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THE EFFECT OF SELECTED CONTAMINANTS ON THE HYGROSCOPICITY OF SODIUM NITRATE

U. S. NAVAL AMMUNITION DEPOT
CRANE, INDIANA

DEPARTMENT OF THE NAVY · BUREAU OF WEAPONS

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by

WILLIAM RIPLEY

This report was reviewed for adequacy and technical accuracy by Duane M. Johnson.

Released

P. P. CORNWELL, Acting Director

Research and Development Department

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ABSTRACT

A preliminary screen is made of the effects of 75 contaminants on the hygroscopicity of sodium nitrate. Results indicate that contaminants exert a significant effect both in increasing and in decreasing hygroscopicity. Various side effects are noted, for example the pronounced anticaking effect of zirconium sulfate and other compounds.

THE EFFECT OF SELECTED CONTAMINANTS ON THE HYGROSCOPICITY OF SODIUM NITRATE

I. Introduction

Studies of chemical components used in pyrotechnic compositions have often shown that considerable variations can exist in the behavior of materials that otherwise meet the military specification requirements. For example, production tests performed on MK 24 Aircraft Parachute Flares in January 1967, indicated that compositions otherwise identical except for the sodium nitrate component showed significantly different burning times. Candles made from sodium nitrate obtained from Supplier A burned in about 150 seconds while candles made from Supplier B burned in about 190 seconds. Furthermore, it was observed that sodium nitrate from Supplier A was a free-flowing powder while sodium nitrate from Supplier B was caked in a hard dense mass.

Subsequent analysis of these two specimens of sodium nitrate revealed a few differences. For example, although both specimens had an average particle diameter of approximately 25 μ, 100% of the test samples taken from Supplier B material passed through a No. 100 U. S. Sieve, while only 60-70% of the test samples taken from Supplier A material passed through a No. 100 U. S. Sieve. Supplier A material showed 0.9% chloride, while Supplier B material showed 0.1%

chloride. It was thought that the difference in particle size distribution might explain the difference in burning time, although this was not conclusively demonstrated. There was no good explanation for why one of the materials caked while the other did not.

Because of the general lack of understanding of the relationship between the properties of sodium nitrate and the behavior of sodium nitrate in pyrotechnic compositions, it was decided to conduct a series of investigations aimed at clarifying this relationship. The subject of the present paper is the effect of various selected contaminants on the hygroscopicity and the caking properties of sodium nitrate.

II. The Problem of Hygroscopicity

According to Shidlovsky, the relative humidity of an enclosed space of air in contact with a saturated solution of a salt containing a definite solid phase at a given temperature is a useful index for evaluating the hygroscopicity of a salt. Any salt with a lower relative humidity than potassium nitrate (92.5% RH at 20°C) is considered hygroscopic, and trouble can be expected in practical use from salts with a figure below about 75-80% RH. Sodium nitrate falls within this range with a RH of 77%.

Ellern comments that this is a simplification of a more complex problem, and calls for studies of the water adsorption per unit time of salts of known purity and particle size under some standard set of conditions. To some extent this has been done for sodium nitrate in the AMCP 706-187 Handbook on military pyrotechnics. The gain in weight of purified sodium nitrate with an apd of 41μ after 120 hours exposure at 70°F is given as 11% at RH 70% and 25.75% at RH 90%. Water adsorbed by 2.000 g of 40-80 mesh sodium nitrate at 25°C is given as 0.0713 g after 3 hours, 0.1355 g after 5.5 hours, 0.1970 g after 7-5 hours, and 0.3924 g after 16 hours. The critical RH is given as 82.7% at 20°C for purified material.

However, the effects of contaminants or of other factors on the hygroscopicity of sodium nitrate are not readily available, although in actual practice they may be significant. For example sodium nitrate admixed with other materials, as it would be in pyrotechnic compositions, may not exhibit the same properties as pure and isolated sodium nitrate. Similarly, the factors and conditions that affect the caking of sodium nitrate are difficult to find in the literature.

The military specifications for sodium nitrate, Mil-S-322B, require limits on certain impurities that appear to be associated with hygroscopicity: e.g., chlorides, chlorates, magnesium, and calcium. (Table V). Chlorides are reported by Shidlovsky to increase the water adsorbing tendencies of alkali metal salts. Sodium chloride and sodium chlorate have RH figures of 75%, indicating that taken by themselves they are slightly more hygroscopic than is sodium nitrate. Calcium nitrate and magnesium nitrate hexahydrate have RH figures of 56%, substantially lower than sodium nitrate, and are both reported as deliquescent in the literature. The premise appears to be that anions that form deliquescent nitrates, or cations that form hygroscopic sodium salts are undesirable because they contribute to the hygroscopicity of sodium nitrate.

III. The Selection of Contaminants

No specific scientific justification can be given for each of the seventy-five contaminants chosen. The general plan was to study a wide variety of anion and cation contaminants in which there would be only one variable. Thus, contaminating the sodium nitrate with sodium fluoride, sodium chloride, sodium bromide, sodium iodide, would introduce only the anion as a variable, while contaminating the sodium nitrate with magnesium nitrate, luthium nitrate, and aluminum nitrate, etc. would introduce only the cation as a variable. Other substances were chosen because of their position in the periodic table, even though they were neither sodium salts or nitrates. for example, zirconium sulfate. Various chlorides were chosen to observe if all chlorides more or less equally affected the hygroscopic nature of sodium nitrate, regardless of the cation. Some insoluble materials such as silicon dioxide were included because of their prevalence in materials. Other contaminants such as boric acid were thrown in on the thinnest hunch. But the overall plan was to screen a wide variety of contaminants to see what kind of variations, if any, they would cause in the water attracting properties of sodium nitrate. Those contaminants which caused any significant deviation from the hygroscopicity of the controls, either positively or negatively, could then be studied more rigorously in the future, either by the present author or by other interested investigators. The same argument applies to contaminants which affect the caking tendency of finely subdivided sodium nitrate.

IV. Preparations of Contaminated Sodium Nitrate Specimens

A saturated solution of sodium nitrate was prepared by dissolving 360 g of purified sodium nitrate, furnished by Olin Mathieson, the only primary producer of sodium nitrate in the United States, in 200 ml of distilled water. Normally, ten grams of the contaminant were dissolved in a minimum amount of distilled water, and added to the hot solution of sodium nitrate. If the contaminant was insoluble in water, it was suspended in 10 ml of distilled water and added to the hot sodium nitrate solution. With rare and expensive contaminants, 0.5% of the contaminant was sometimes used. The mixture was stirred and then placed in an ice bath maintained at 0°-5°C. During cooling, the sodium nitrate solution was stirred intermittently until it reached the 0°-5°C temperature range. The sodium nitrate crystals were then separated from the mother liquor by immediate filtration through a Buchner funnel fitted to a flask which was attached to a vacuum aspirator. The yield was dried first in a conventional oven at 100°C and then in a vacuum oven at 80°C. The dry sodium nitrate was then weighed and the yield recorded. Any unusual observations were also recorded. Finally, the sodium nitrate was ground by mortar and pestle, redried, and the average particle diameter and porosity was determined using the Fisher Sub Sieve Sizer. The percent yield which was obtained on each of the seventy-five samples is shown in Table I, along with any significant or unusual observation concerning the effect the particular contaminants might have had on the crystallization, drying, or grinding properties. It was during these operations that the anticaking effect of zirconium sulfate and tungsten hexachloride were observed.

V. Treatment in the Humidity Chamber

Studies of control sodium nitrate samples in a small constant temperature - constant humidity chamber indicated variations in different runs of the same sample. Therefore, in the first screening test, it was decided to run all the samples simultaneously in a large humidity chamber. The argument for this approach was that even if variations in the temperature-humidity conditions of the chamber should occur, all the samples would suffer the same fate.

In the original run, 72 samples were exposed simultaneously, of which five were controls placed in different positions in the humidity chambers. The large humidity chamber did not in fact maintain a constant humidity. On the first day of the four day run the dry bulb temperature cycled between 33°C and 35°C while the wet bulb temperature cycled between 25°C and 31°C. On the succeeding days the wet and dry bulb temperatures cycled but in a narrower range, the dry bulb averaging about 33°C and the wet bulb about 30°C. This temperature cycling, which could not be corrected, caused the humidity to vary although it was generally in the 70-80% RH range. The air in the humidity chamber is constantly circulated by a blower. All samples in the original run were exposed a total of 23 hours; 5 hours on the first day and 6 hours on the next three succeeding days. The sample bottles were capped overnight, stored at room temperature outside the humidity chamber, and reweighed the next morning before being placed back in the humidity chamber.

A second run was made in the small humidity chamber on seven samples and two controls which were run simultaneously. The conditions were the same as in the original run except the humidity was more constantly controlled, with a wet bulb temperature of 30°-31°C and a dry bulb temperature of 31-32°C indicating between 80-85% RH.

III. Discussion of Results

The preliminary results obtained in this study are shown in Figures 1-81. Moisture gain in percent is plotted against time in hours. Table I alphabetically lists the 75 contaminants along with the rough yield obtained upon crystallization and any unusual observations. Table II shows the contaminated sodium nitrate specimens arranged according to their increasing gain in total weight of adsorbed water for 23 hours. Table III shows this same arrangement for the first five hours and Table IV for the next six hours of the exposure.

Variations in the moisture gain of the controls are an indication of the reproducibility of results using this technique. After the first five hours results in the original run varied from 0.8% gain to 1.93% gain, although four of the five samples were between 1.60% and 1.93%. During the next six hours the gain ranged from 3.14% to 6.20%, and the total gain varied from 11.40% to 17.67%. On the second run in the small humidity chamber, the controls varied from 1.7% to 2.26% for the first 5 hours, 3.2% - 3.6% for the next six hours, and 12.7% to 15.9% for the total adsorbed water. From these results it can be seen that considerable variations occur due primarily to conditions of the experiment. Thus, only results that deviate somewhat spectacularly from the range of the controls would be considered as evidence of unusual effects due to the contaminants. The data shows that such effects exist.

Contaminants which consistently showed moisture adsorption significantly below the control samples are as follows:

1. Sodium fluoride

2. Sodium carbonate

3. Mercuric nitrate

4. Various soluble elements of the first transitional group including manganese nitrate, cobalt nitrate, nickel nitrate, chromic nitrate, and ferric nitrate.

5. Aluminum nitrate

6. Uranyl acetate

7. Various other anions including the perchlorate, hypochlorite, nitrite, bromide, dichromate, borate, thiosulfate

and peroxide.

8. Both sodium hydrochlorite and sodium peroxide form significantly alkaline solutions.

Contaminants which showed moisture adsorption significantly above the control samples are as follows:

1. Sodium chloride
2. Sodium sulfite
3. Sodium formate
4. Cerium nitrate
5. Stannic chlorates

Of contaminants restricted in the Military Specification, Mil-S-3226, alkalinity values represented by sodium salts that hydrolyze in water to form basic solutions were scattered over the entire range. For example, sodium carbonate and sodium hypochlorite specimens were conspicuously low in adsorption, sodium peroxide and sodium acetate in the middle range, and sodium formate and sodium sulfite were conspicuously high in adsorption.

Sodium chlorate caused water adsorption on the high side of the controls, but this was not true of either sodium sulfate, calcium nitrate, or magnesium nitrate.

While sodium chloride was associated with one of the highest values of water adsorption, other chlorides did not consistently follow this trend. Neither antimony trichloride, rhenium trichloride, gold chloride, or tungsten hexachloride were unusual in their effects, although stannic chloride was definitely on the high side.

The anticaking effect of certain contaminants was recognized early in the investigation. Most spectacular of these was the effect of zirconium sulfate. On drying, sodium nitrate contaminated with zirconium sulfate formed a kind of "growth" on the surface that was unlike anything observed with either pure sodium nitrate or with any of the other contaminants. Chemical analysis showed the presence of about 0.15% zirconium. X-ray diffraction studies revealed no differences in the pattern of the $Zr_2(SO_3)_3$ doped sodium nitrate and the control sodium nitrate. However, differential thermal analysis showed a very large endotherm at 150°C. The dried and ground material had a dull, chalky appearance. It formed no lumps after standing for six months and remained free-flowing and powdery. Four experimental MK 24 Flares were prepared and their burning characteristics compared with four control candles. The average burning time of the four control flares was 190 seconds, the average candlepower was 1,900,000 cp integrated over the full burning time, and the candlepower efficiency was 53,000 cp-sec/g. The average burning time of the four experimental candles made with zirconium sulfate doped sodium nitrate was 164 seconds, the average candlepower was 1,964,000 cp, and the candlepower efficiency was 49,000 cp-sec/g. Thus, as might have been anticipated, the doped candles burned faster and at a lower efficiency than the control candles.

Other components that showed significant anticaking effects were antimony trichloride, sodium fluoride, sodium carbonate, aluminum nitrate, magnesium nitrate, erbium sulfate, sodium sulfate, and tungsten hexachloride. Further study of these materials has not yet been accomplished.

VII. Conclusion and Future Plans

It should be repeated that the first phase of the present experiment has been to screen the effect of a large number of contaminants on sodium nitrate in order to evaluate the nature of the problem. The second phase would dictate that any contaminants which caused significant deviations from the hygroscopic properties of the controls should be more rigorously tested in a follow-up study. Since such verification has not yet been accomplished, no serious conclusions can be proposed in the present report. The purpose of the report is rather to inform and to suggest areas of potentially useful study.

Future plans include a thorough reexamination of tendencies indicated in the present screening phase. Particularly, a more extensive study of the effect of anticaking agents on the burning and other performance characteristics of sodium nitrate will be made. Finally, theoretical explanations for these phenomena should be attempted when the original work is verified and fulfilled.

