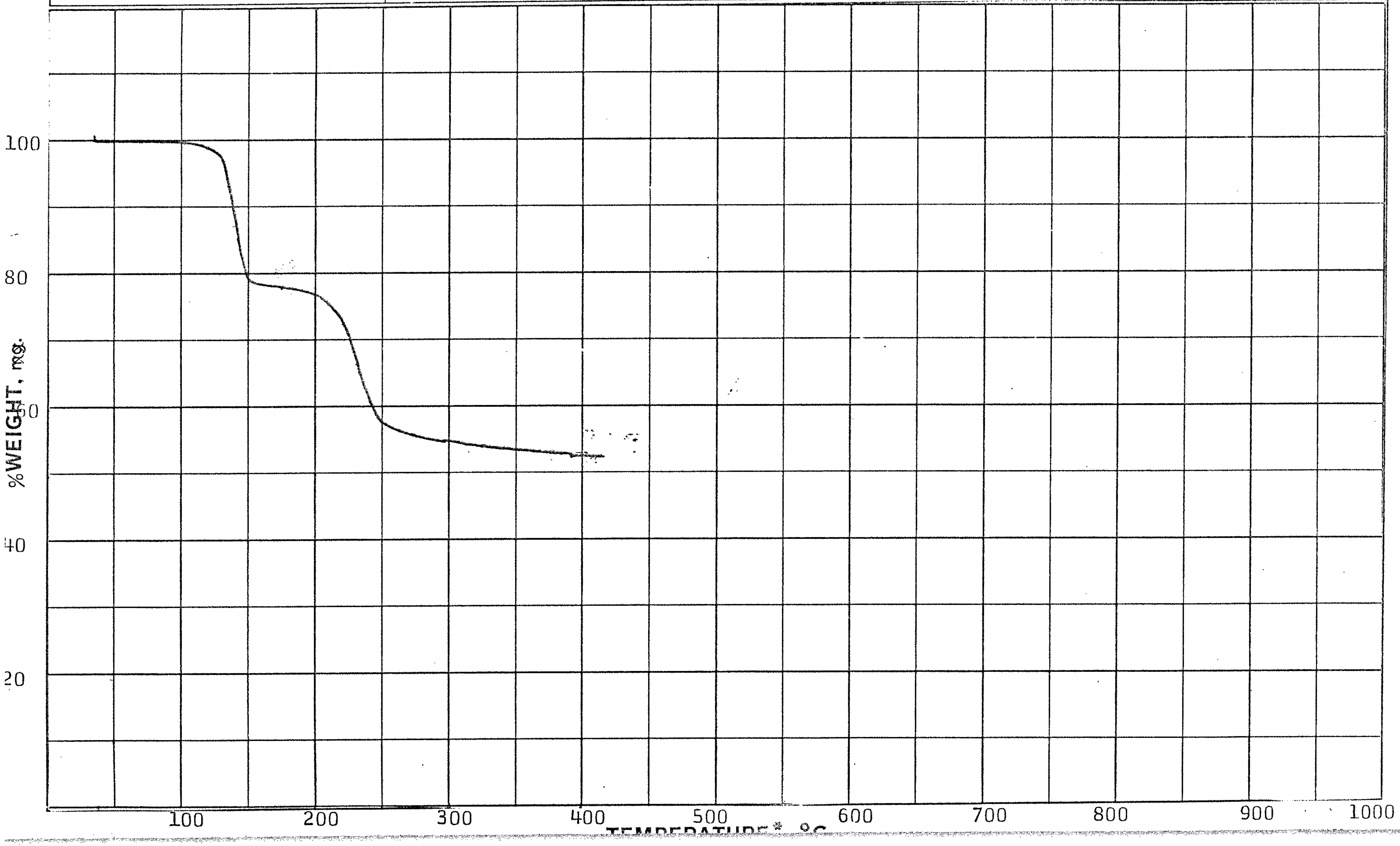
RUN NO. 1 **DATE** 11/20/74

OPERATOR RM

HEATING RATE 10 °C/min.

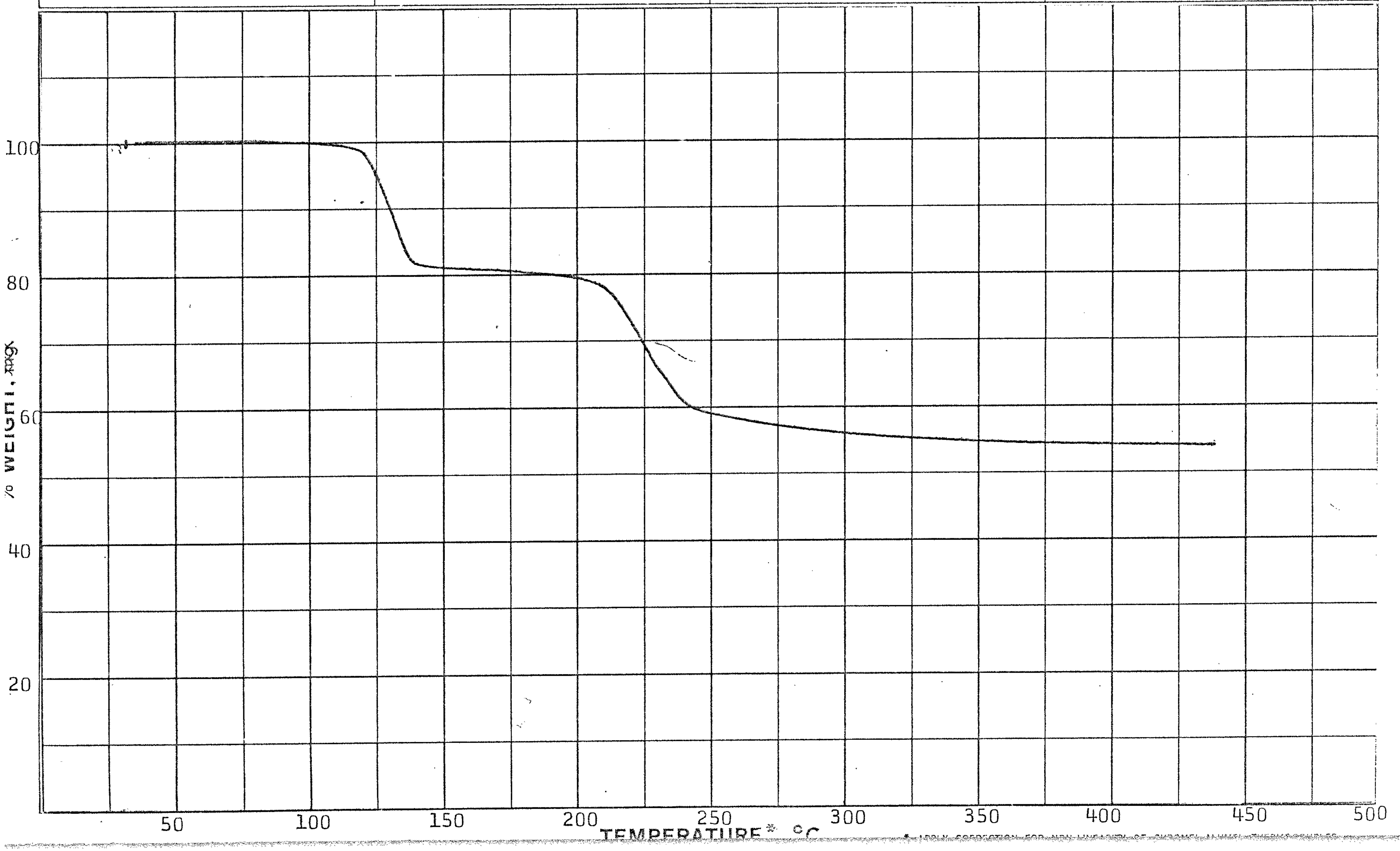
ATM. self-generated

TIME CONSTANT 1 sec.



