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The Thermal Dehydration of Magnesium Sulfite Hexahydrate (MgSO3.6H2O) and Magnesium Sulfite Trihydrate (MgSO3.3H2O);

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

BY

RAAFAT F. ABDEL-MALEK

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE

AT

NEW JERSEY INSTITUTE OF TECHNOLOGY

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ABSTRACT

The thermal dehydration of MgSO₃.3H₂O and MgSO₃.6H₂O 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 MgSO3.6H2O, under equilibrium conditions, dehydrates in two steps through the intermediate formation of MgSO3.3H2O.

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.

i

APPROVAL OF THESIS

The Thermal Dehydration of Magnesium Sulfite Hexahydrate (MgSO3.6H2O) and Magnesium Sulfite Trihydrate (MgSO3.3H2O);

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

BY

RAAFAT F. ABDEL-MALEK

FOR

DEPARTMENT OF CHEMISTRY

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1975

ii

ACKNOWLEDGMENT

iii

The author wishes to express his gratitude to Professor Leonard Dauerman for his interest, suggestions, advice, encouragement and guidance which made the conduct of this investigation possible.

TABLE OF CONTENTS

ABSTRACT	i
APPROVAL PAGE	ii
ACKNOWLEDGMENT	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	v
LIST OF FIGURES	vi
INTRODUCTION	1
EXPERIMENTAL	4
RESULTS AND DISCUSSION	6
APPLICATION	11
REFERENCES	15
TABLES 1-6 inclusive	16-21
FIGURES 1-22 inclusive	22- 43

/

iv

LIST OF TABLES

<u>No</u> .		<u>Page</u>
1.	Starting Temperature of Thermal Dehydration	16
	of MgS0 ₃ . ^{3H} 20	
2.	Starting Temperature of Thermal Dehydration	17
	of MgSO ₃ .6H ₂ 0	
3.	Calculated and Observed Values of Water	18
	Content in Synthetic Mixtures	
4.	MgS0 3.3H 0 Content from TGA	19
5.	MgS0 ₃ . ^{6H} 2 ⁰ Content from TGA	20
6.	TGA Results of a Synthetic Mixture	21
	Containing Thermally Inactive Material	

v

LIST OF FIGURES

	No.	<u>.</u>	Page
	1	DTA of MgSO ₃ .3H ₂ O	. 22
•	2	DTA of MgS0 ₃ .6H ₂ 0	23
	3	DSC of MgS0 ₃ . ^{3H} 2 ⁰	24
	4	DSC of $MgSO_3.6H_2O$	25
	5	TGA of MgS0 ₃ .3H ₂ 0	26
	6	TGA of MgS0 ₃ .6H ₂ 0	27
	7	TGA of $MgSO_3.3H_2O$ under self-generated atmosphere	28
	8	TGA of $MgSO_{3}^{6H}2^{0}$ under self-generated atmosphere	29
	9	TGA of Std #1	30
	10	TGA of Std #2	31
	11	TGA of Std #3	32
	12	TGA of Std #4	33
	13	TGA of Std #5	34
	14	TGA of Std #6	. 35
	15	TGA of Std #7	36
	16	TGA of Std #8	37
	17	TGA of Std #9	38
	18	B TGA of Std #10	39
	19) TGA of Std #11	40
	20) TGA of a mixture of $MgSO_3.3H_2O$, $MgSO_3.6H_2O$ and	41
		glass beads	
	2]	L Water content versus % MgSO3.3H20	42
	22	2 Water content versus % MgSO ₃ .6H ₂ O	43

vi

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 $(MgSO_3 \cdot 3H_2O)$ 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 MgSO₃ are formed; also MgSO₄ 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 MgSO₃; the coke reduces MgSO₄ to MgSO₃. The useful products of calcination are MgO, which is recycled back to the slurry, and SO₂, 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 MgSO₃. $6H_2O$ loses three water molecules between $60^{\circ}C$ and $100^{\circ}C$ to form MgSO₃. $3H_2O$. The latter at 200°C completely dehydrates to yield amorphus anhydrous MgSO₃. 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 h ave o c c urred without any change in the infrared spectra. The band in the 3500 cm⁻¹ region is obviously an 0-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 EPAsponsored 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 MgSO₃.6H₂O takes place in one step starting at 100°C and that MgSO₃.3H₂O dehydrates in one step, starting at 160°C.