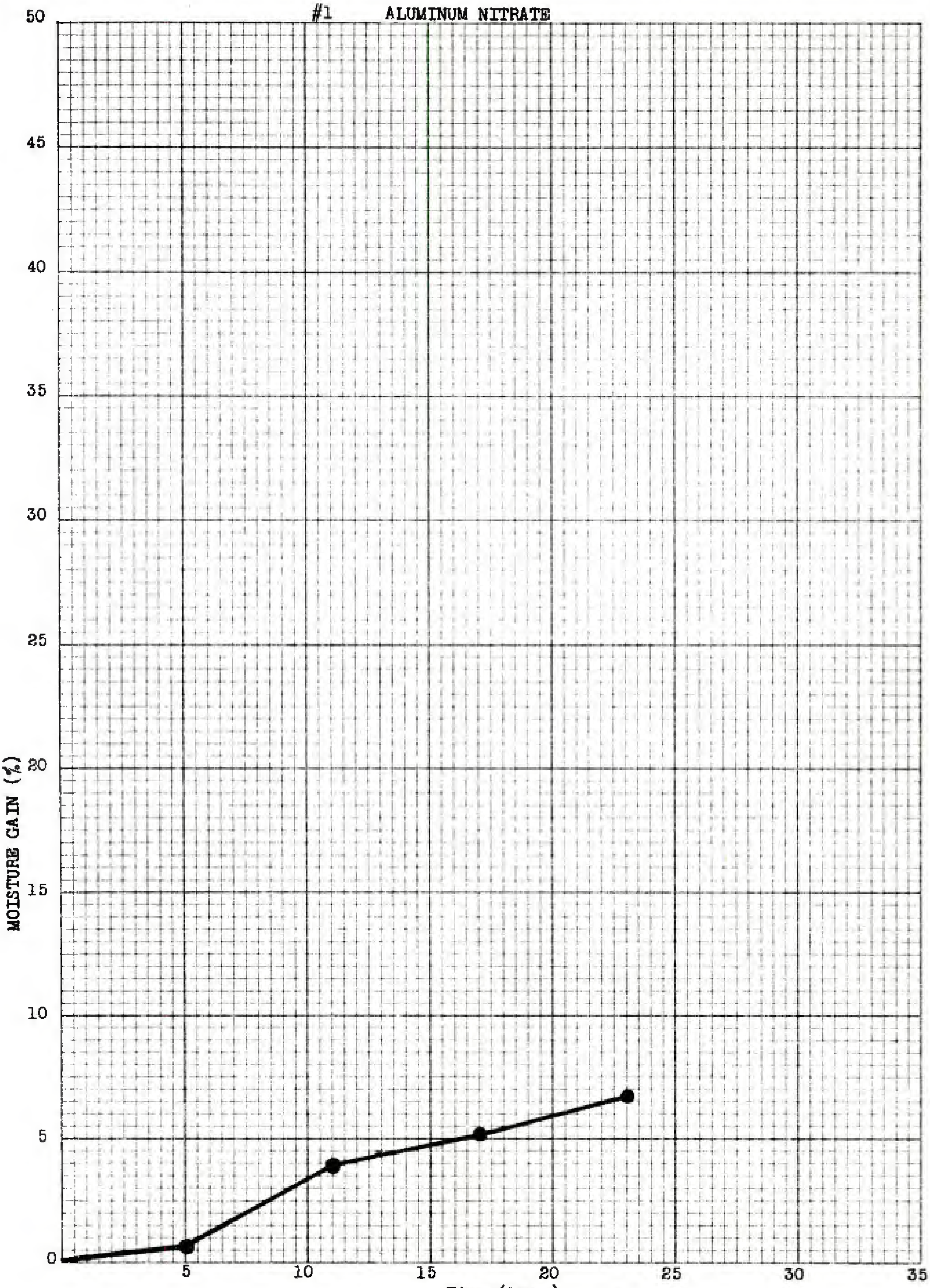
BIBLIOGRAPHY

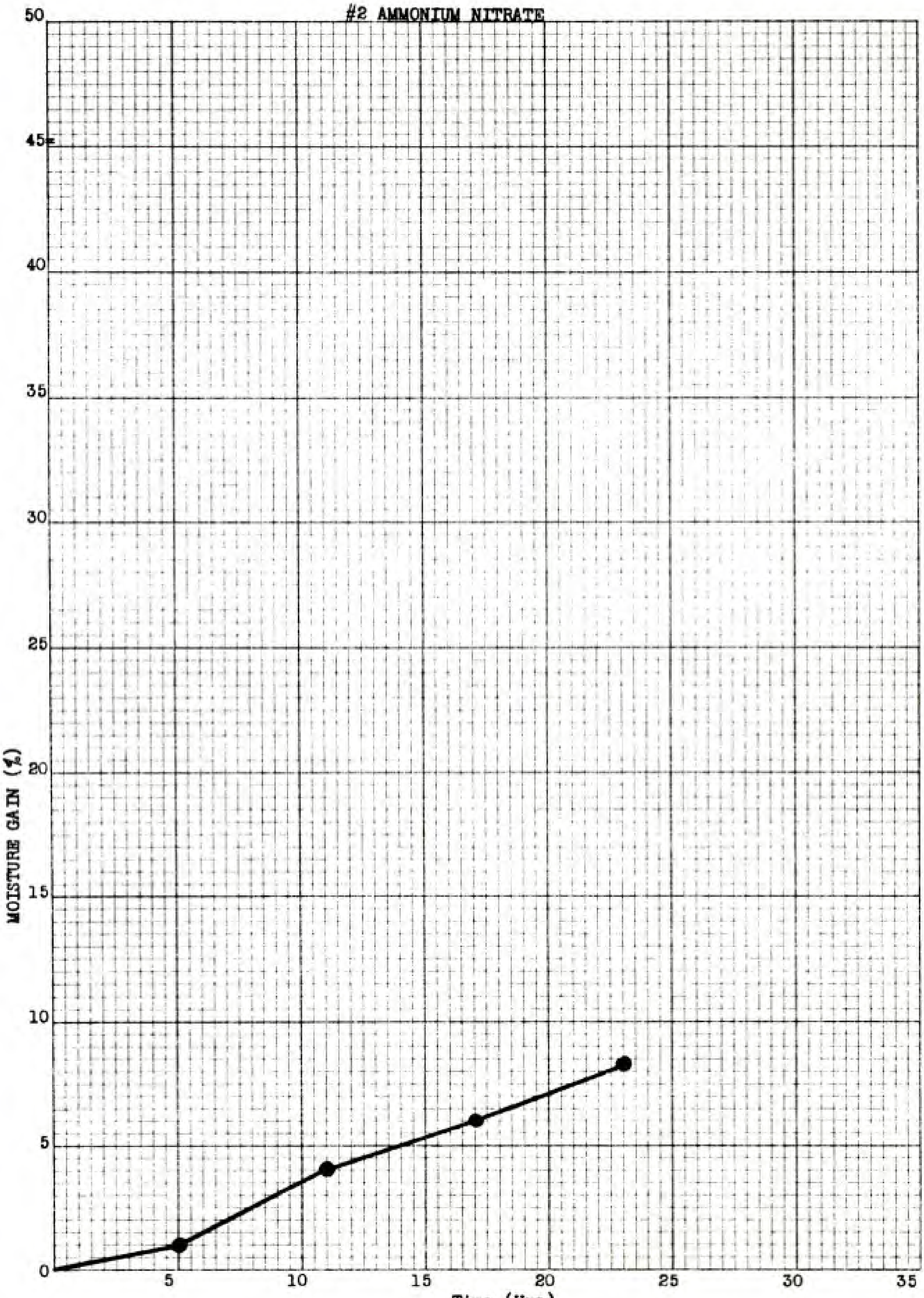
1. Ellern, Herbert, Modern Pyrotechnics, Chemical Publishing Company, Inc., New York, 1961, pp. 219-220.

2. Shidlovsky, A. A., OSNOVY PIROTEKHNIKI (Fundamentals of Pyrotechnic), Government Publication of the Defense Industry, 1st Edition, Moscow 1943, Part I, pp 11-15.

3. AMCP 706-187. Research and Development of Material. Engineering Design Handbook, Military Pyrotechnic Series. Part III - Properties of Materials used in Pyrotechnic Compositions. Headquarters, U. S. Army Material Command. Washington. D. C.. October 1963. p 273.

APPENDIX I


#1 ALUMINUM NITRATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs.)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MOISTURE GAIN (%)
Time (Hrs)
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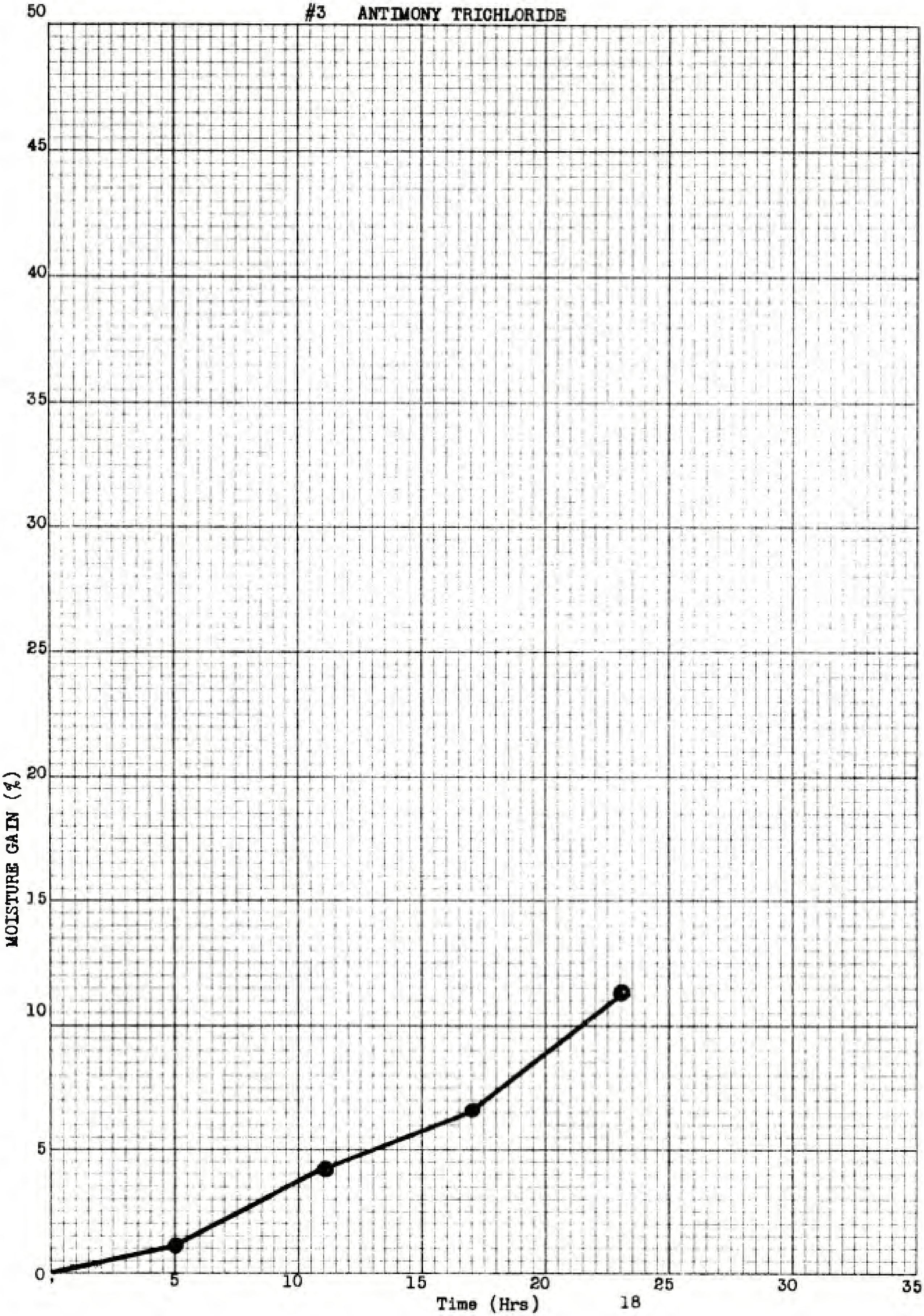
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35


#3 ANTIMONY TRICHLORIDE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
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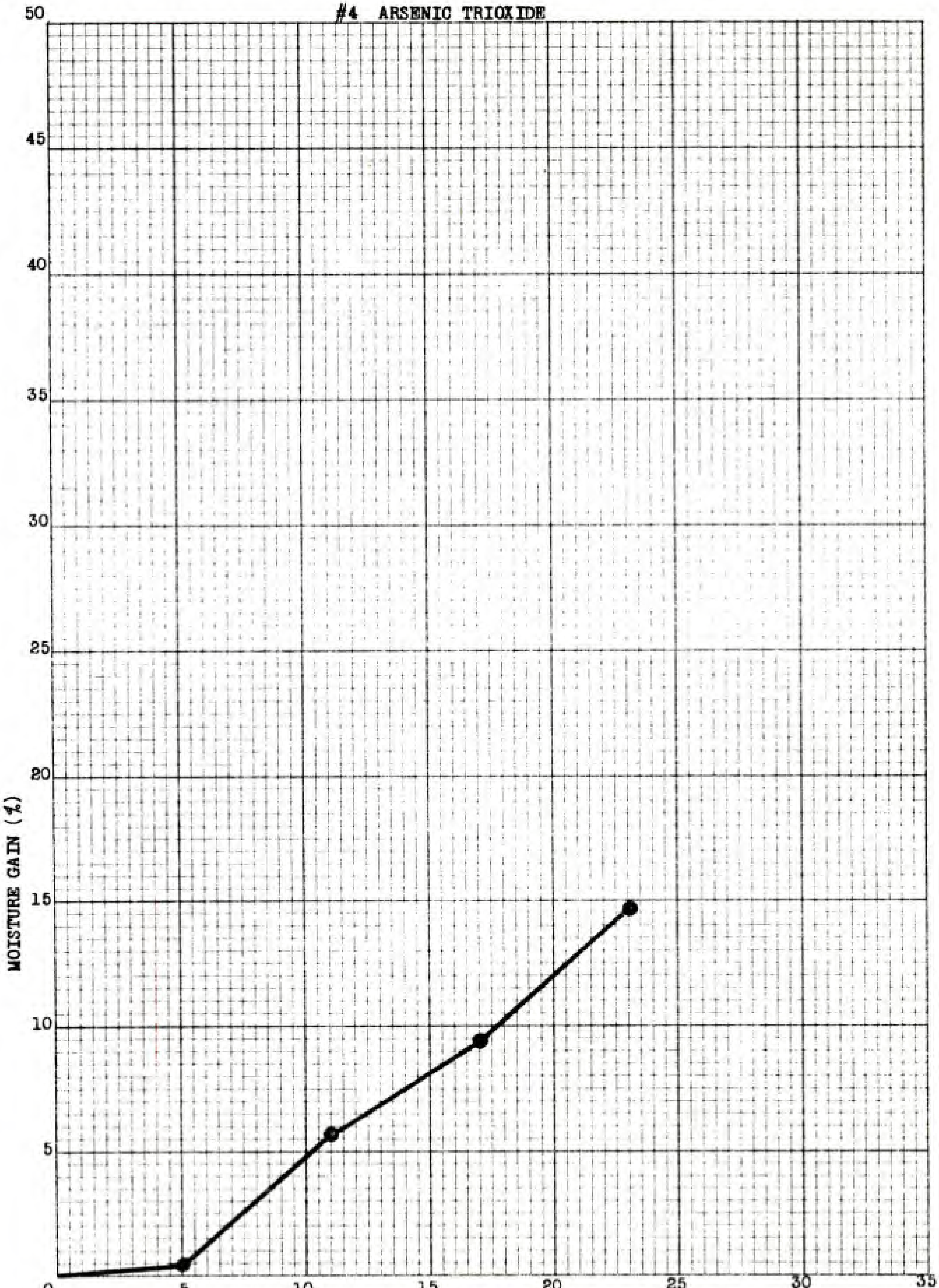
30
35
Time (Hrs)
18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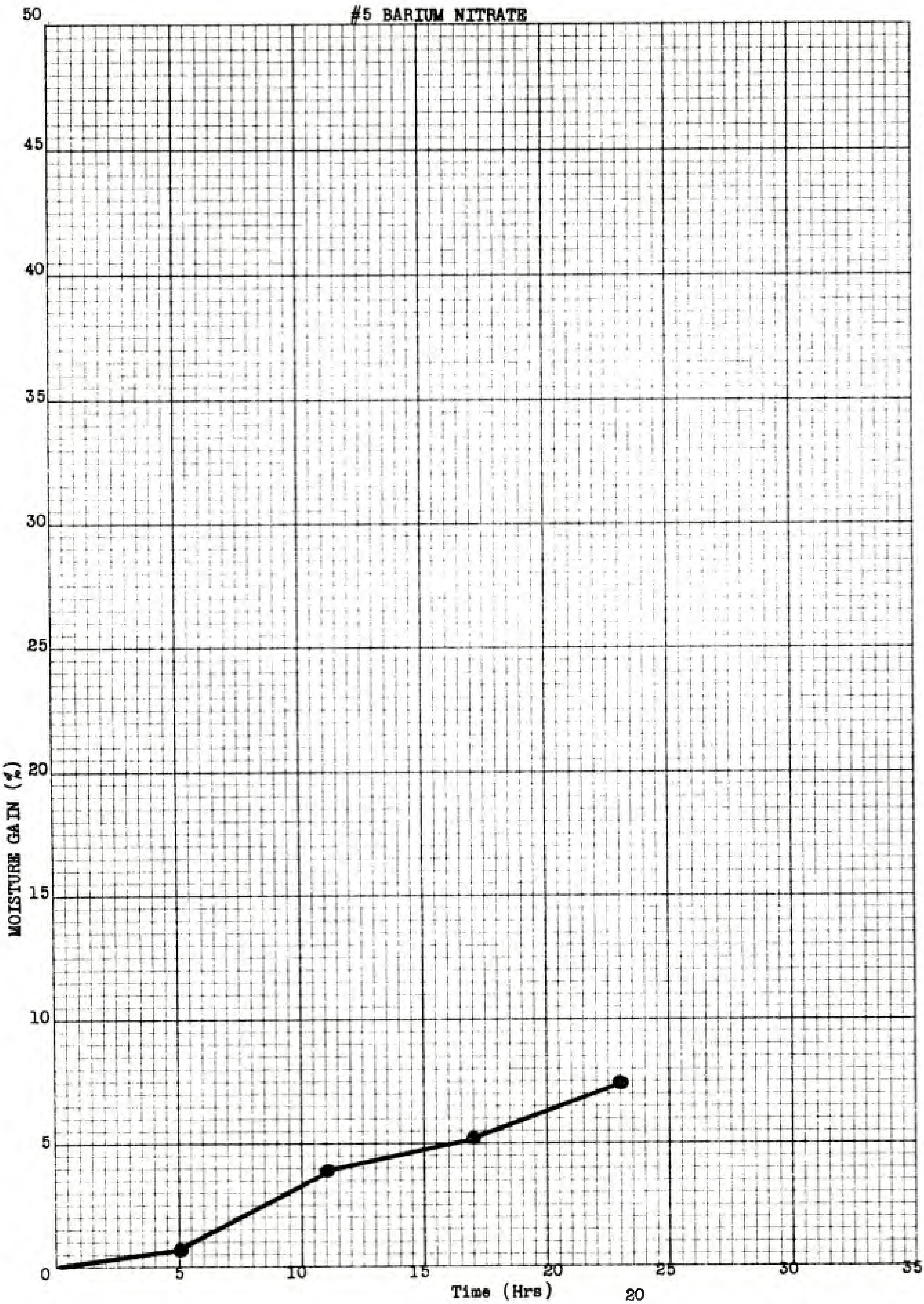
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)