INSTRUMENTS

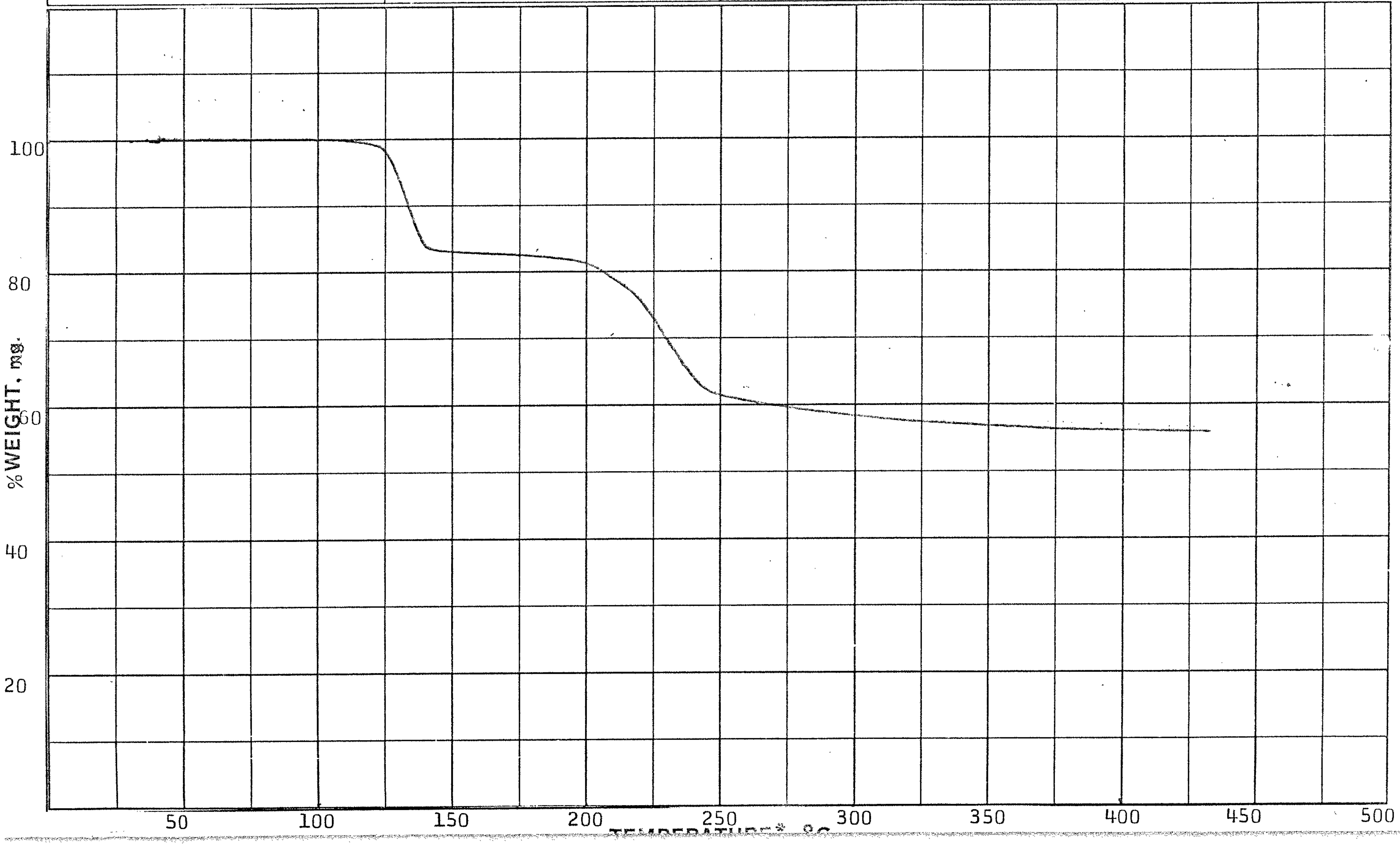
SAMPLE: Std #3 18.96% $MgSO_3 \cdot 3H_2O$ 81.04% $MgSO_3 \cdot 6H_2O$ Fig. No. 11 **SIZE** 15 mg.	**X-AXIS** **TEMP. SCALE** 50 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)**	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 50 mg.	**RUN NO.** 1 **DATE** 11/21/74 **OPERATOR** RM **HEATING RATE** 10 °C/min. **ATM.** self-generated **TIME CONSTANT** 1 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DUPONT INSTRUMENTS

SAMPLE: Std #4 29.37% $MgSO_3 \cdot 3H_2O$ 70.63% $MgSO_3 \cdot 6H_2O$ Fig. No. 12 **SIZE** 10 mg.	**X-AXIS** **TEMP. SCALE** 50 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)**	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 50 mg.	**RUN NO.** 1 **DATE** 11/22/74 **OPERATOR** RM **HEATING RATE** 10 °C/min. **ATM.** self-generated **TIME CONSTANT** 1 sec.