In the other study, Hatfield and co-workers reported that MgSO₃.6H₂O 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 hexa-hydrate 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 $100^{\circ}C$.

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

MgSO₃.3H₂O (97.9%) and MgSO₃.6H₂O (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 MgSO₃.3H₂O is shown in Figure 1. Only one endothermic transition is observed, starting at 190°C. On the other hand, in the thermogram of MgSO₃.6H₂O 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 $100^{\circ}C$ with a peak maximum at $160^{\circ}C$. 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, $100^{\circ}C$, in contrast to the DTA data from which it is inferred that $190^{\circ}C$ is the starting temperature.

The DSC thermogram of MgSO₃.6H₂O 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 MgSO₃.6H₂O

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 selfgenerated 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 $100^{\circ}C$ 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 $70^{\circ}C$ 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. MgSO₃.3H₂O, 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 selfgenerated 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, MgSO₃.6H₂O 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 MgSO3.3H20, then, to the anhydrous MgSO3. 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 MgSO₃.6H₂O, i.e., 50% of the water content of the hexaform. Thus the water content can be calculated, from the TGA thermogram, as follows:

% H₂O in MgSO₃.6H₂O in a mixture = (% weight loss

in the first step at 175°C) (2)

 $\% H_20$ in MgSO₃.3H₂0 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:

% H₂⁰ in MgSO₃.6H₂⁰ in a mixture = % MgSO₃.6H₂⁰ in the mixture

 $\frac{X \ 6H_20}{MgSO_3.\ 6H_20}$ X 100 = % MgSO_3.\ 6H_20 in the mixture $\frac{X \ 108}{212.3} \ X \ 100$ = % MgSO_3.\ 6H_20 in the mixture X 50.9 x 50.9

% H₂0 in MgSO₃.3H₂0 in a mixture = % MgSO₃.3H₂0 in the mixture

 $\frac{X \ 3 \ H_20}{MgSO_3 \ 3H_20} \times 100$

= % MgSO_{3.3H2}0 in the mixture $\frac{X 54}{158.3} \times 100$

= % MgSO3.3H20 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 MgSO₃.3H₂O and in Figure 22 for MgSO₃.6H₂O.

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:

% MgSO₃. $6H_20$ in a mixture = % weight loss at 175°C X 2 X $\frac{100}{50.9}$ % MgSO₃. $3H_20$ in a mixture = (% weight loss between 175° and 400°C __% weight loss at 175°C)

$\frac{100}{34.1}$

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 \pm 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 MgSO₃.³H₂O, MgSO₃.⁶H₂O and glass beads. The mixture was subjected to the same experimental conditions of a selfgenerated 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.

REFERENCES

- (1) Griffith, E.J., <u>Anal. Chem.</u>, 29, 198 (1957)
- (2) Honda, K., Sci. Rept. Tohoku Uni., 4,97 (1915)
- (3) Karchmer, J.H., The Analytical Chemistry of Sulfur and its Compounds. New York, Wiley Interscience, Vol. 29, Part I pp 225-226 (1970)
- (4) LeChatelier, H., <u>Bull. Soc. Franc. Mineral</u>, 10, 203 (1887)
- (5) Okabe, T. and Hori, S., <u>Tohoku University Technology</u> <u>Report</u>, 23(2), pp 85-89 (1959)
- (6) McGlamery, G.G., Torstrick, R.L., Simpson, J.P., and Phillips, J.F., <u>Conceptual Design and Cost Study</u>. <u>Sulfur Oxide Removal From Power Plant Stack Gas</u>. <u>EPA-R2-73-244</u>, pp 33-34, (1973)
- (7) Ray, A.B., Chemical Construction Corporation, Private Communication (1974)
- (8) Shah, I.S., Chemical Construction Corporation, <u>Recovery</u> of <u>Sulfur Dioxide From Waste Gases</u>. U.S. 3, 577, 219 (1971)
- Wendlant, W.W., <u>Thermal Methods of Analysis</u>, Second Edition. New York, Wiley Interscience, pp 134-201 (1974)
- (10) Wendlant, W.W., Hoiberg, J.A., <u>Anal. Chem. Acta</u>, 28, 506 (1963)