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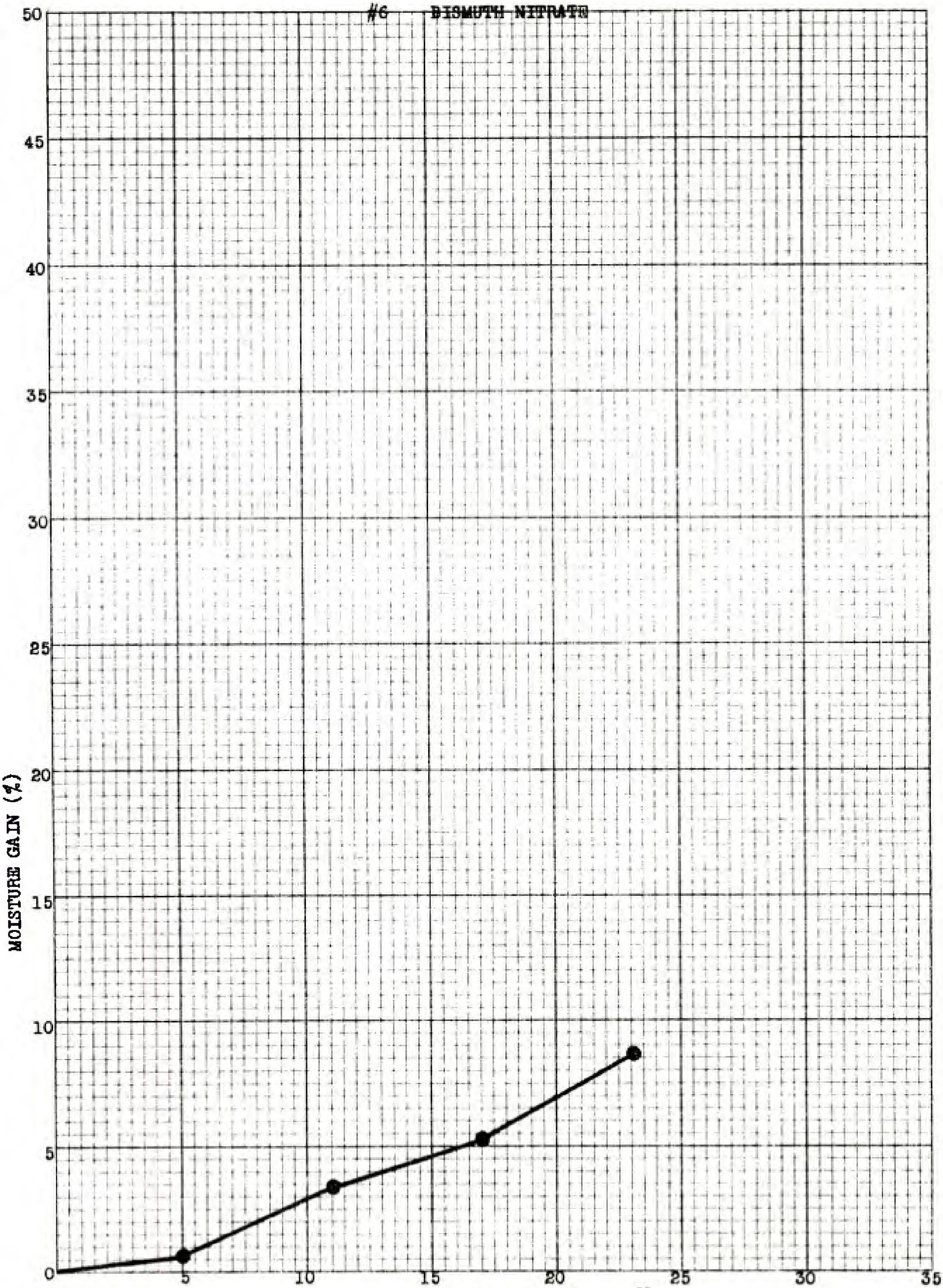
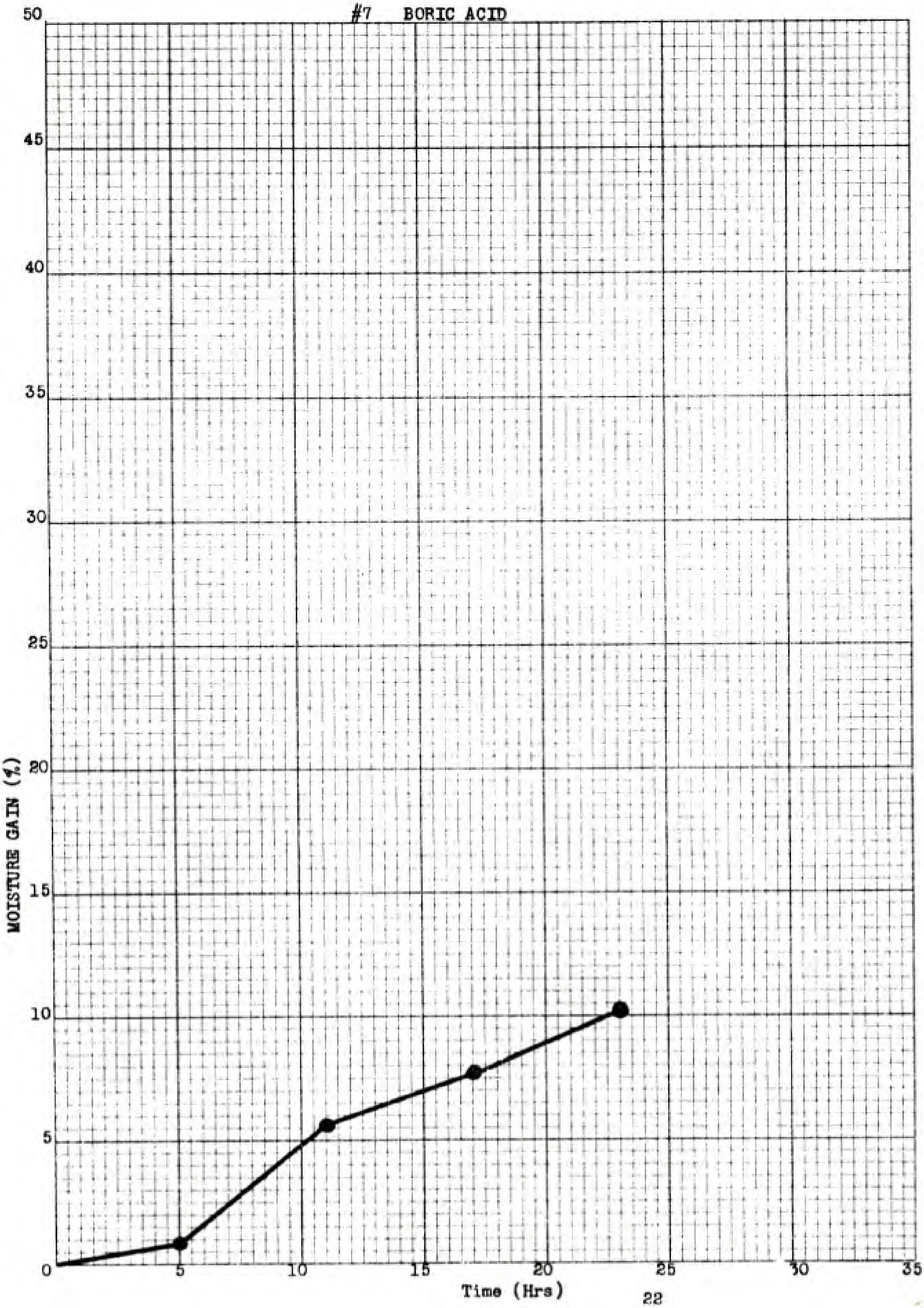
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50


#6 BISMUTH NITRATE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs)
5
10
15
20
25
30
35


#7 BORIC ACID
MOISTURE GAIN (%)
Time (Hrs)
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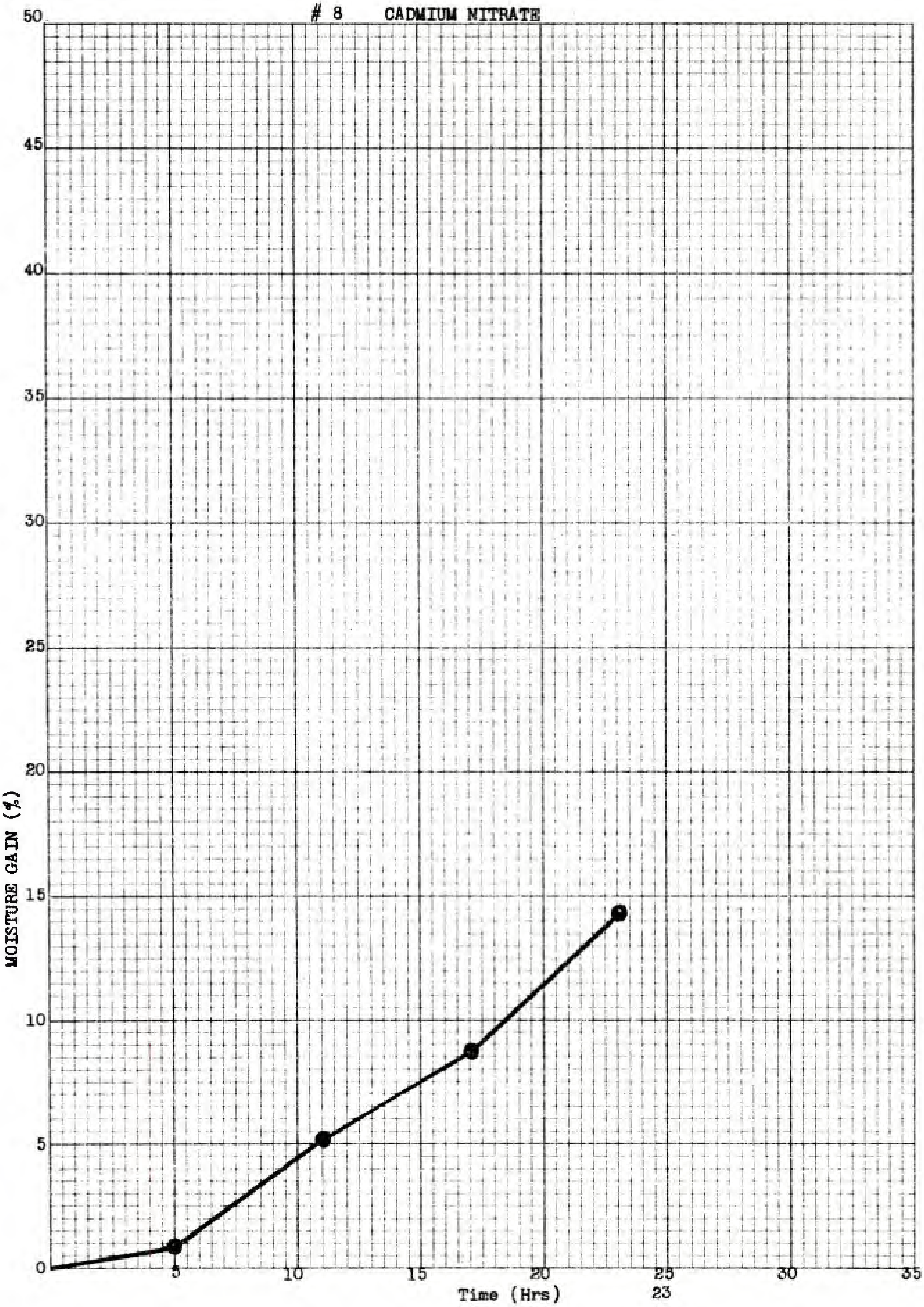
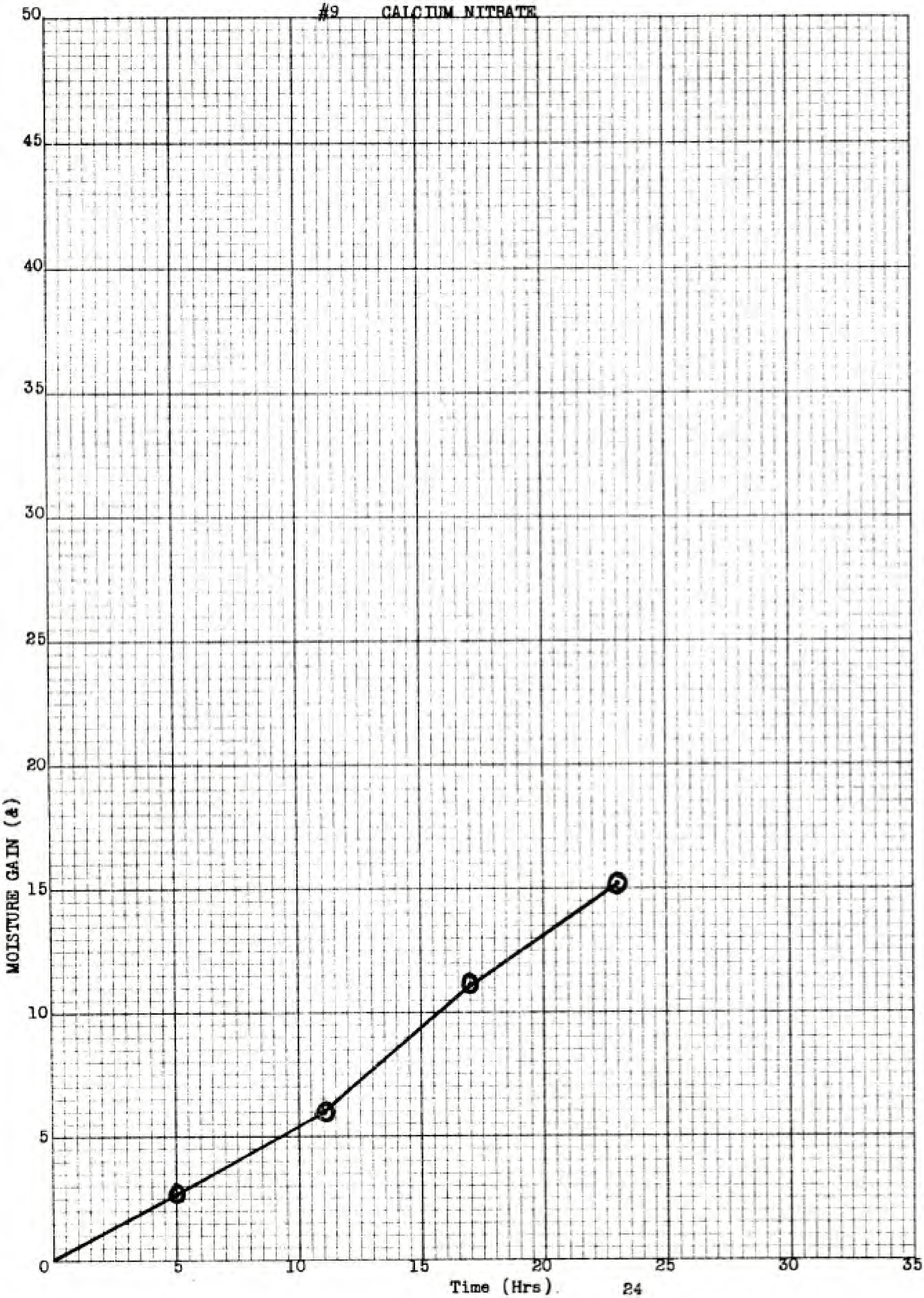
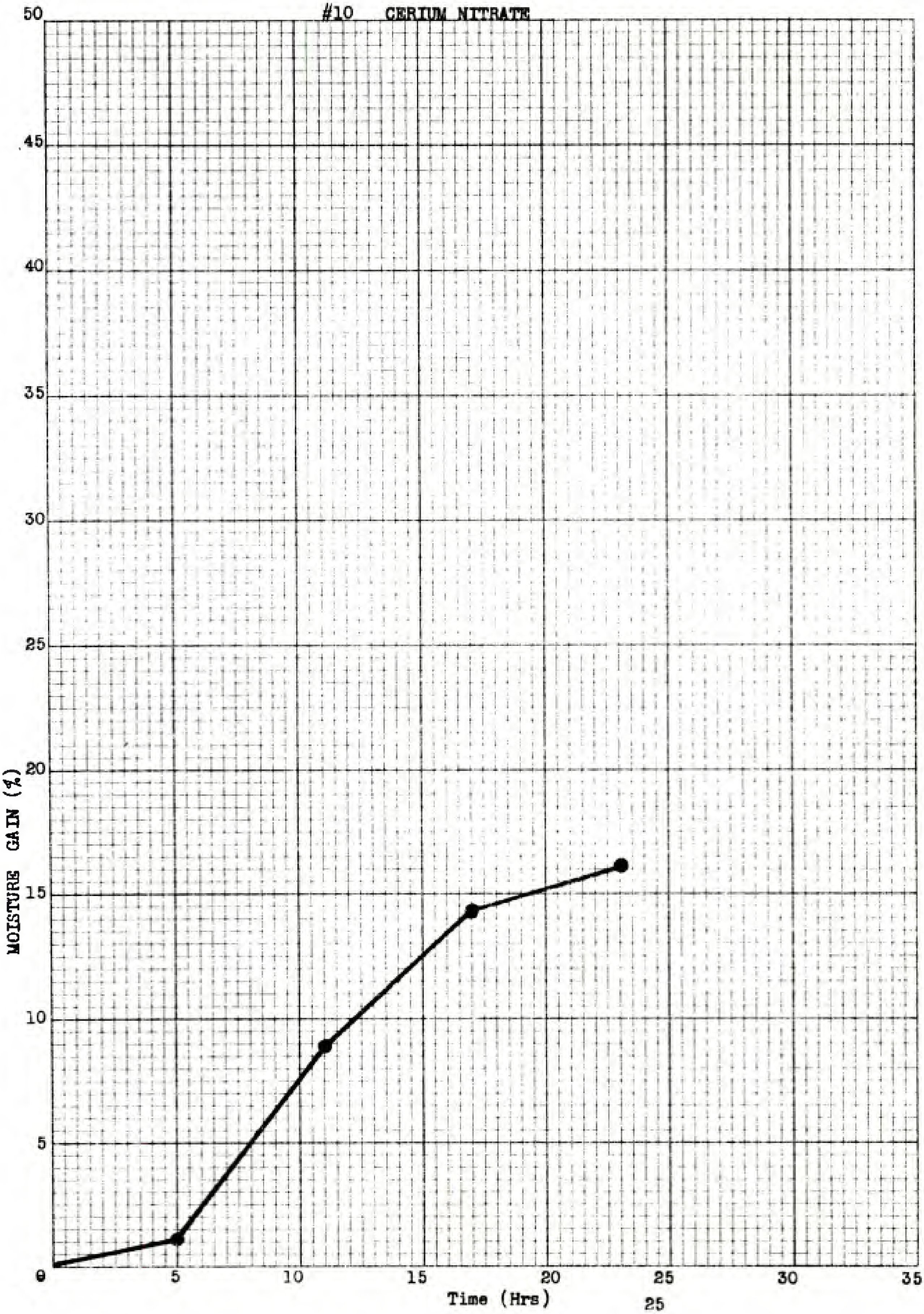
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
30
35