DUPONT INSTRUMENTS

SAMPLE: Std #5
38.24% $MgSO_3 \cdot 3H_2O$
61.76% $MgSO_3 \cdot 6H_2O$

Fig. No. 13

SIZE 12 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

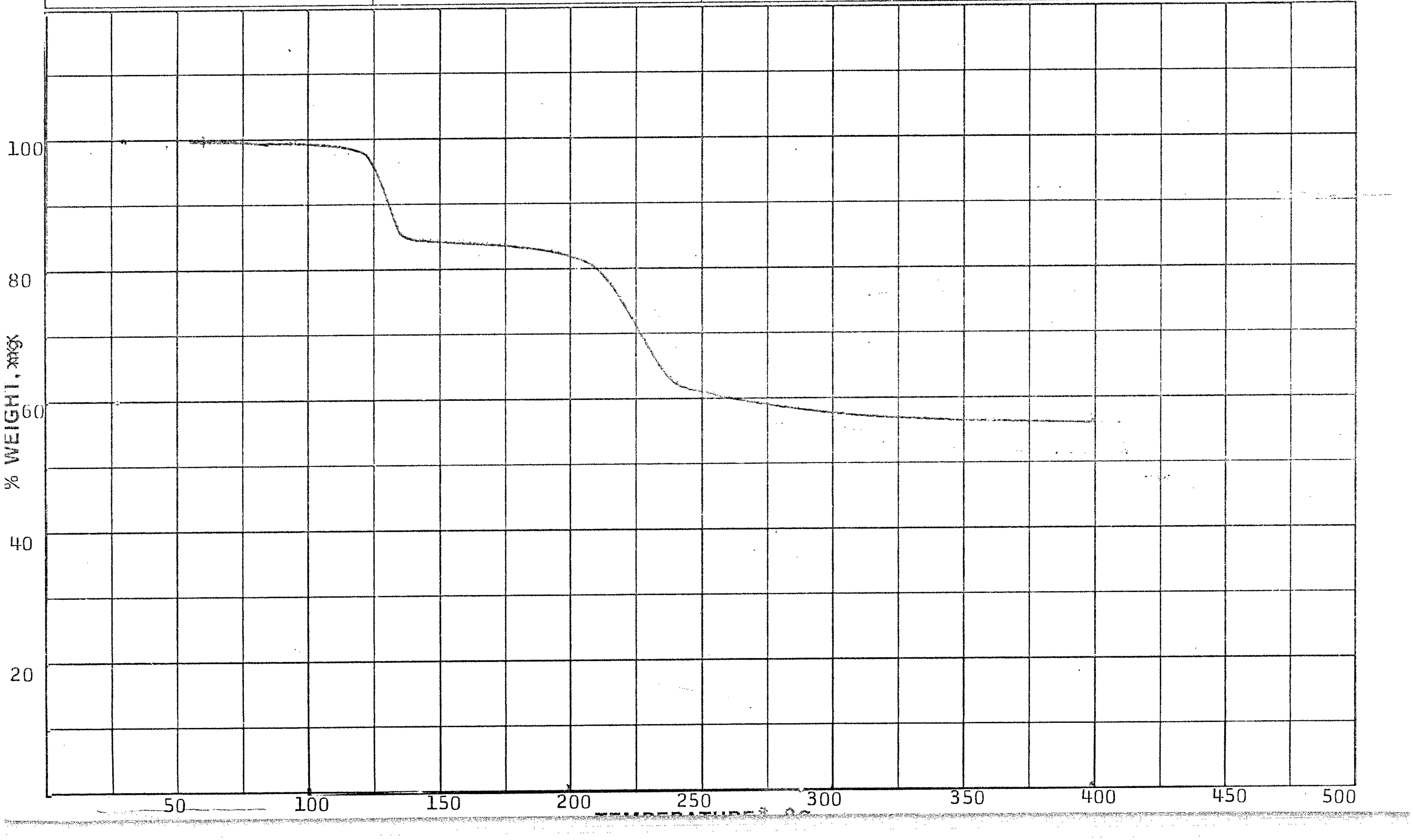
RUN NO. 1 **DATE** 11/25/74

OPERATOR RM

HEATING RATE 10 °C/min.

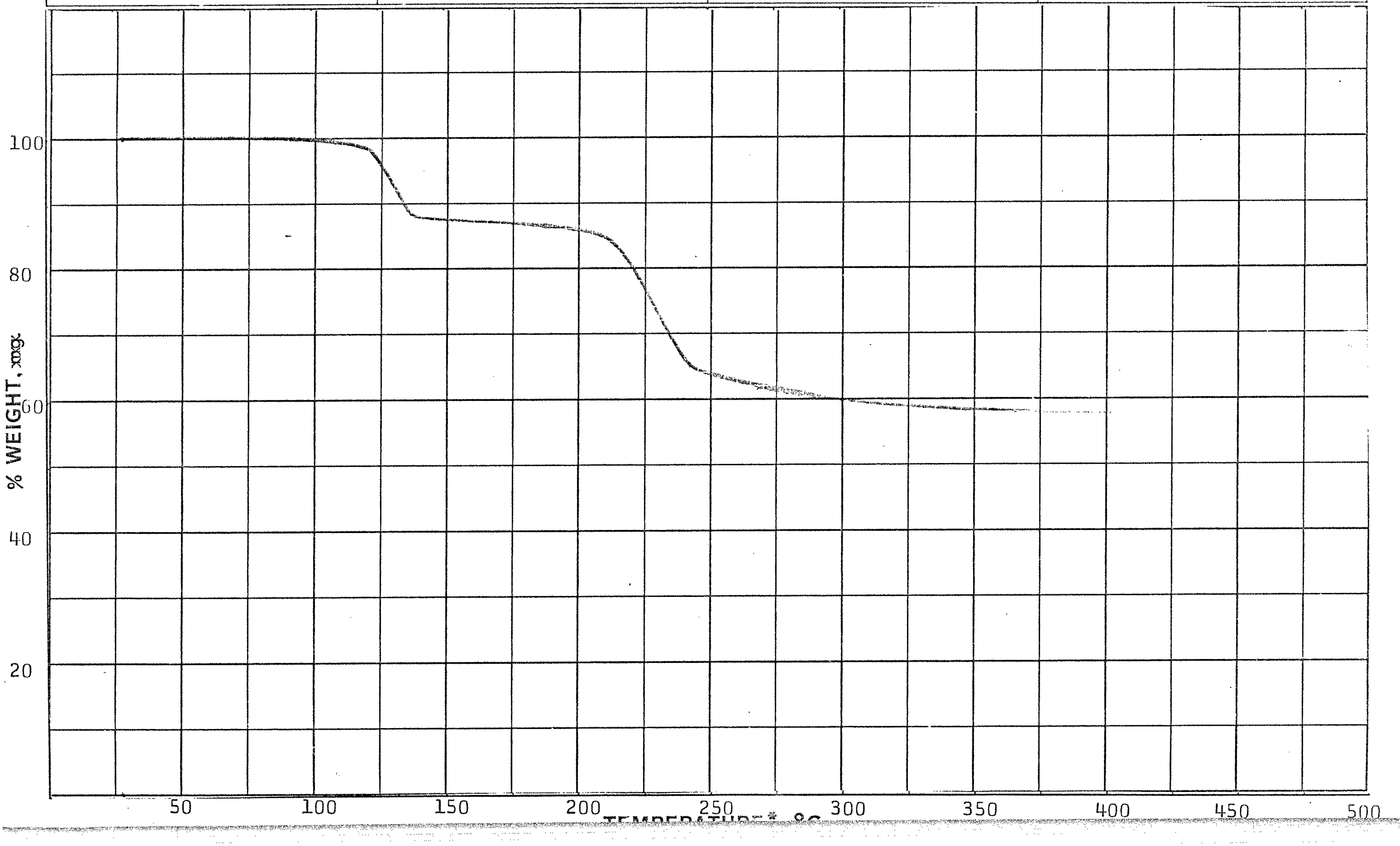
ATM. self-generated

TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

SAMPLE	X-AXIS	Y-AXIS	
SAMPLE: Std #6 50% $MgSO_3 . 3H_2O$ 50% $MgSO_3 . 6H_2O$	**TEMP. SCALE** 50 °C/inch	**SCALE** 2 mg./inch **(SCALE SETTING X 2)**	**RUN NO.** 1 **DATE** 11/25/74 **OPERATOR** RM
Fig. No. 14	**SHIFT** 0 inch		**HEATING RATE** 10 °C/min. **ATM.** self-generated
SIZE 10 mg.	**TIME SCALE (ALT.)**	**SUPPRESSION** mg.	**TIME CONSTANT** 1 sec.