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Starting Temperature of Thermal

Dehydration of MgS03.3H20

<u>Technique</u>	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

<u>Table 2</u>

Starting Temperature of

Thermal Dehydration of MgS03.6H20

Tec hnique	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

1

of Water Content in

Synthetic Mixtures

Composition			Calculate	Calculated H20 content in		Observed H20 content		in	
<u>Std#</u>	2023.3H20	26H2036H20	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%	3 9%	
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%	

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 4

· . .

1

MgSO3.3H20 Content from TGA

Std#	Theoretical Value	Observed Value	<u>Deviation</u>
1	100%	102.2%	+2.2%
2	89.71%	87.3%	-2.41%
3	81.04%	78.45%	-2. 54%
4	7 0.63%	68.8%	-1.83%
5	61.7 6%	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%

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MgSO3.6H20 Content

From TGA

Table 6

TGA results of a synthetic

mixture containing thermally

inactive compound

	Theoretical Value	Observed Value
MgSO ₃ .3 _{H2} 0	44.3%	43.2%
MgSO ₃ .6H ₂ 0	30.0%	29.3%
glass beads	25.7%	27.5%*

*This value was obtained by difference

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SAMPLE: MgSO3.6	1 ₂ 0	SIZE		<u>8 mg</u>			ATM.	self-	genera	ated	MM	RUN	NO]		-
Fig No 2		REF.	gla	ss_bea	ds				<u>T</u>		<u> </u>	DATE		11/8/7	'4		-
		PROG	S. MOE)E	hea	<u>t</u>	SCAL	E	<u>50 </u>	<u>.</u>	2 <u>°c</u> IN.	OPEF	RATOR	RM			
ORIGIN:		RATE	10	_ <u>min</u> ,S7	ART_	<u>30</u> °C	SHIFT	•	<u> </u>	1	<u>0</u> IN.	BASE	E LINE	SLOP	ν <u>Ε 0</u>	T	-
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SAMPLE: MgSO ₃ .3H ₂ O	SIZE 12 mg	ATMN2,	<u>30 MM</u>	RUN NO1
Fig. No. 3	REF. empty pan	T	<u> </u>	DATE
	PROG. MODEheat	SCALE 50 °C	<u>] °c</u> IN.	OPERATORRM
ORIGIN :	RATE10 <u>*c</u> ,START_25_°C	SHIFTIN	<u> </u>	BASE LINE SLOPE 0
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SAMPLE	: MgSO ₃	.6H_0 2		SIZE_	5	mg			АТМ	N2	9	30	MM	RUN	NO	1	
	Fig. N	o . 4		REF	empty	y pan					<u>T</u>		<u> </u>	DATE		11/9/74	,
				PROG	. MOE)Eh	eat		SCALE		50 <u>°c</u>	·	<u>1</u> <u>•c</u> in.	OPER	ATOR_	RM	
ORIGIN	;			RATE.	10	_ <u>*c</u> ,ST	ART_	<u>30</u> °C	SHIFT		<u> </u>	0	IN.	BASE	LINE	SLOPE_	0
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) INSTRUMENTS