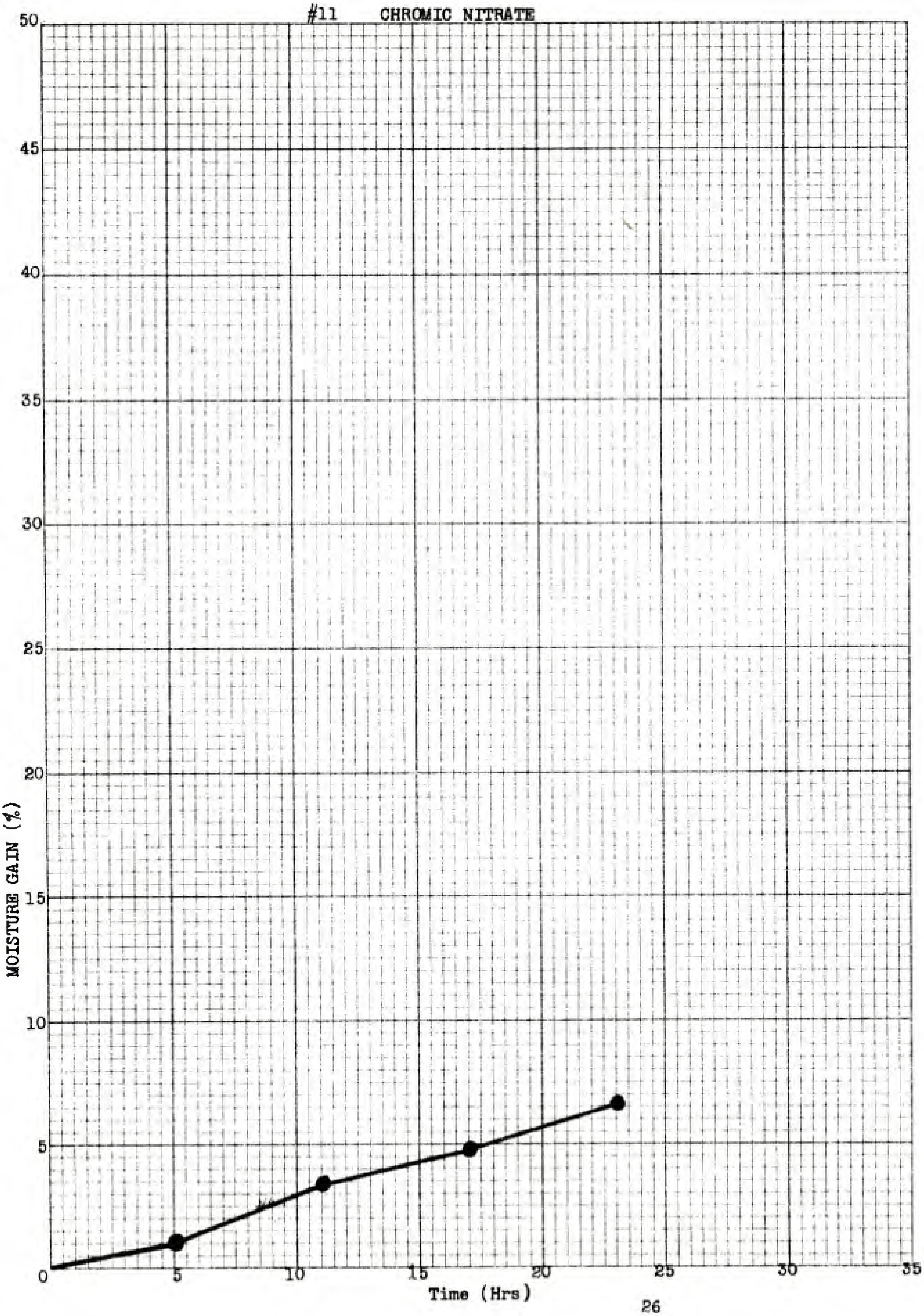
8 CADMIUM NITRATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)
23

#9 CALCIUM NITRATE

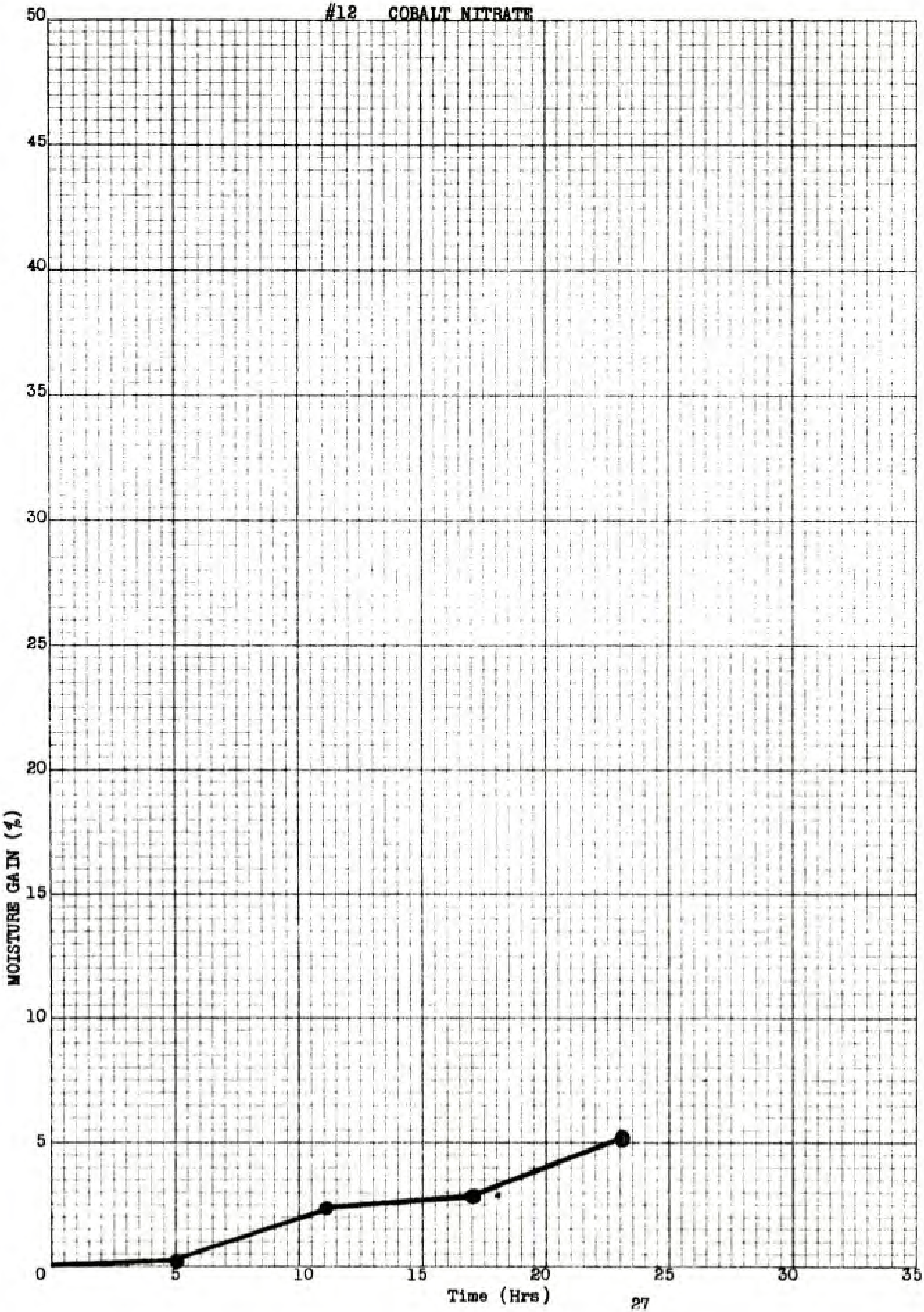




#10 CERIUM NITRATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)

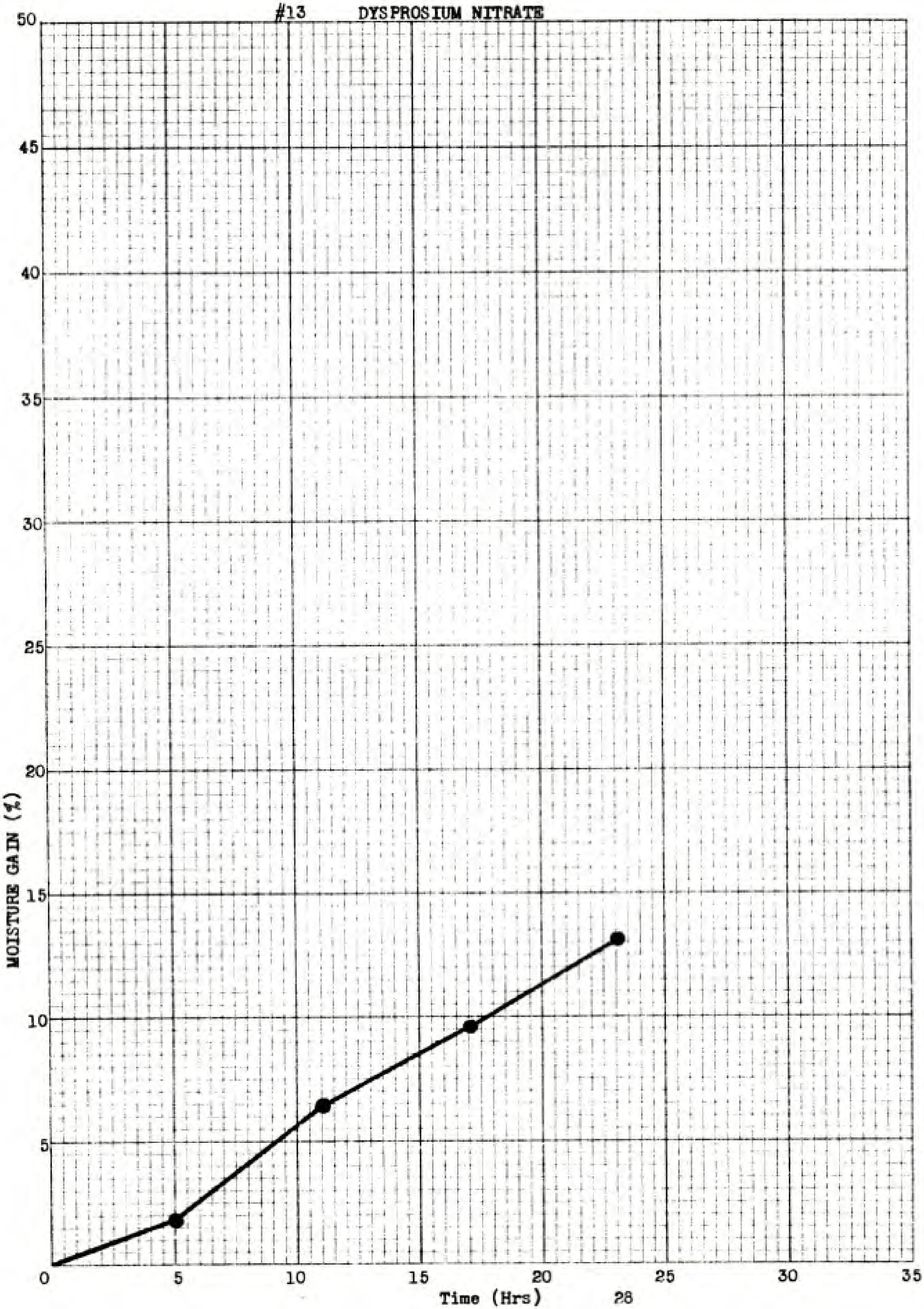


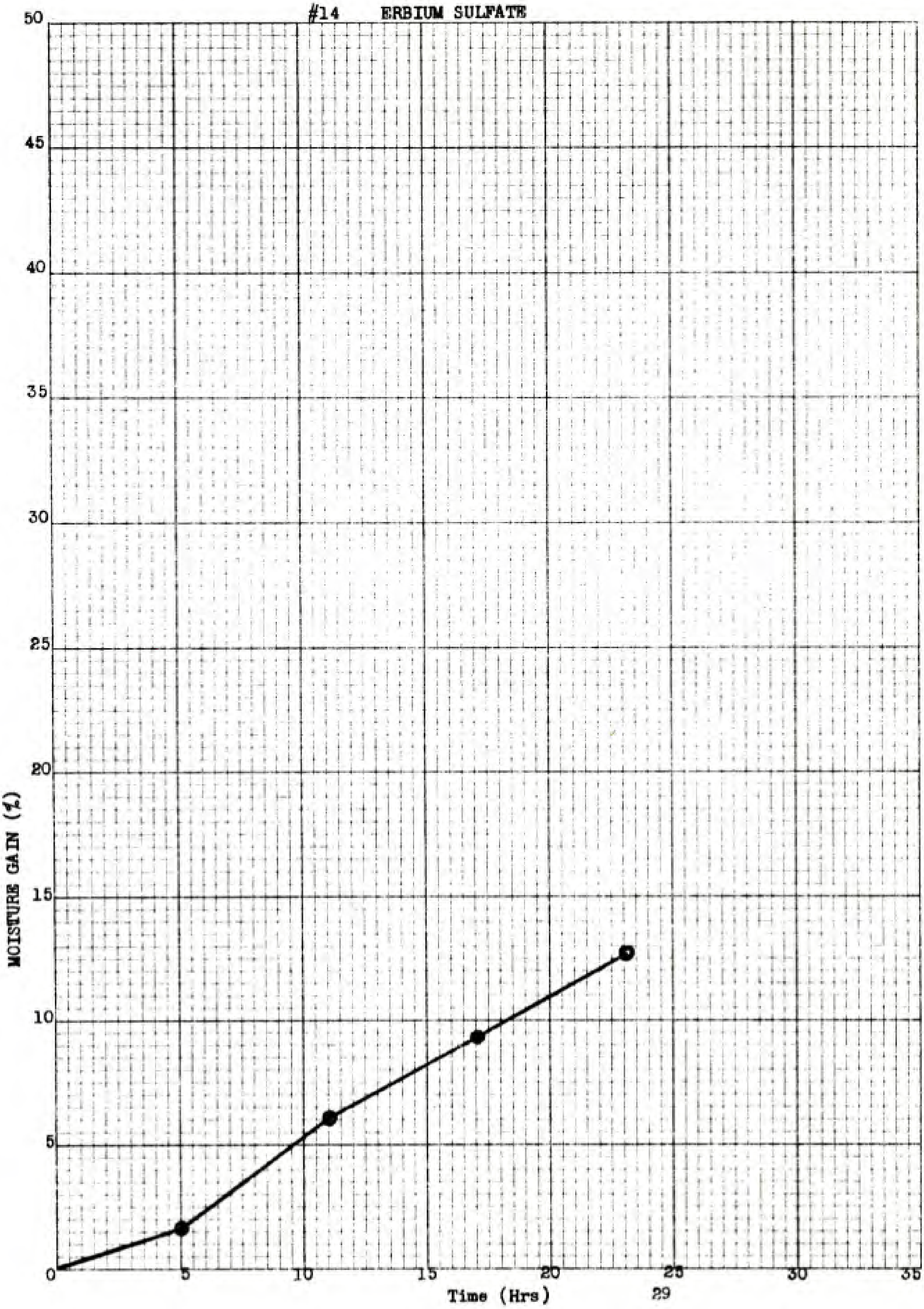
#11 CHROMIC NITRATE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs)

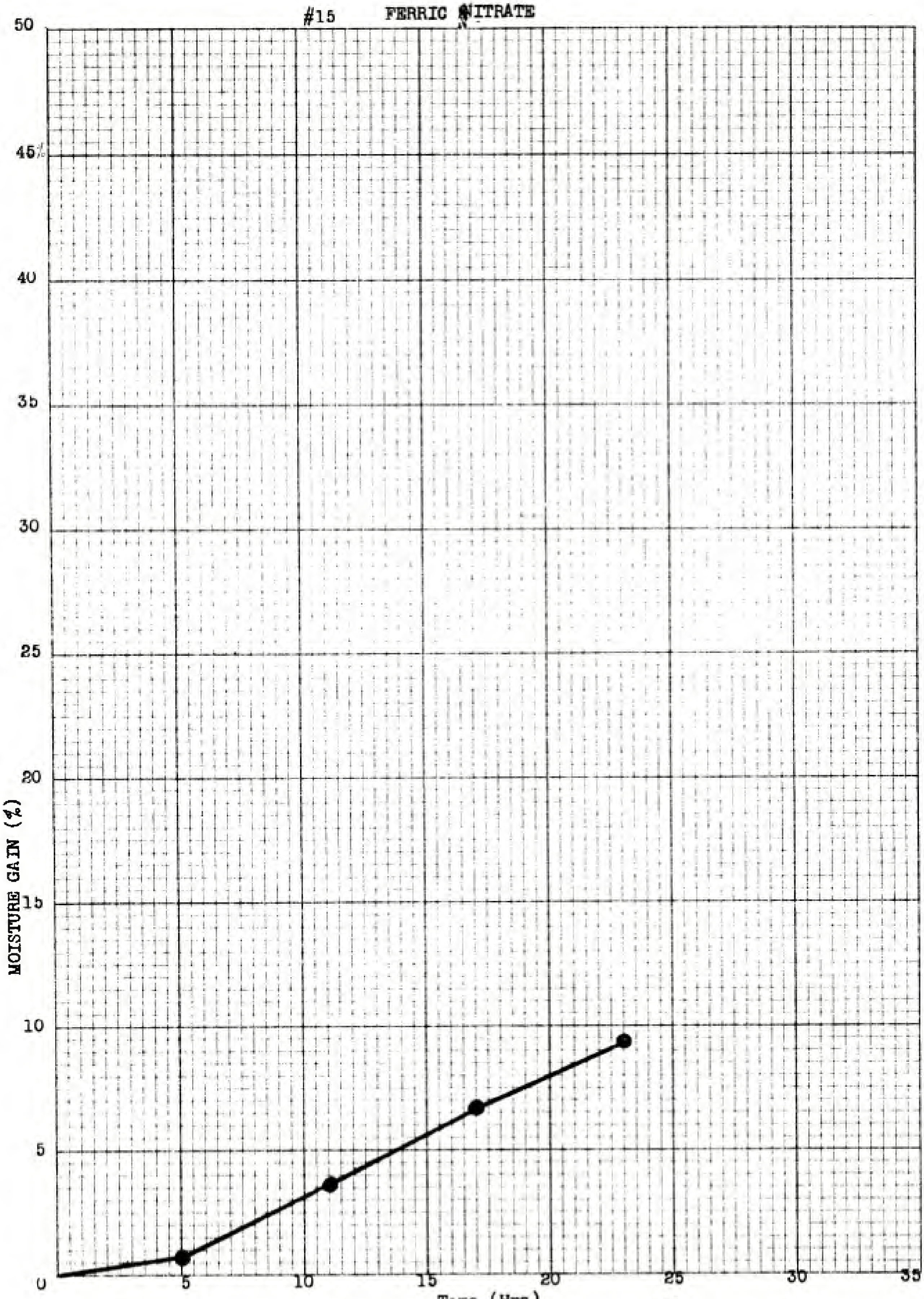


#12 COBALT NITRATE
50
45
40
35
30
25
20
15
10
5
0
MOISTURE GAIN (%)
5
10
15
20
25
30
35
Time (Hrs)