DU PONT INSTRUMENTS

SAMPLE: Std #7
59.84% $MgSO_3 \cdot 3H_2O$
40.16% $MgSO_3 \cdot 6H_2O$

Fig. No. 15

SIZE 12 mg.

X-AXIS

TEMPERATURE SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

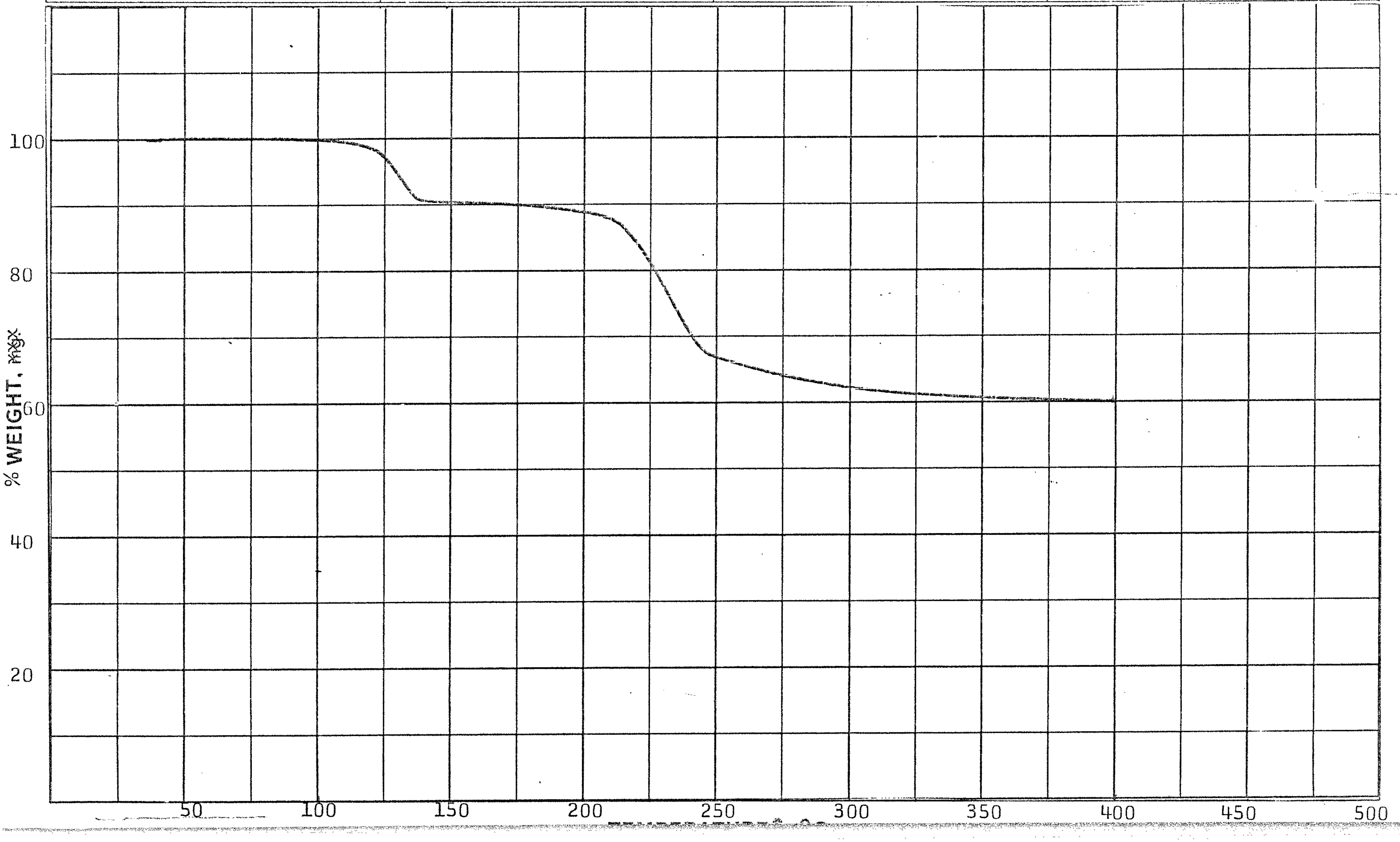
RUN NO. 1 **DATE** 11/27/74

OPERATOR RM

HEATING RATE 10 °C/min.

ATM. self-generated

TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

SAMPLE: Std #8
70.19% $MgSO_3 . 3H_2O$
29.81% $MgSO_3 . 6H_2O$

Fig. No. 16

SIZE 12 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg./inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