SAMP	LE:	MgS0 ₃	3.6H2)			X-AXIS	5				Y-AXI	S		RUN	NO. 1	D	ATELI	/16/74
Fig.	No.	8	L		TEM	P. SC/	NLE5	inch	°C nch	SCA (scal	LE_1_	mc inc IG X 2)	<u>3.</u> h		OPEI HEAT	RATOF TING R self	RATE -gener	10 lo ated	°C min.
SIZE	5	mg.		4	ТІМЕ	SCAL	E (AL)	Г.)	····	SUP	PRESS	ION_	60	mg.	ТІМЕ	CONS	STANT_		sec
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	SAMP Fig. SIZE	SAMPLE: Fig. No. SIZE 5 	SAMPLE: MgSO	SAMPLE: MgSO ₃ .6H ₂ (Fig. No. 8 SIZE 5_mg.	SAMPLE: MgSO ₃ .6H ₂ 0 Fig. No. 8 SIZE5mg.	SAMPLE: MgSO ₃ . 6H ₂ O Fig. No. 8 SIZE 5_mg. TIME	SAMPLE: MgSO ₃ .6H ₂ O Fig. No. 8 SIZE_5_mg. TIME SCAL	SAMPLE: MgSO3.6H20 X-AXIS Fig. No. 8 TEMP. SCALE_5 SIZE_5_mg. TIME SCALE (ALT) Image: Solution of the second se	SAMPLE: MgSO3.6H20 X-AXIS Fig. No. 8 TEMP. SCALE _50	SAMPLE: MgSO3.6H20 X-AXIS Fig. No. 8 TEMP. SCALE _50 _ °C _ inch SIZE _5 _ mg. TIME SCALE (ALT.)	SAMPLE: MgS03.6H20 X-AXIS Fig. No. 8 TEMP. SCALE_50_°C SCA SIZE_5_mg. TIME SCALE (ALT.) SUP	SAMPLE: MgSO3.6H20 X-AXIS Fig. No. 8 TEMP. SCALE_50_OC SCALE_1 SIZE_5_mg. TIME SCALE (ALT.) SUPPRESS	SAMPLE: MgSO3.6H20 X-AXIS Y-AXIS Fig. No. 8 TEMP. SCALE 50 °C inch SCALE 1 mm incline SCALE 20 °C inch SIZE 5 mg. TIME SCALE (ALT.) SUPPRESSION	SAMPLE: MgSO3.6H20 X-AXIS Y-AXIS Fig. No. 8 TEMP. SCALE_50OC SCALE_1_mg. inch SCALE_1_mg. inch SCALE_1_mg. inch SUPPRESSION60 SIZE5_mg. TIME SCALE (ALT.) SUPPRESSION60 SUPPRESSION60 Image: State of the second seco	SAMPLE: MgSO3.6H20 X-AXIS Y-AXIS Fig. No. 8 TEMP. SCALE_50_°C SCALE 1_mg. inch SIZE_5_mg. TIME SCALE (ALT.) SUPPRESSION_60_mg.	SAMPLE: MgSO3.6H20 X-AXIS Y-AXIS RUN Fig. No. 8 TEMP. SCALE 50 °C SHIFT 0 inch SCALE 1 mg. inch SHIFT 0 inch SCALE 1 mg. inch SUPPRESSION 60 mg. HEAT ATM. SIZE 5 mg. TIME SCALE (ALT.) SUPPRESSION 60 mg. TIME Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State setting x a) Image: State set	SAMPLE: MgSO3.6II20 X-AXIS Y-AXIS RUN NO. J Fig. No. 8 TEMP. SCALE_50_°C SCALE_1_mg. inch SCALE_1_mg. inch ATMself SIZE_5_mg. TIME SCALE (ALT.) SUPPRESSION_60_mg. TIME CONS	SAMPLE: MgSO3.6H20 X-AXIS Y-AXIS RUN NO. 1D OPERATOR MSO3.1D OPERATOR ME Fig. No. 8 TEMP. SCALE 50 °C SCALE_1_mg. SCALE_1_mg. Inch SCALE_1mg. HEATING RATE ATMself-gener SIZE 5 mg. TIME SCALE (ALT.) SUPPRESSION_60 mg. TIME CONSTANT. IME CONSTANT. SIZE 1 Ime Ime <td>SAMPLE: Ng803.6/J20 X-AXIS Y-AXIS RUN NO. 1 DATEI1 Fig. No. 8 TEMP. SCALE_50°C SHIFT_0_inch SCALE_1_mg. (SCALE string x.) SCALE_1_mg. (SCALE string x.) MEATING RATE_10 ATM_solf-generated. SIZE_5_mg. TIME SCALE (ALT.) SUPPRESSION_60 mg. TIME CONSTANT Image: Size string x.) TIME SCALE (ALT.) SUPPRESSION_60 mg. TIME CONSTANT Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Si</td>	SAMPLE: Ng803.6/J20 X-AXIS Y-AXIS RUN NO. 1 DATEI1 Fig. No. 8 TEMP. SCALE_50°C SHIFT_0_inch SCALE_1_mg. (SCALE string x.) SCALE_1_mg. (SCALE string x.) MEATING RATE_10 ATM_solf-generated. SIZE_5_mg. TIME SCALE (ALT.) SUPPRESSION_60 mg. TIME CONSTANT Image: Size string x.) TIME SCALE (ALT.) SUPPRESSION_60 mg. TIME CONSTANT Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Size string x.) Image: Si