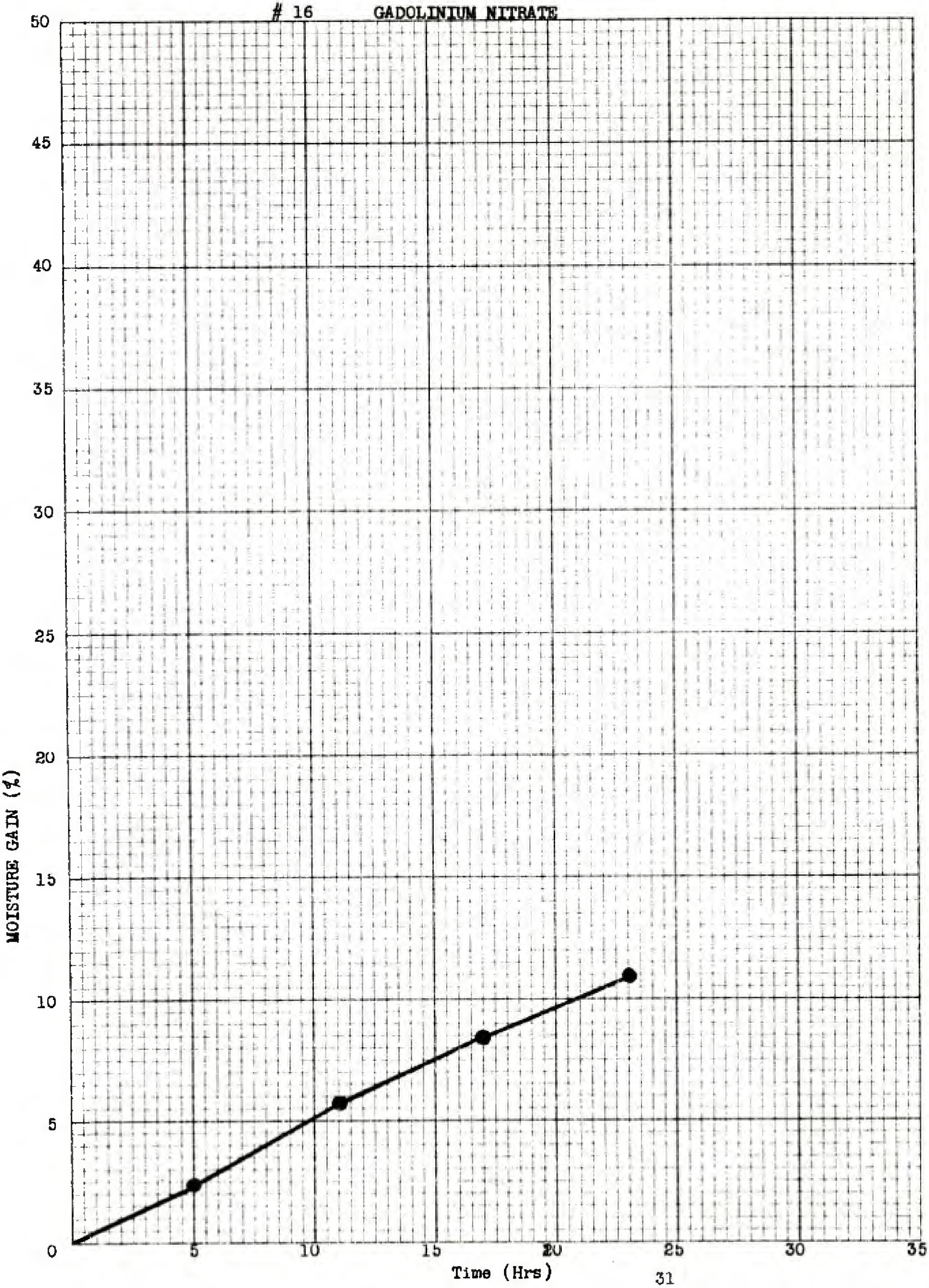
#13 DYSPROSIUM NITRATE



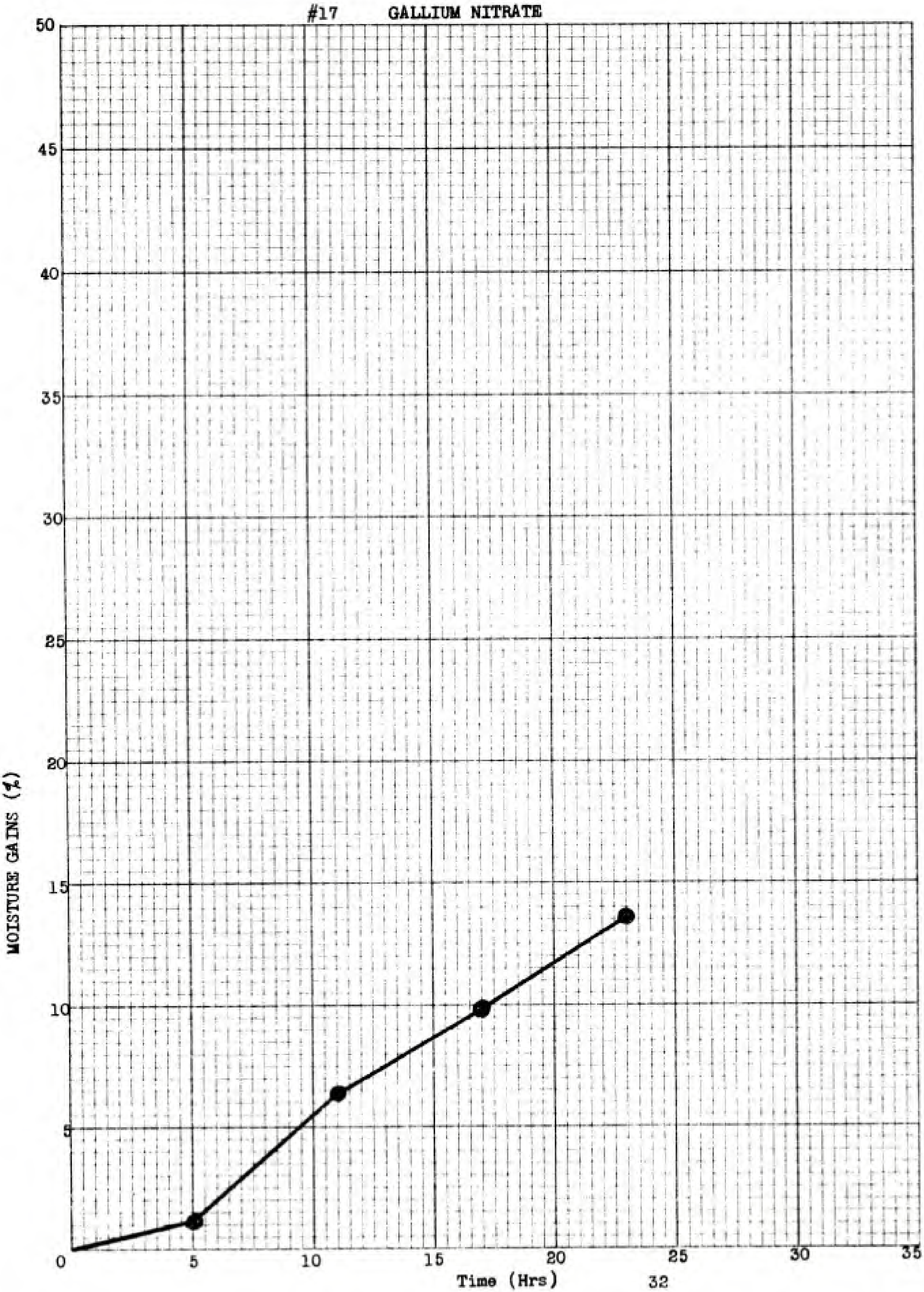

#14 ERBIUM SULFATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)



#15 FERRIC NITRATE
MOISTURE GAIN (%)
Time (Hrs)
50
45%
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35



16 GADOLINIUM NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



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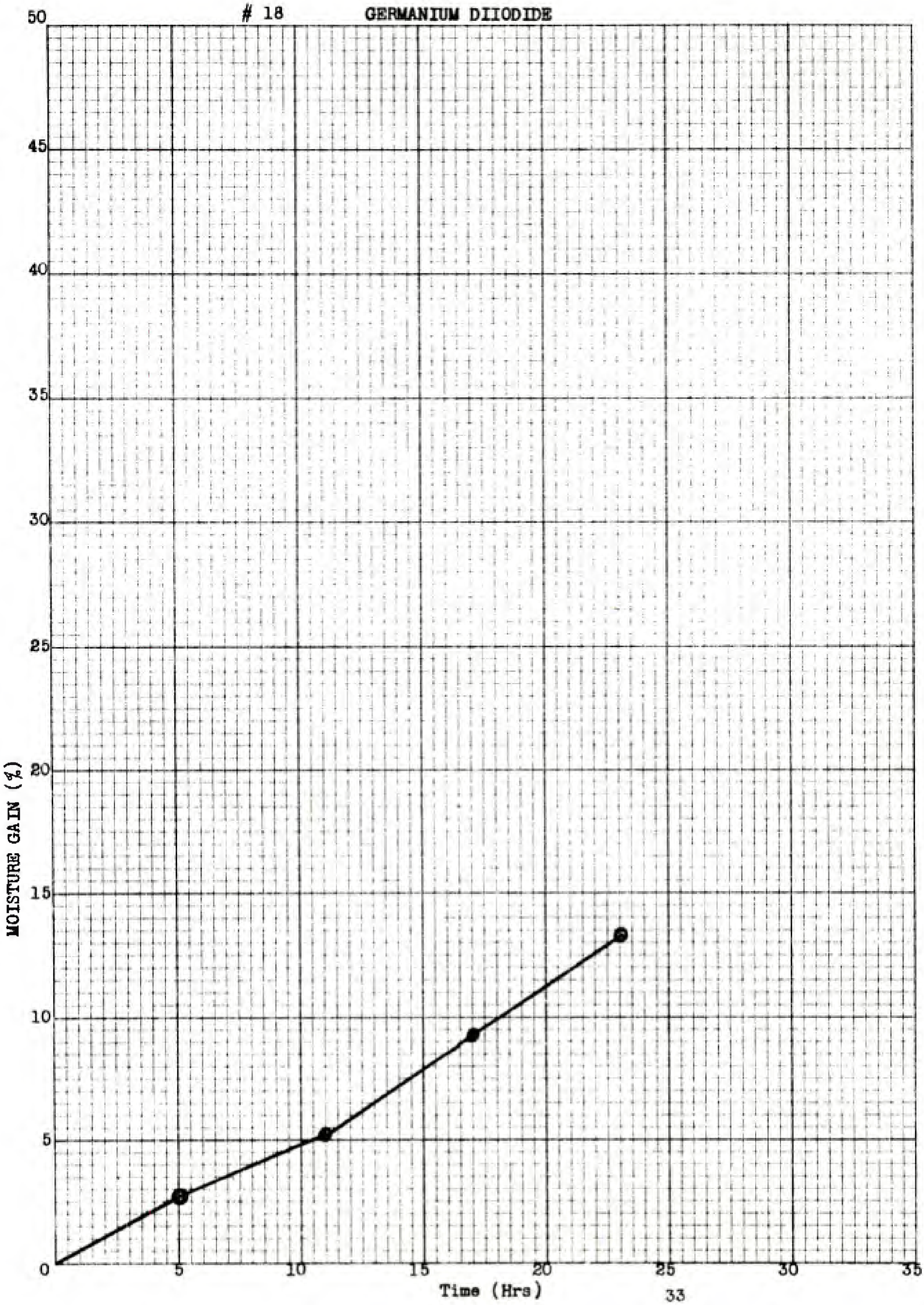
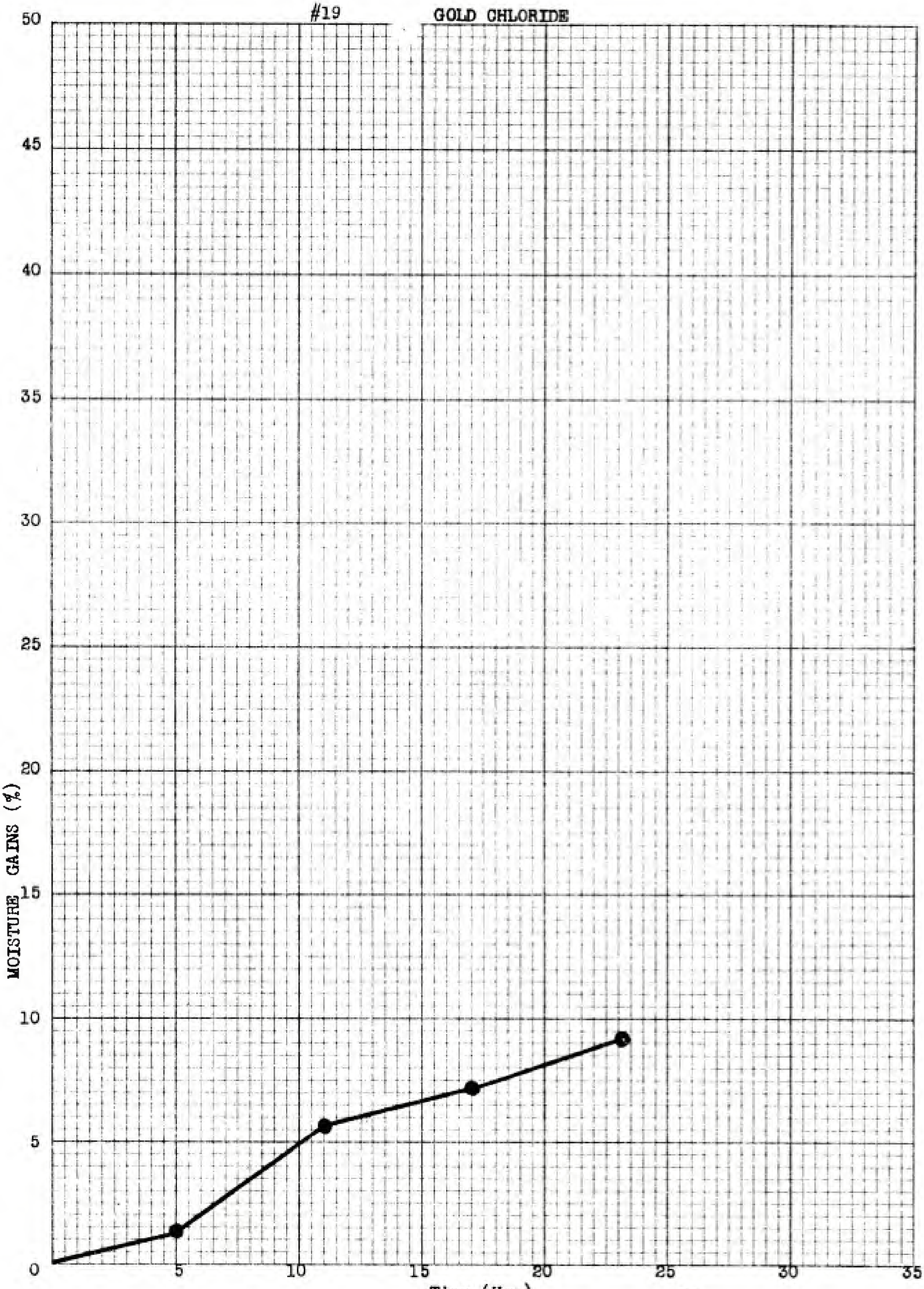
MOISTURE GAINS (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