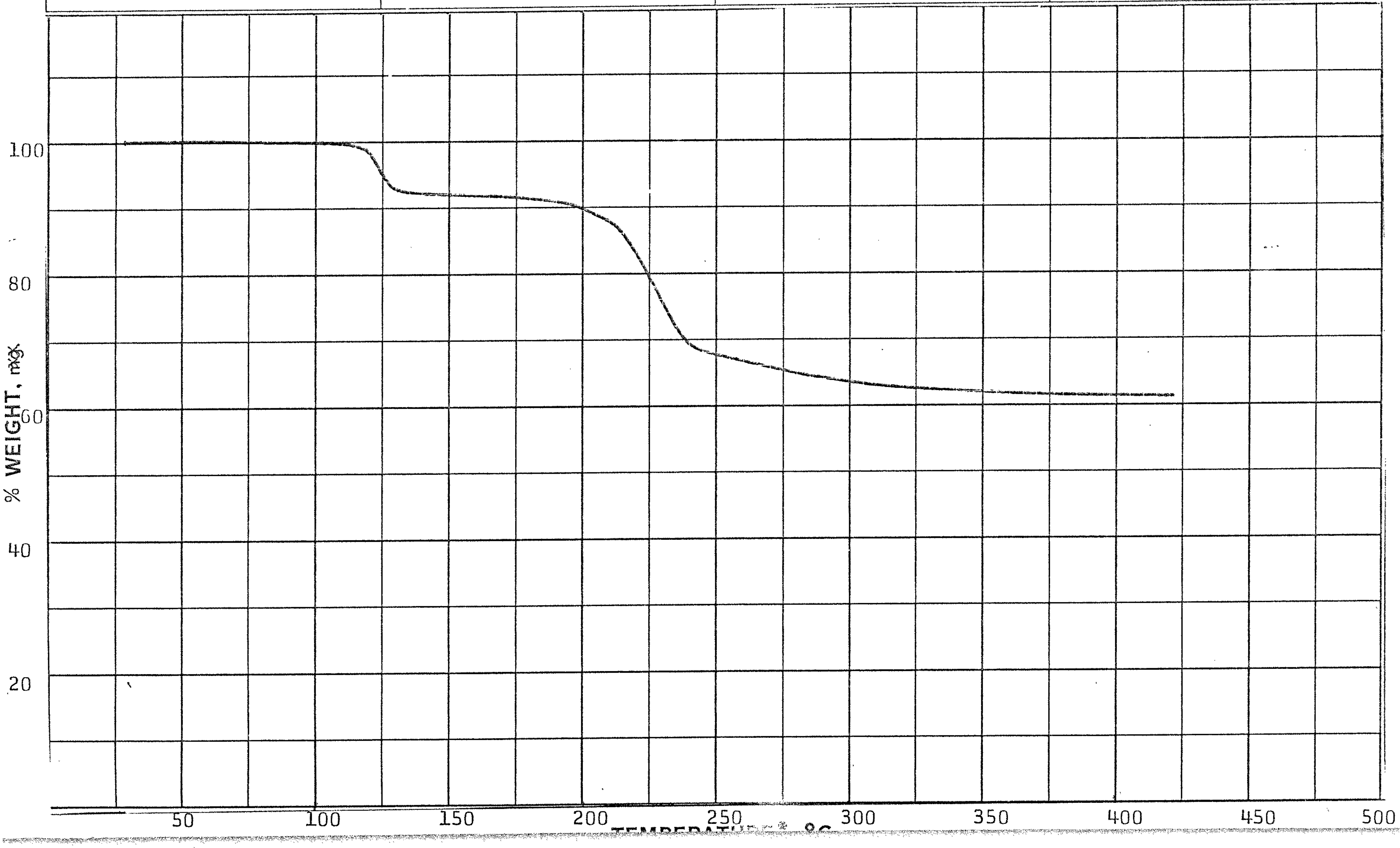
RUN NO. 1 DATE 11/25/74

OPERATOR RM

HEATING RATE 10 °C/min.

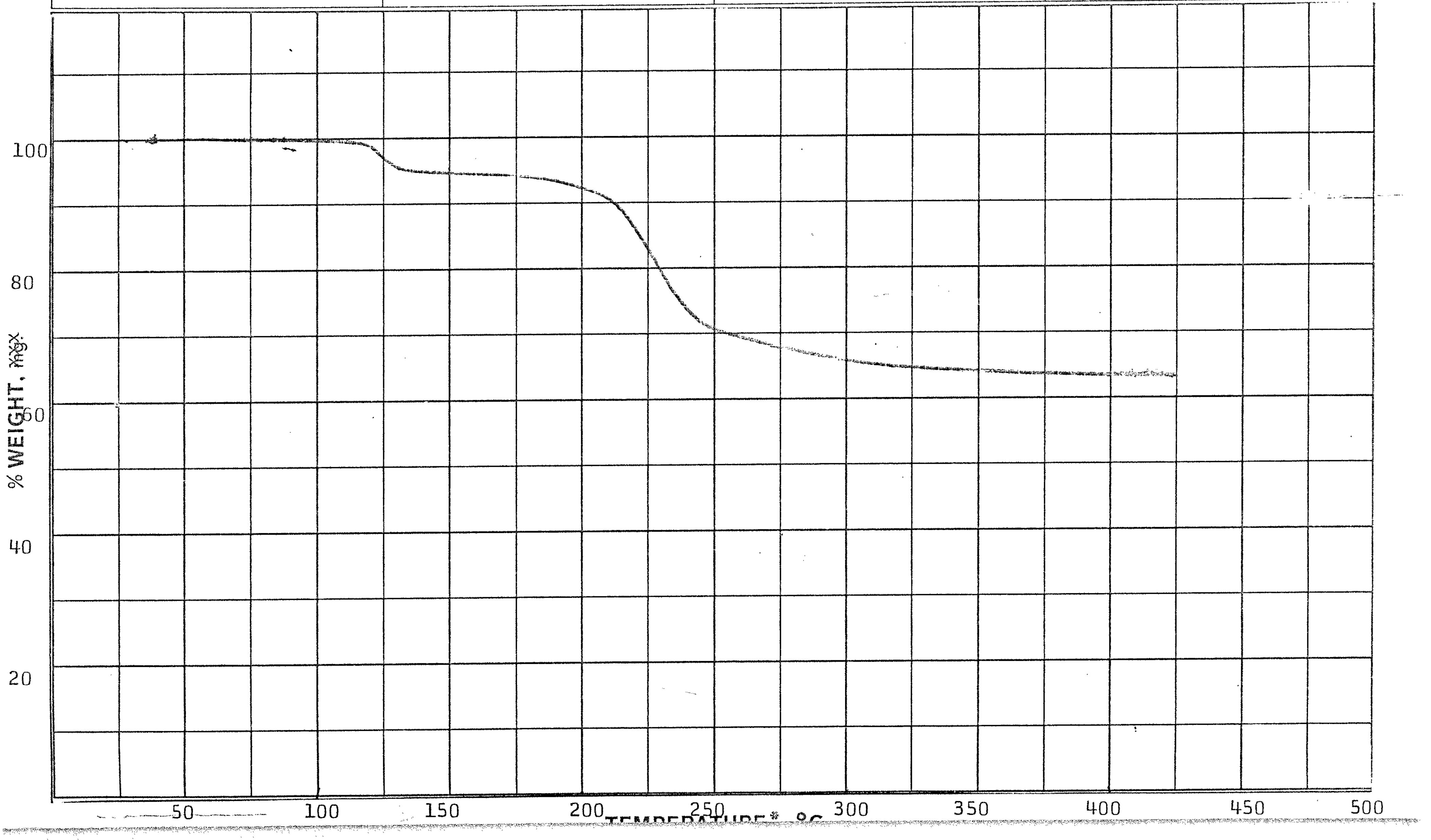
ATM. self-generated

TIME CONSTANT 1 sec.