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30	SAM	PLE:	Std #)0% Mg	1 SO ₂ , 6F				X-AXI	S				Υ-ΑΧΙ	S		RUN	NO.	L D	ATE 11 RM	/17/74
	Fi	g. No.	, 9	3	.20	TEM	P. SCA	LE	50 inch	°C inch	SCA (SCAL	LE_2 .e settii	mo inc NG X 2)	<u>g.</u> h		HEAT	FING R	ATE	10 rated	°C min.
	SIZE	12	mg.			ТІМЕ	SCAL	.E (AL	r.)		SUP	PRESS	SION_	50	mg.	TIME	CONS	STANT	1	sec
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SAM	PLE: S	td #2					X-AXI	S				γ-ΑΧΙ	S		RUN	NO.	<u>l</u> c	ATE 1	L/20,
Fig SIZE	10.29 89.71 g. No. 10	% MgS % MgS 10 mg.	0 ₃ .3н 0 ₃ .6н	20 2 ⁰	TEM SHIF TIME	P. SCA	ALE 1 0 E (AL	00 i inch T.)	°C nch	SCA (sca) SUP	LE_2 LE SETTI	mc inc NG X 2) 5ION	9h h50	mg.	HEAT ATM. TIME	ring R self	ATE E-gene	10 rated 1	ەر m sec
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0	SAMF	PLE:	Std #3	}				X-AXIS	3				Y-AXIS	5		RUN	NO. 1	DATE	1/21/74
	Fig.	18.9 81. No.	6% Mg9 04% Mg 11	50 ₃ .3H 550 ₃ .6)	2 ⁰ H ₂ 0 2	TEM SHIF	P. SCA	0	inch	°C nch	SCAI (scal	E 2 E SETTIN	mg inch IG X 2)	<u>. </u>		HEAT	TING RAT self-	E l() °C min. ed
ŝ	SIZE	15	mg.			TIME	SCAL	.E (AL1	「.)		SUPI	PRESS	ION	50	mg.	ТІМЕ	CONST	ANT 1	sec
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	SAMP	LE :	Std #	4				X-AXIS	5				Y-AXIS	5		RUN	NO	1 D	ATE 11	/22/74
	Fig.	29.3 70.6 No.	57% Mg 53% Mg 12	SO ₃ .3H SO ₃ .6H	^I 2 ⁰ ^I 2 ⁰	TEM SHIF TIME	P. SCA T	LE 5	50 c inch	°C nch	SCAI (scal SUP	E ² E SETTIN	mg incl IG X 2)		mg.	OPEF HEAT ATM. TIME	RATOR ING R self CONS	ATE -genei STANT	RM 10 rated	°C min.
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S	AMPL	LE: St	d #5	30	n			X-AXIS	5				Y-AXIS	3		RUN	NO.	1 D/	ATE ¹¹	/25/74
F	5 6 Sig.	8.24% 1.76% No. 13	mgs0 MgS0	3• ⁵⁶ 2 3• ^{6H} 2	0	TEM	P. SCA	LE 50) c inch	°C nch	SCAI (scal	E 2 SETTI	mg inch NG X 2)	<u>.</u> 1		HEAT	ING R	ATE f-gene	10 rated	°C min.
SI	IZE	12	mg.			TIME	SCAL	.e (AL ⁻	Г.)		SUPI	PRESS	SION	50	mg.	TIME	CONS	TANT	1	sec.
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SA	MPLE: 50%	Std #0 MgSO	б ЗН ₂ 0			>	(-AXIS					Y-AXIS	5		RUN	NO. RATOR	1D/	ATE11/ RM	/25/7
Fig	50% z. No. 1	мgSO ₃ . 4	6H ₂ 0		TEMP SHIF	P. SCA	LE <u>5</u>	0 ° in inch	C ich	SCAL (SCALI	E 2 SETTIN	mg inch IG X 2)	ı		HEAT	TING R self	ATE	10 ated	°C min