18 GERMANIUM DIIODIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50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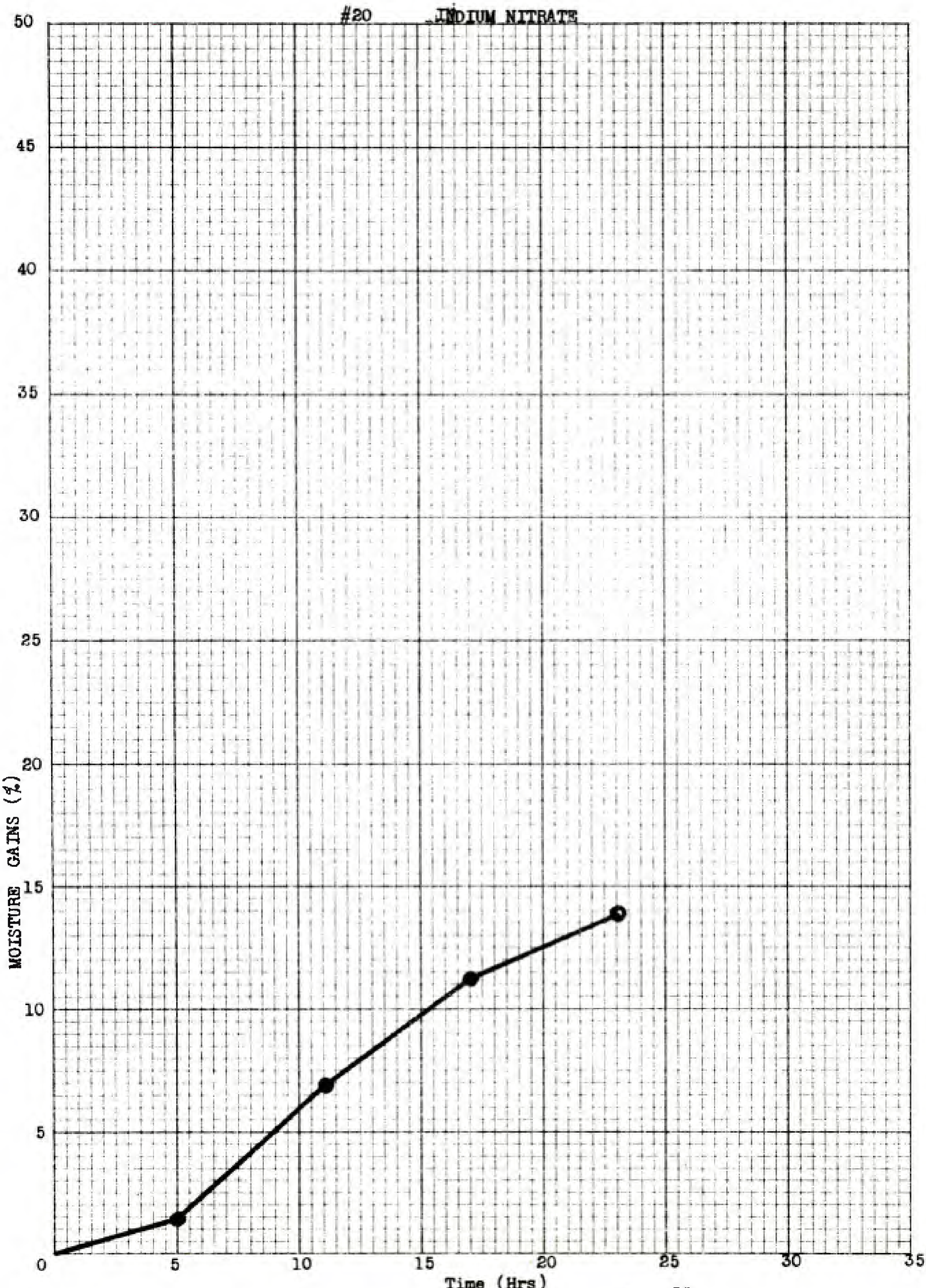
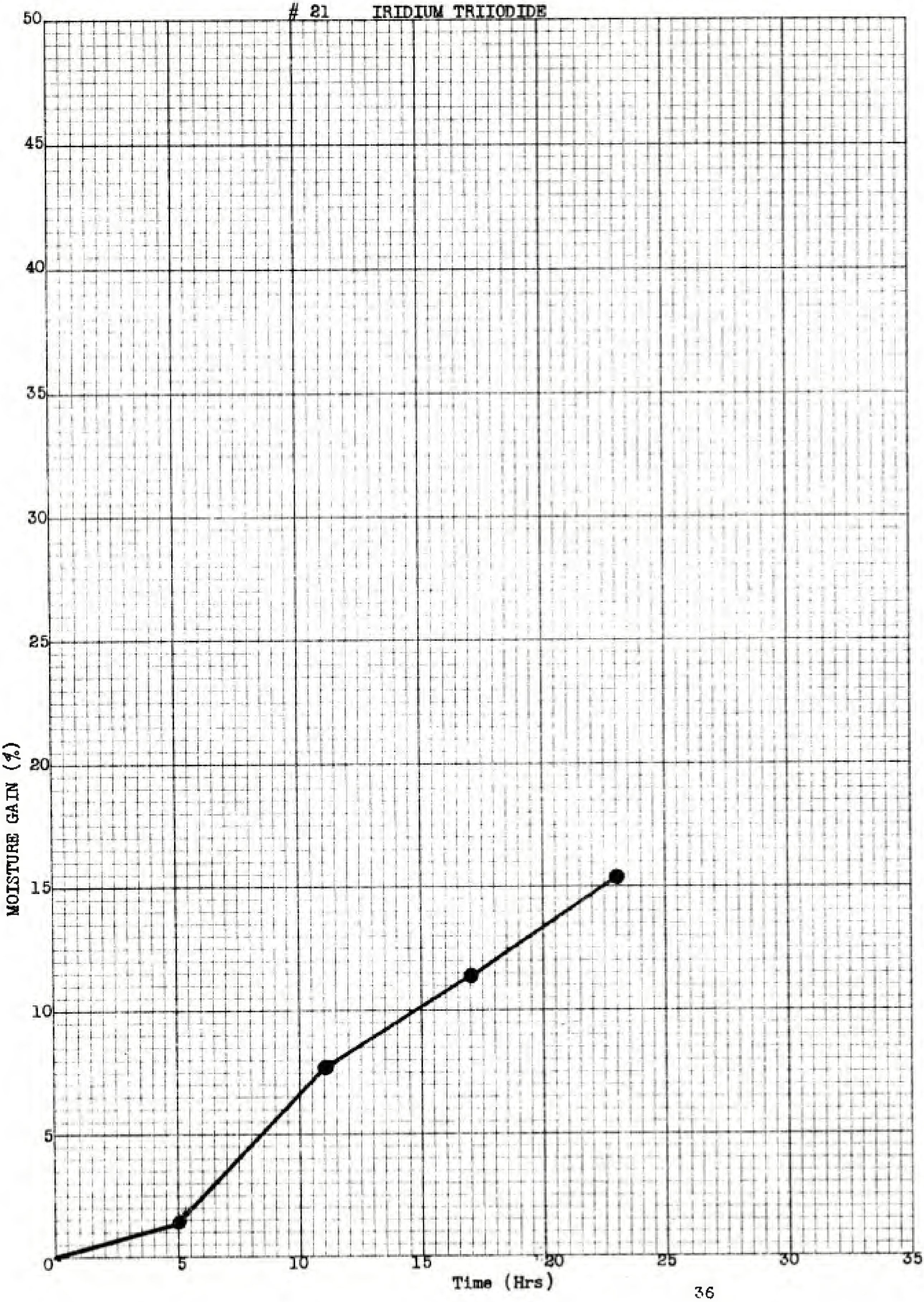
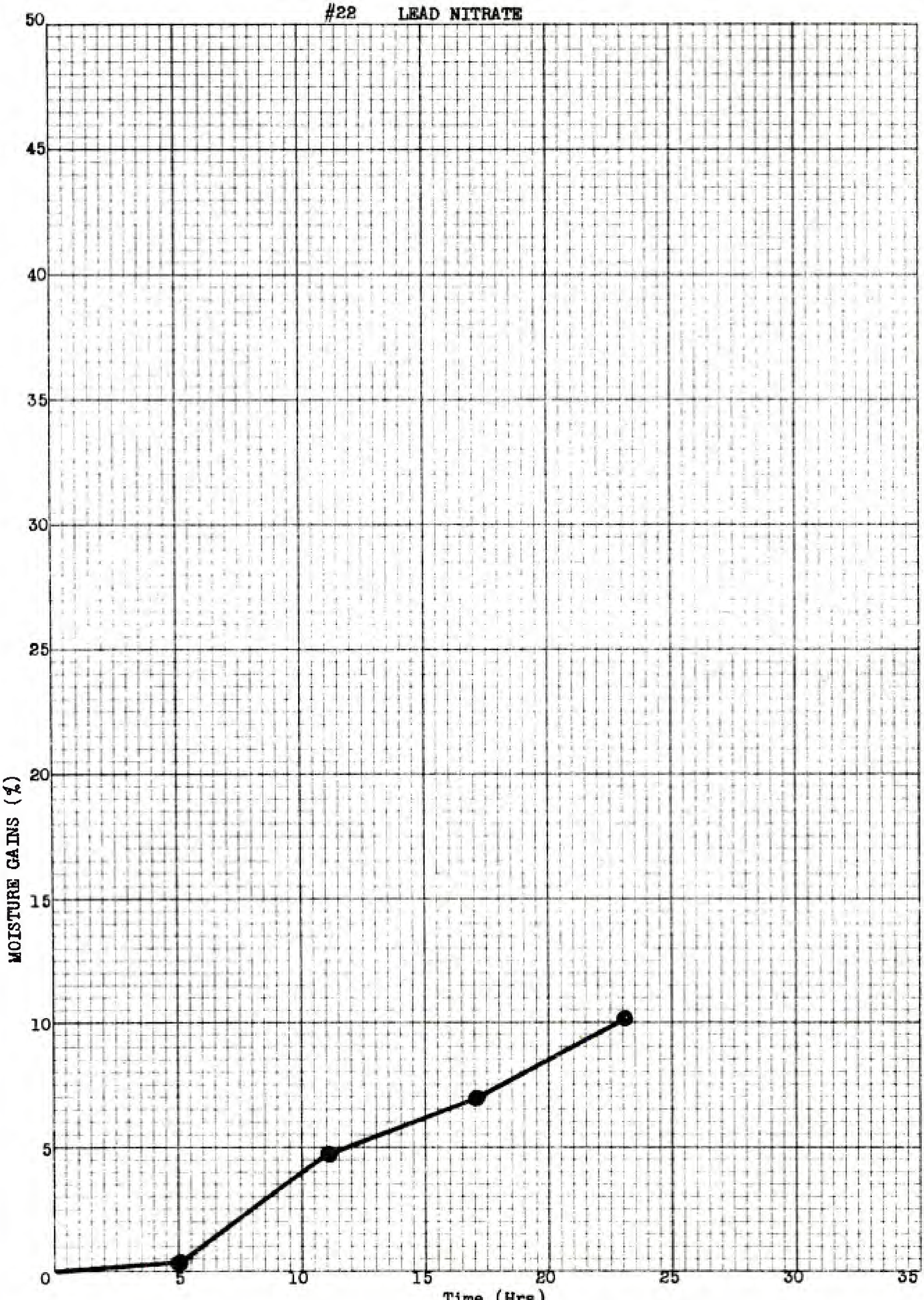
GOLD CHLORIDE
MOISTURE GAINS (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)

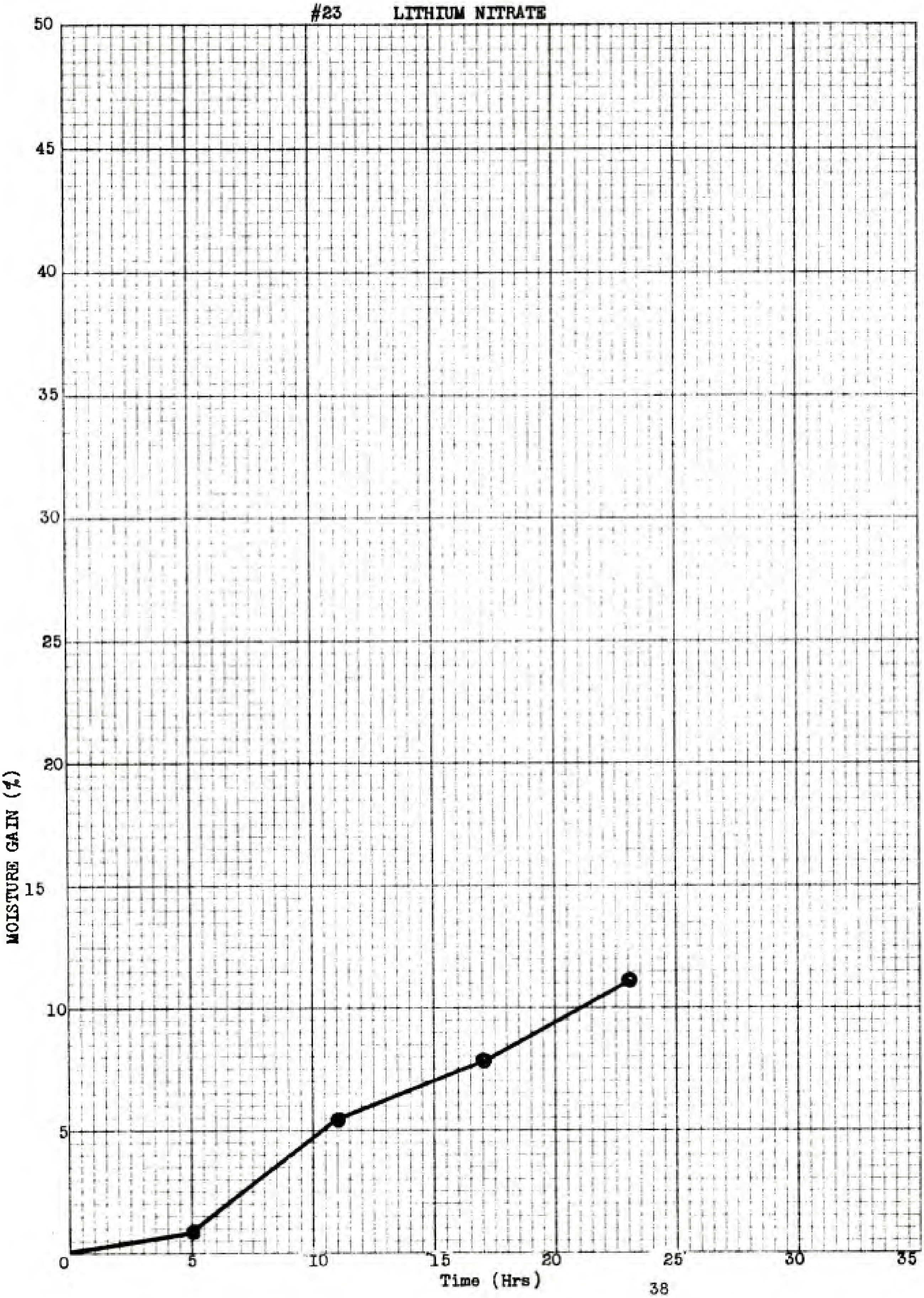

#20 INDIUM NITRATE
MOISTURE GAINS (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



21 IRIDIUM TRIIODIDE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)



#22 LEAD NITRATE
MOISTURE GAINS (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)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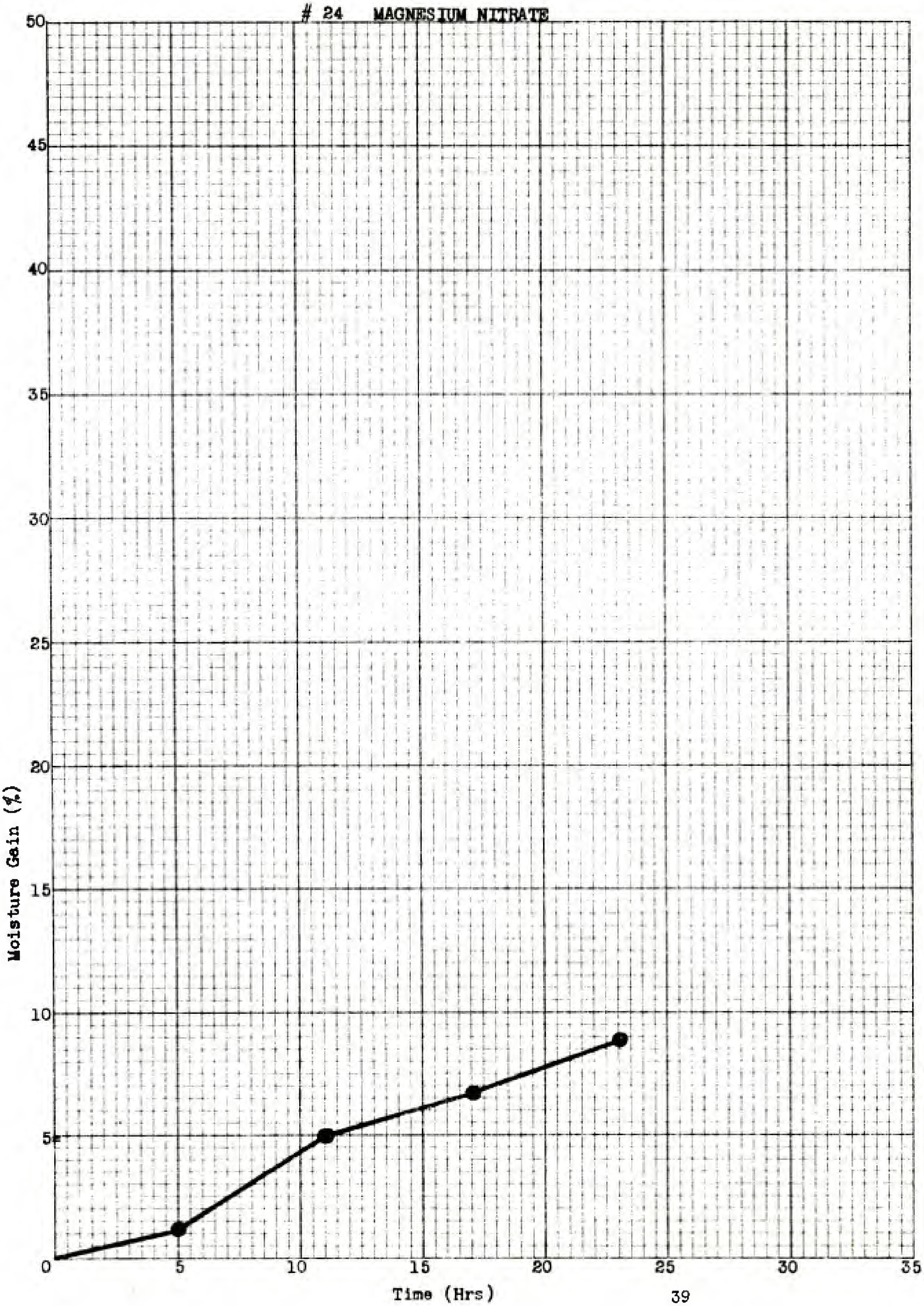
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