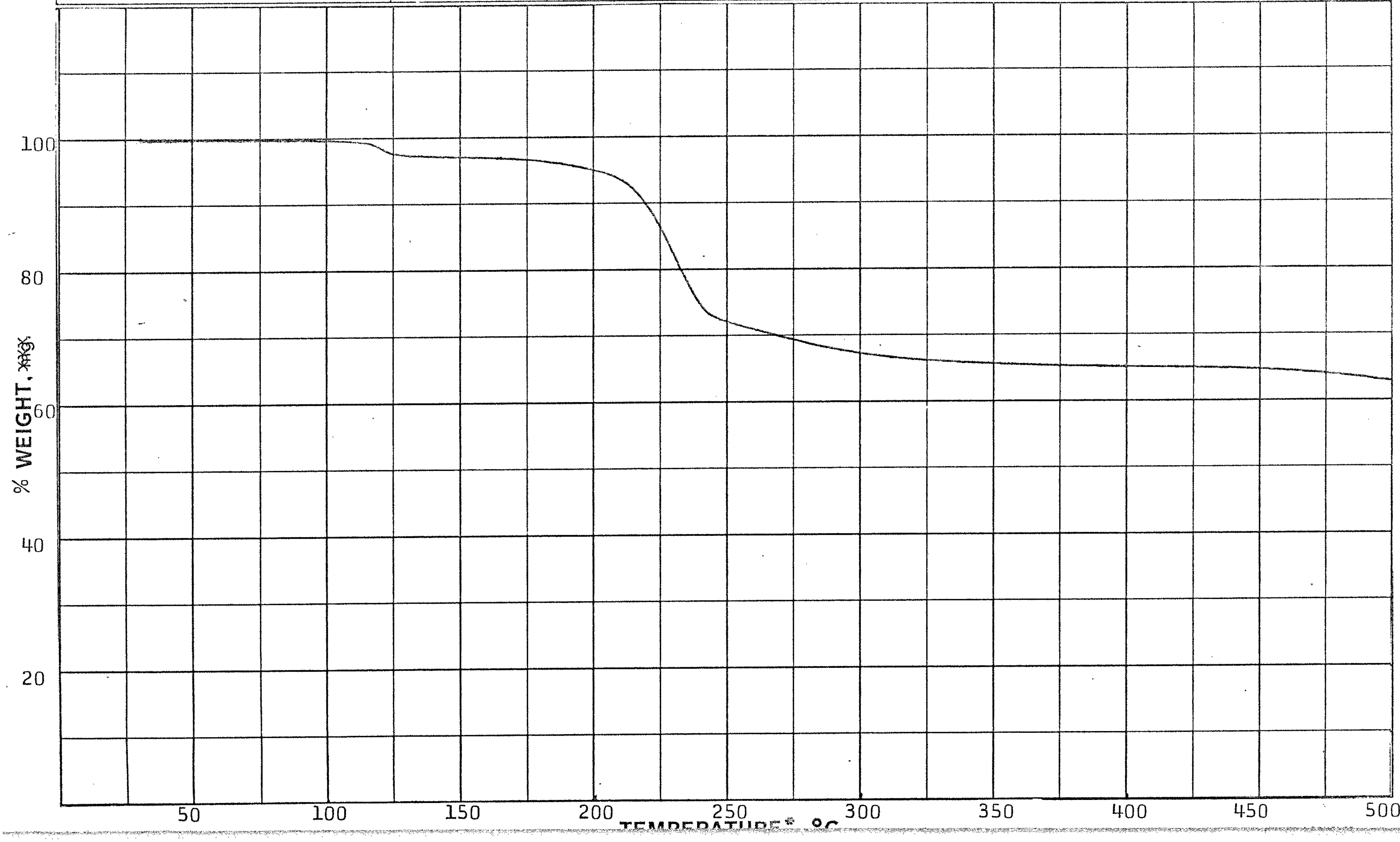
DU PONT INSTRUMENTS

SAMPLE: Std #9 79.34% $MgSO_3 \cdot 3H_2O$ 20.66% $MgSO_3 \cdot 6H_2O$ Fig. No. 17 **SIZE** 14 mg.	**X-AXIS** **TEMP. SCALE** 50 °C/inch **SHIFT** 0 inch **TIME SCALE (ALT.)**	**Y-AXIS** **SCALE** 2 mg./inch (SCALE SETTING X 2) **SUPPRESSION** 50 mg.	**RUN NO.** 1 **DATE** 11/27/74 **OPERATOR** RM **HEATING RATE** 10 °C/min. **ATM.** self-generated **TIME CONSTANT** 1 sec.



DUPONT INSTRUMENTS

SAMPLE: Std #10 90.18% $MgSO_3 \cdot 3H_2O$ 9.82% $MgSO_3 \cdot 6H_2O$	**X-AXIS**	**Y-AXIS**	RUN NO. 1 DATE 11/30/74
Fig. No. 18	TEMP. SCALE 50 °C/inch	SCALE 2 mg./inch (SCALE SETTING X 2)	OPERATOR RM
SIZE 16 mg.	SHIFT 0 inch		HEATING RATE 10 °C/min.
	TIME SCALE (ALT.)	SUPPRESSION 50 mg.	ATM. self-generated
			TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

SAMPLE: Std #11
100% $MgSO_3 . 3H_2O$
Fig. No. 19

SIZE 14 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)

SUPPRESSION 50 mg.