SIZ	2E 10	mg.			TIME	SCAL	E (ALT	.)		SUPF	RESS	ION		mg.	тіме	CONS	STANT	1	sec.
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 	<u>.</u>		*******						5 - 5				S.T.FGC	RUN	NO.	5 1 D/	TE 11	/27/74
SAMPL	E: Std 59.84% M 40.16% M 5. 15 _12mg	#7 gSO ₃ .3; gSO ₃ .6;	^H 2 ⁰ H2 ⁰	TEM SHIF TIME	P. SCA T SCAL	LE 5 0 E (ALT	0 ° ir inch	°C nch	SCAL (scali	E 2 E SETTIN	mg inch G X 2)	50	mg.	OPEF HEAT ATM. TIME	RATOR ING RA sel CONS	ATE f-gene TANT	RM 10 rated 1	°C min. sec
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SAMPLE: Std #8 70.19% MgSO ₃ .3H ₂ 0 29.81% MgSO ₃ .6H ₂ 0 Fig. No. 16 SIZE 12 mg.					X-AXIS TEMP. SCALE <u>50 °C</u> inch SHIFT0inch TIME SCALE (ALT.)					Y-AXIS SCALE 2 mg. inch (SCALE SETTING X 2) SUPPRESSION 50 mg.					RUN NO.1DATE 11/25/74OPERATORRMHEATING RATE10C°CATM.self-generatedTIME CONSTANT1sec.sec.				
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s	SAMPLE: Std #9 79.34% MgSO ₃ .3H ₂ O 20.66% MgSO ₃ .6H ₂ O Fig. No. 17 SIZE14mg.					X-AXIS						40G (Y-AXIS	5		RUN NO. 1 DATE 11/27/74					
F						TEMP. SCALE 50 °C inch SHIFT 0 inch TIME SCALE (ALT.)					SCALE 2 mg. inch (SCALE SETTING X 2) SUPPRESSION 50 mg.					OPERATOR RM HEATING RATE 10 °C min ATM. self-generated TIME CONSTANT 1 sec.					
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6	SAMF	PLE :	Std #	10		X-AXIS							Y-AXIS	5		RUN NO. 1 DATE 11/30/74					
Ω,	ç Fig.	0.18% 9.82% No. 1	MgSO MgSO 8	3.3H ₂ 0 3.6H ₂ 0		TEMP. SCALE 50 °C inch inch						SCALE 2 mg. inch (SCALE SETTING X 2)					OPERATOR RM HEATING RATE 10 °C Min. min.				
	SIZE	16	mg.			TIME	SCAL	E (ALT	.)		SUPI	PRESS		50	mg.	TIME	CONS	TANT	1	_sec	
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s	SAMPLE: A mixture of: 44.3% MgSO _{3.6H2} O 30.0% MgSO ₃ .3H ₂ O 25.7% glass beads Fig. No. 20					X-AXIS						Y-AXIS					RUN NO. 1 DATE 12/1/74					
F						TEMP. SCALE 50 °C inch inch SHIFT 0 inch					SCALE 2 mg. inch (SCALE SETTING X 2)						HEATING RATE ATM. self-generation			°C min		
SI	IZE	15	; mg.				TIME SCALE (ALT.)					SUPPRESSION 50 mg.						TIME CONSTANT				
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