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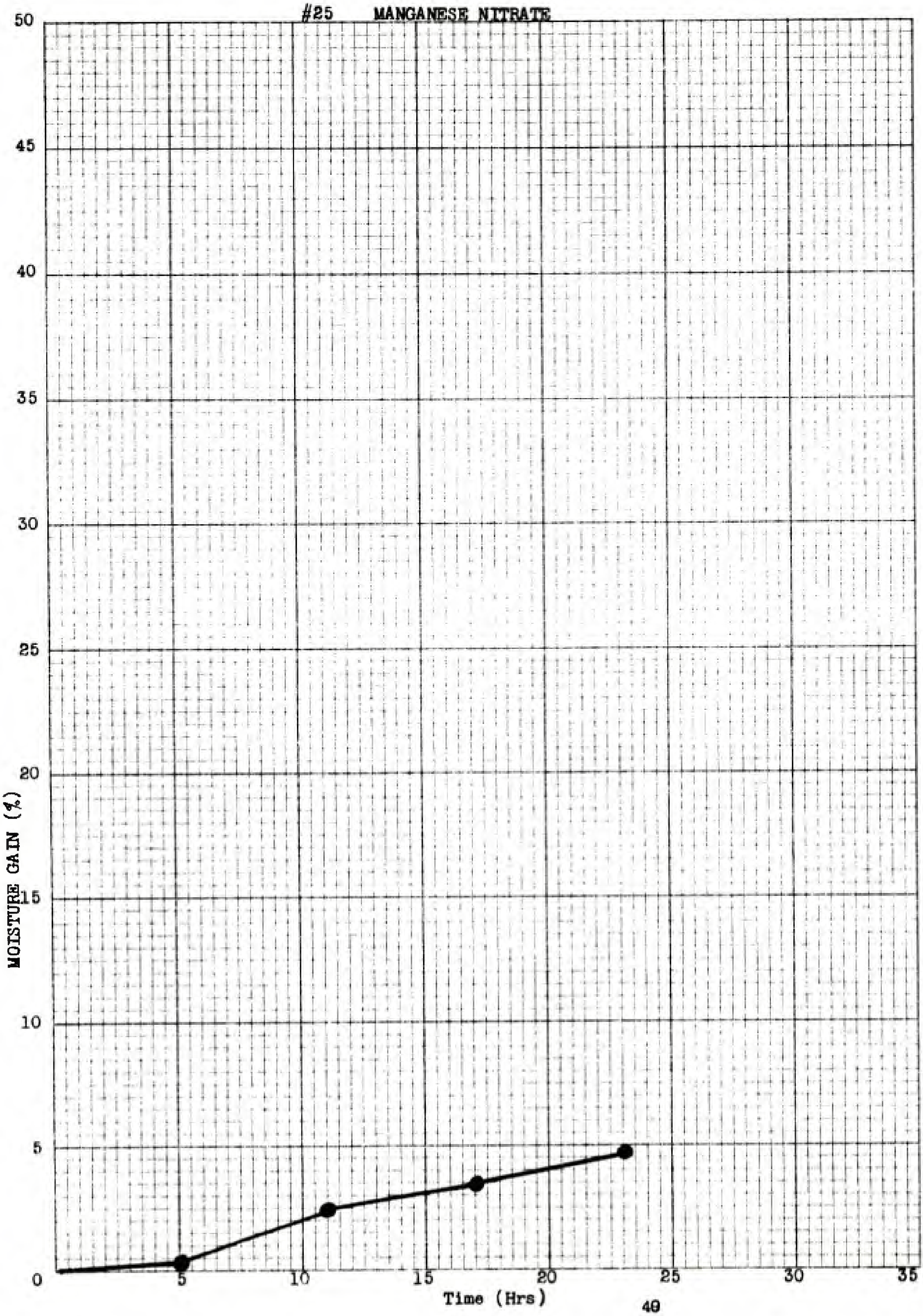
Moisture Gain (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50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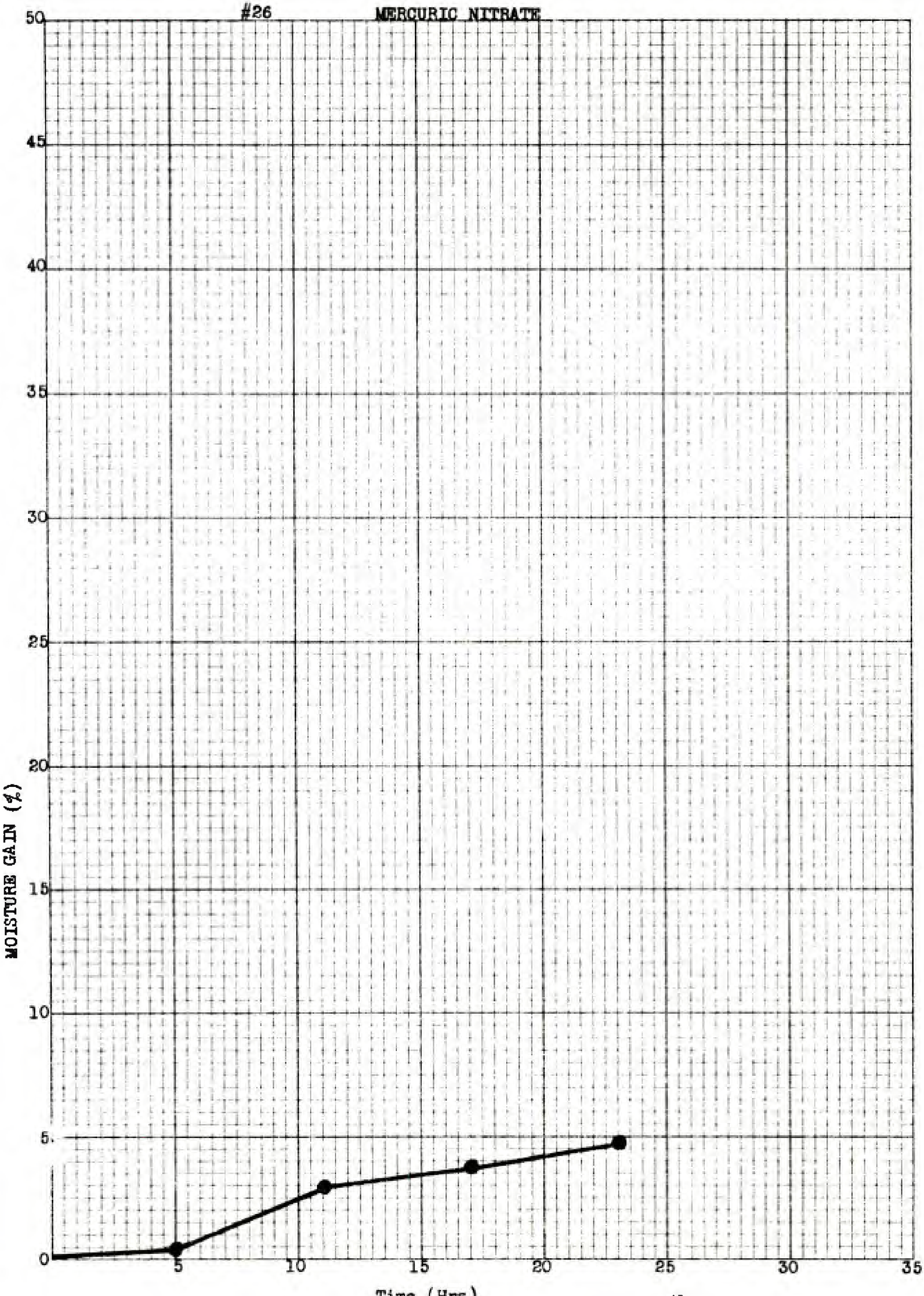
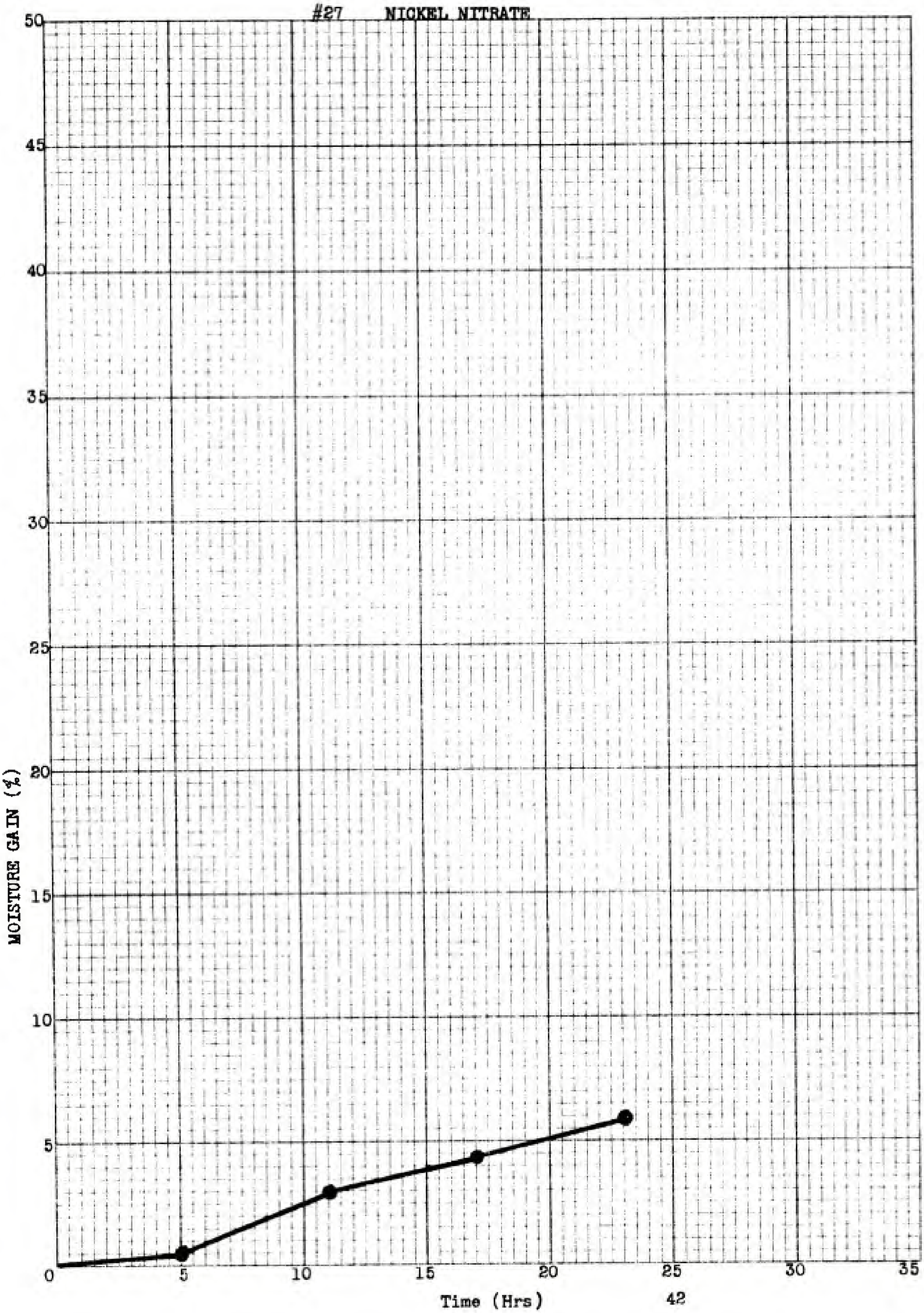
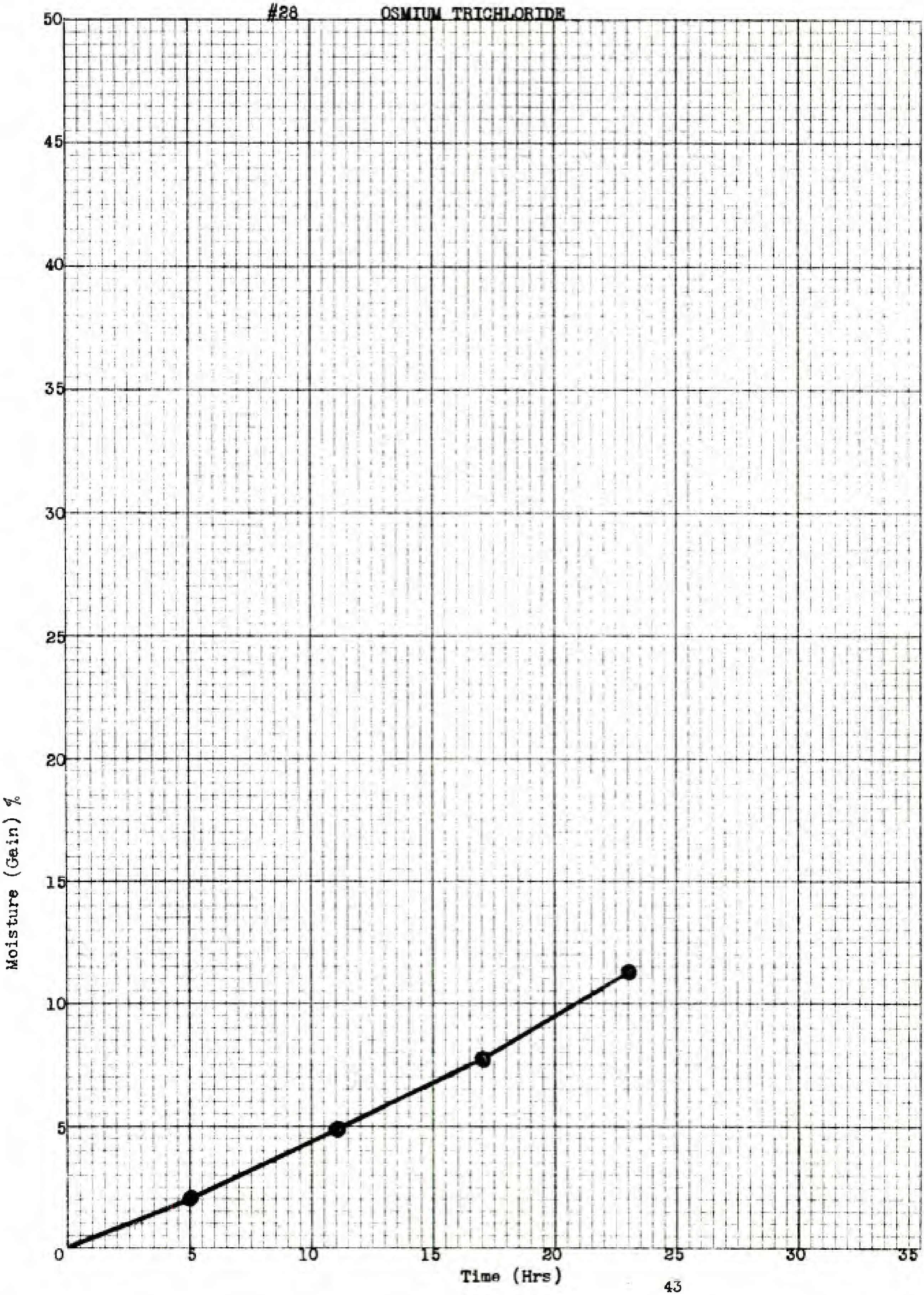
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
30
35