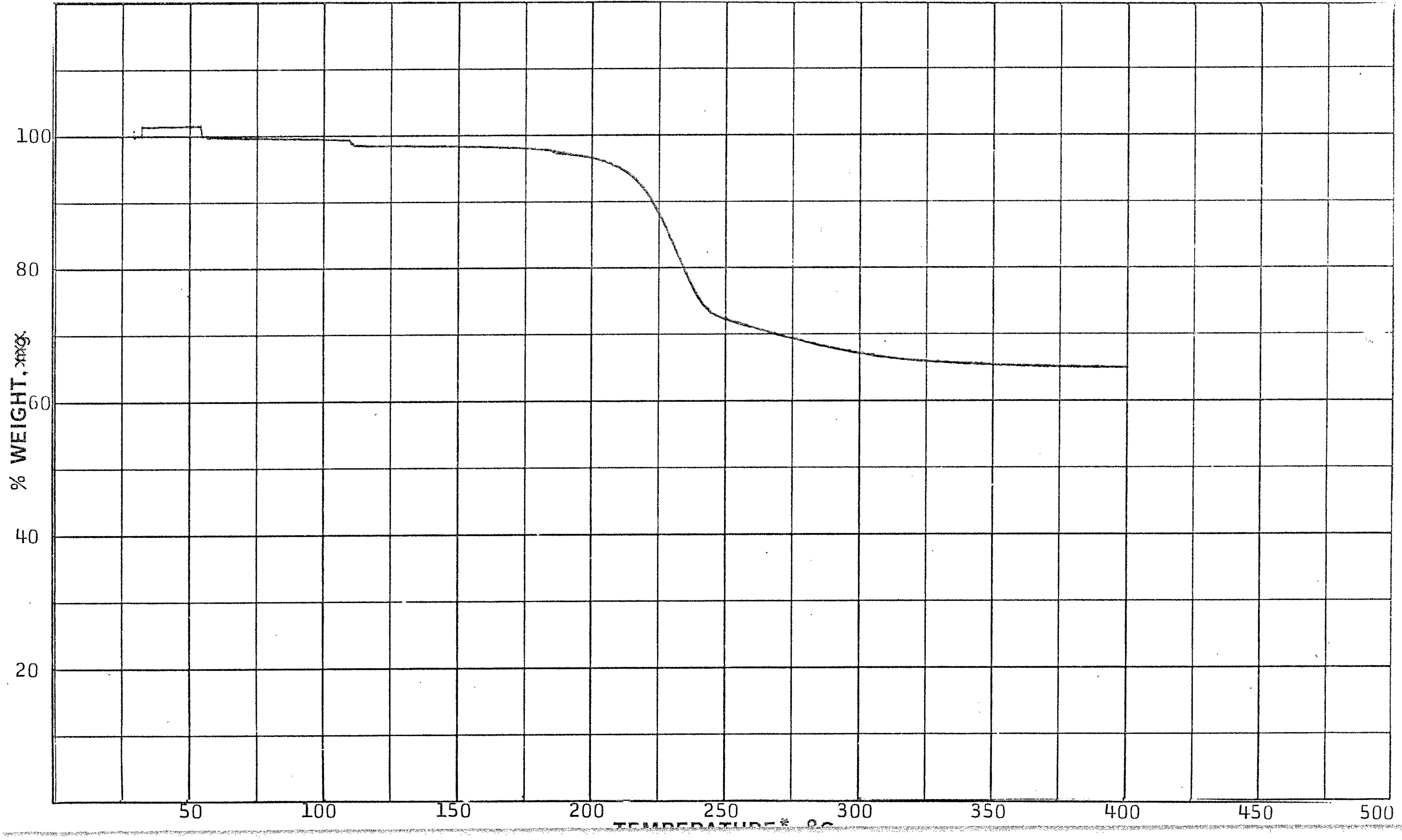
RUN NO. 1 **DATE** 12/1/74

OPERATOR RM

HEATING RATE 10 °C/min.

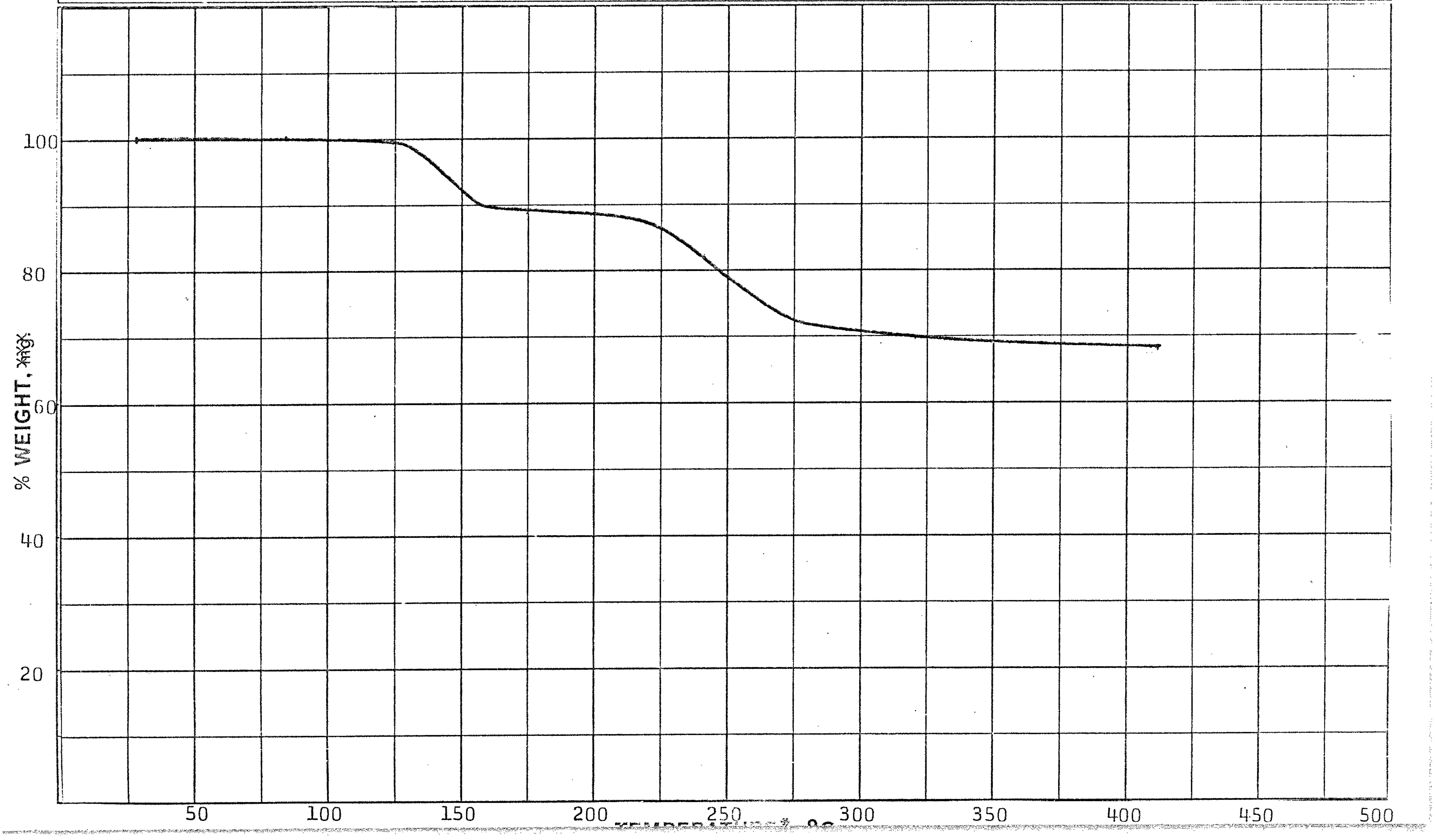
ATM. self-generated

TIME CONSTANT 1 sec.



DUPONT INSTRUMENTS

SAMPLE: A mixture of: 44.3% $MgSO_3.6H_2O$ 30.0% $MgSO_3.3H_2O$ 25.7% glass beads Fig. No. 20	**X-AXIS**	**Y-AXIS**	**RUN NO.** 1 **DATE** 12/1/74
	TEMP. SCALE 50 °C/inch	**SCALE** 2 mg./inch (SCALE SETTING X 2)	**OPERATOR** RM
	SHIFT 0 inch		**HEATING RATE** 10 °C/min.
			ATM. self-generated
SIZE 15 mg.	**TIME SCALE (ALT.)**	**SUPPRESSION** 50 mg.	**TIME CONSTANT** 1 sec.



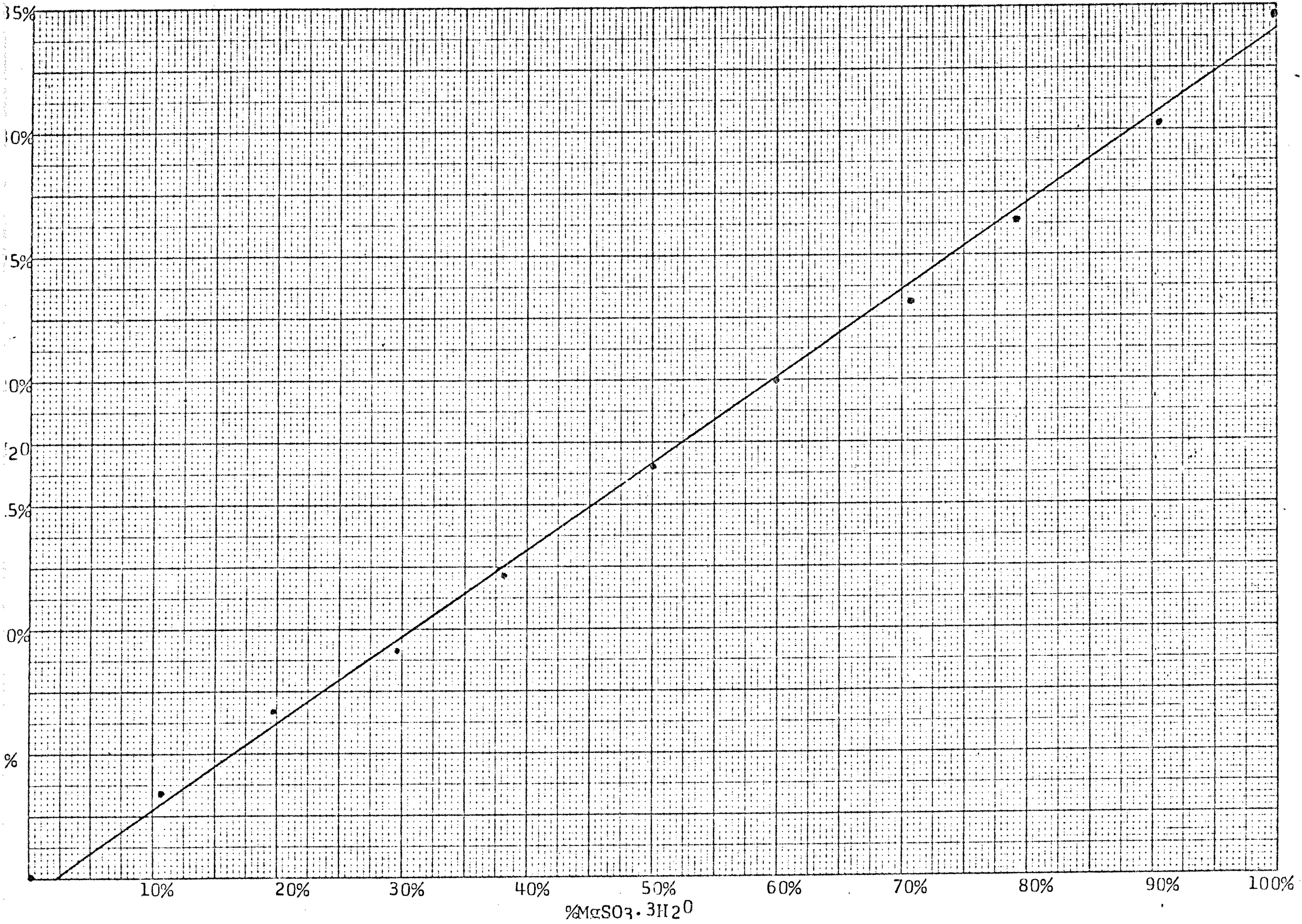


Fig. No. 21

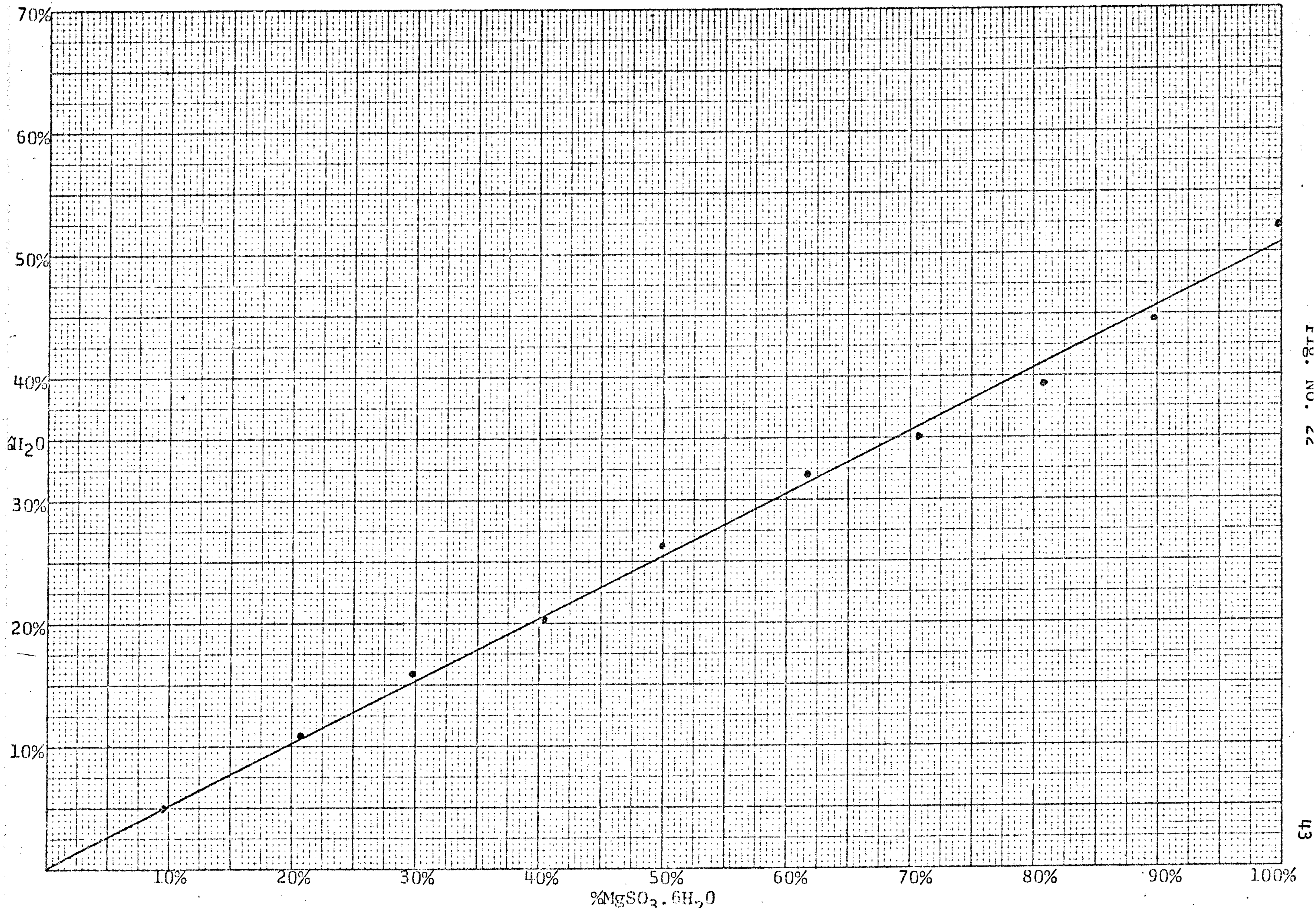


Fig. No. 22