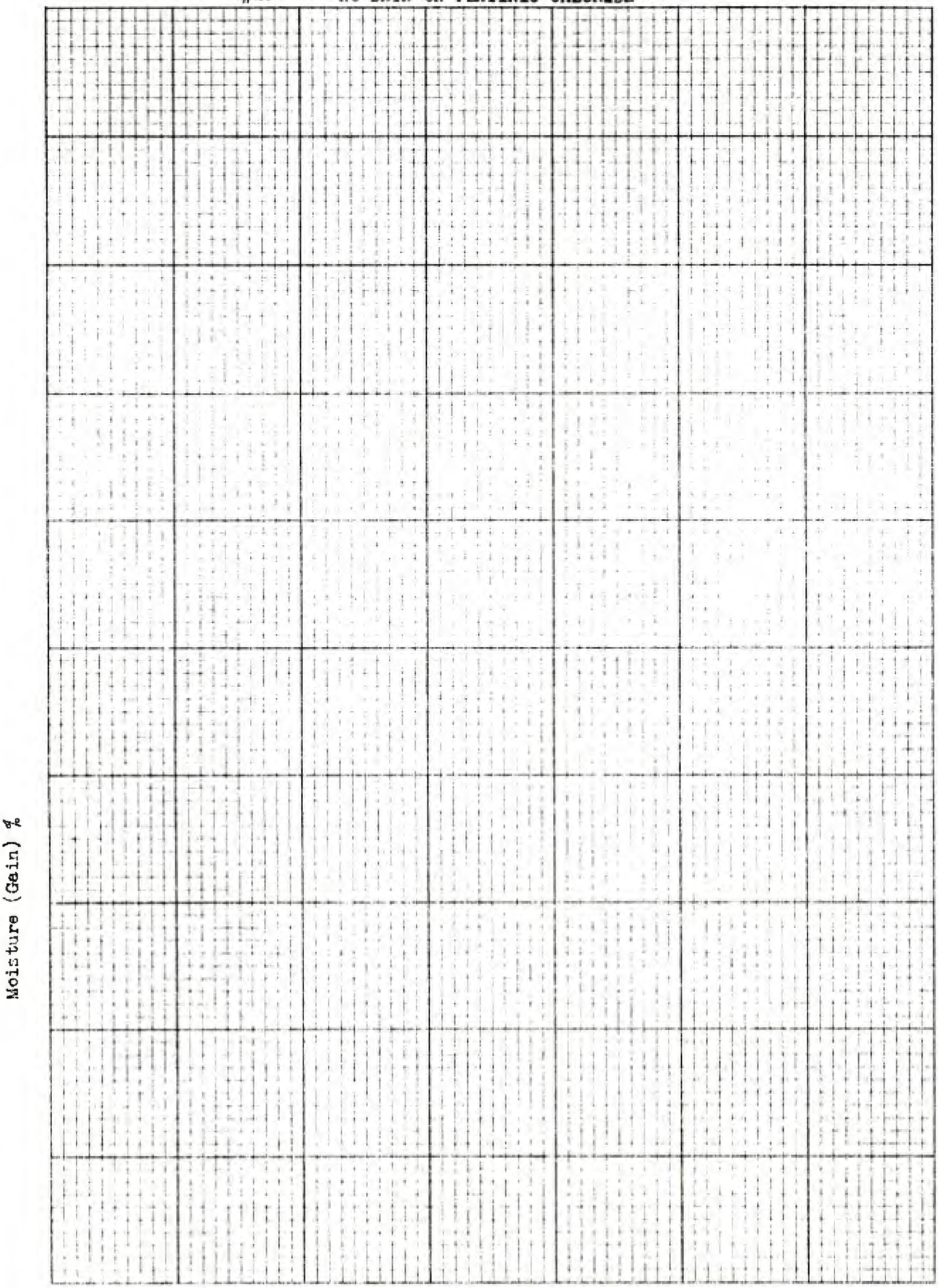
#26
MERCURIC NITRATE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35
Time (Hrs)

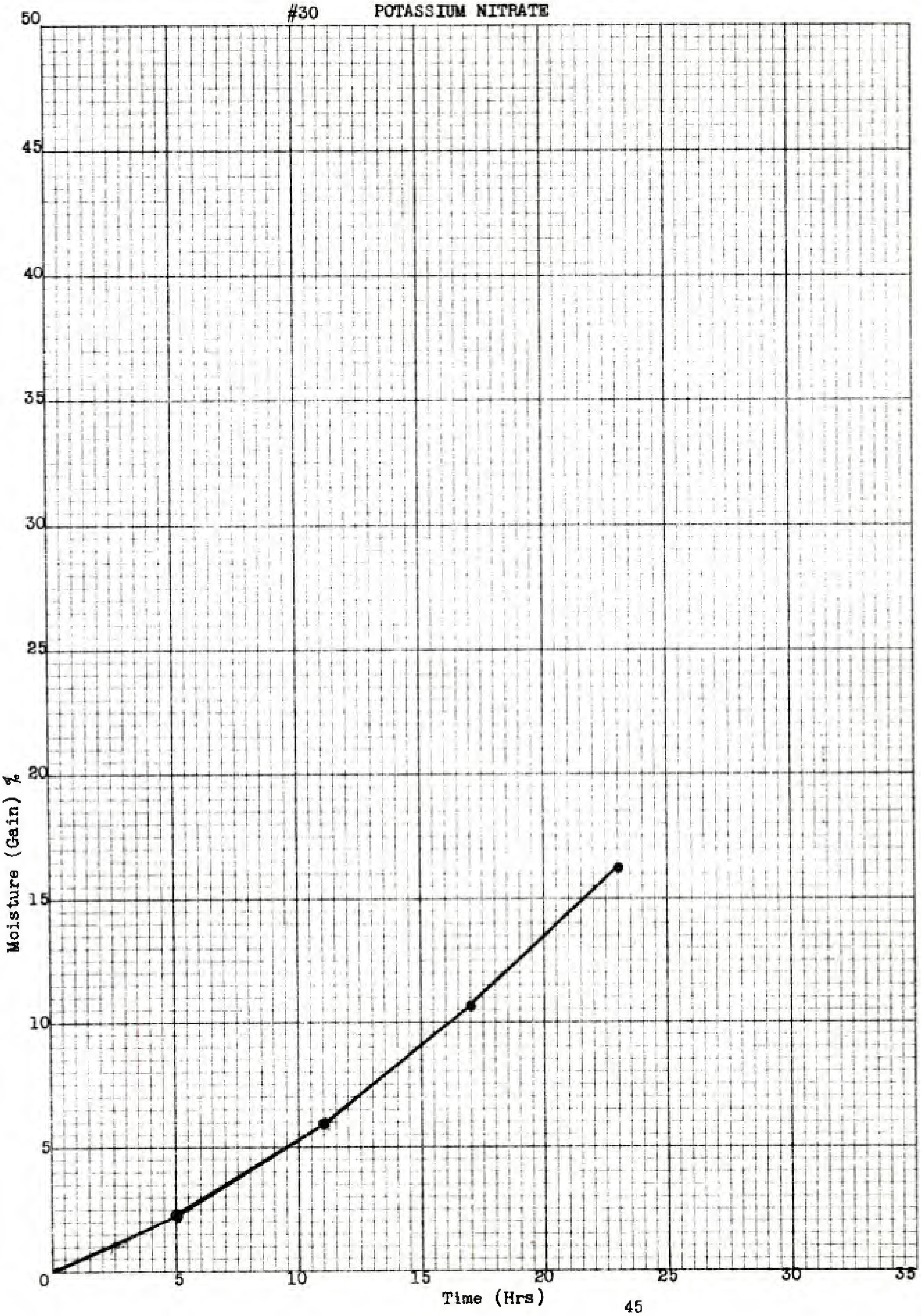
#27 NICKEL NITRATE



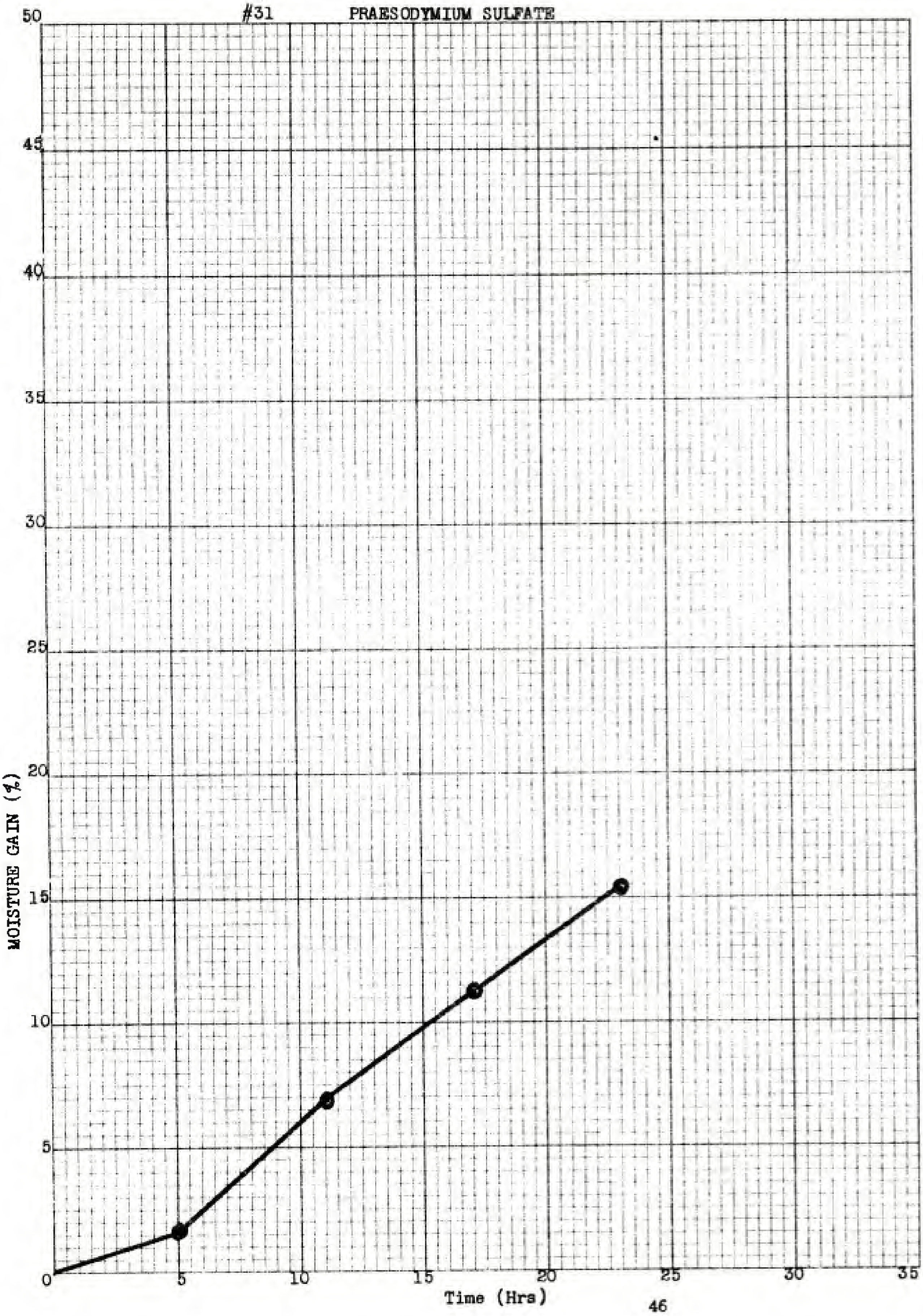

#28 OSMIUM TRICHLORIDE
Moisture (Gain) %
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
30
35

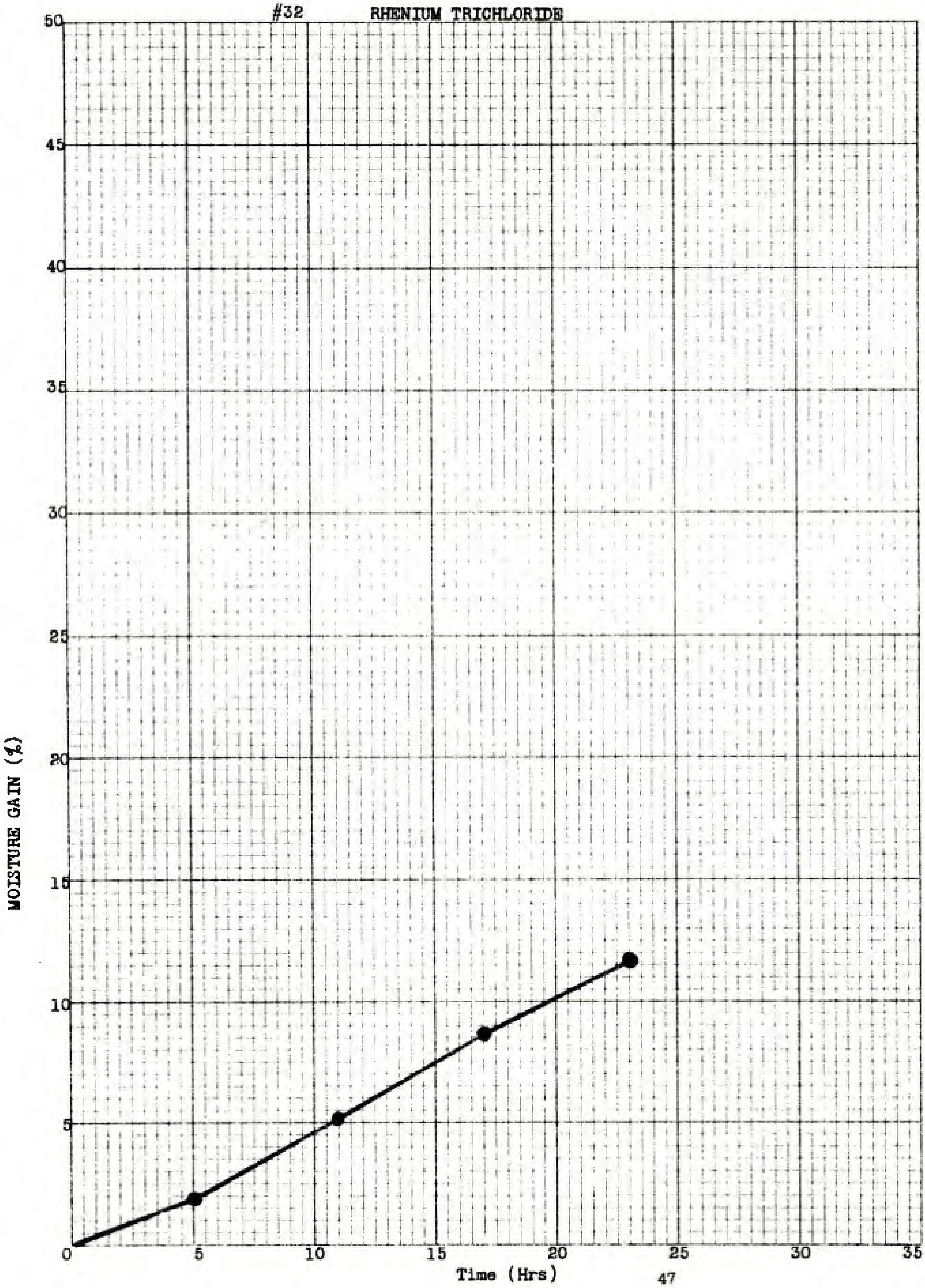
#29 NO DATA ON PLATINIC CHLORIDE

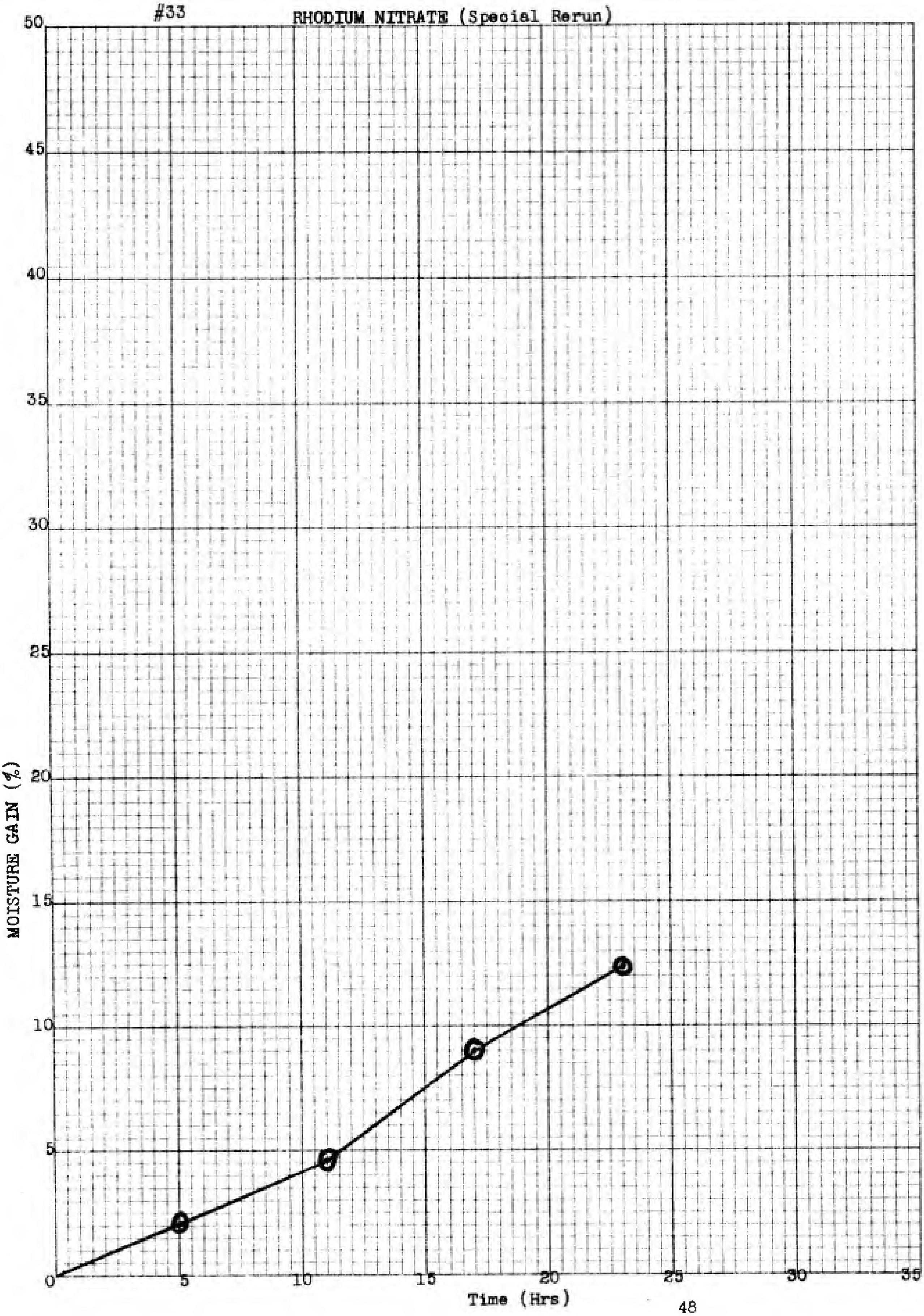



#30 POTASSIUM NITRATE
Moisture (Gain) %
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
30
35

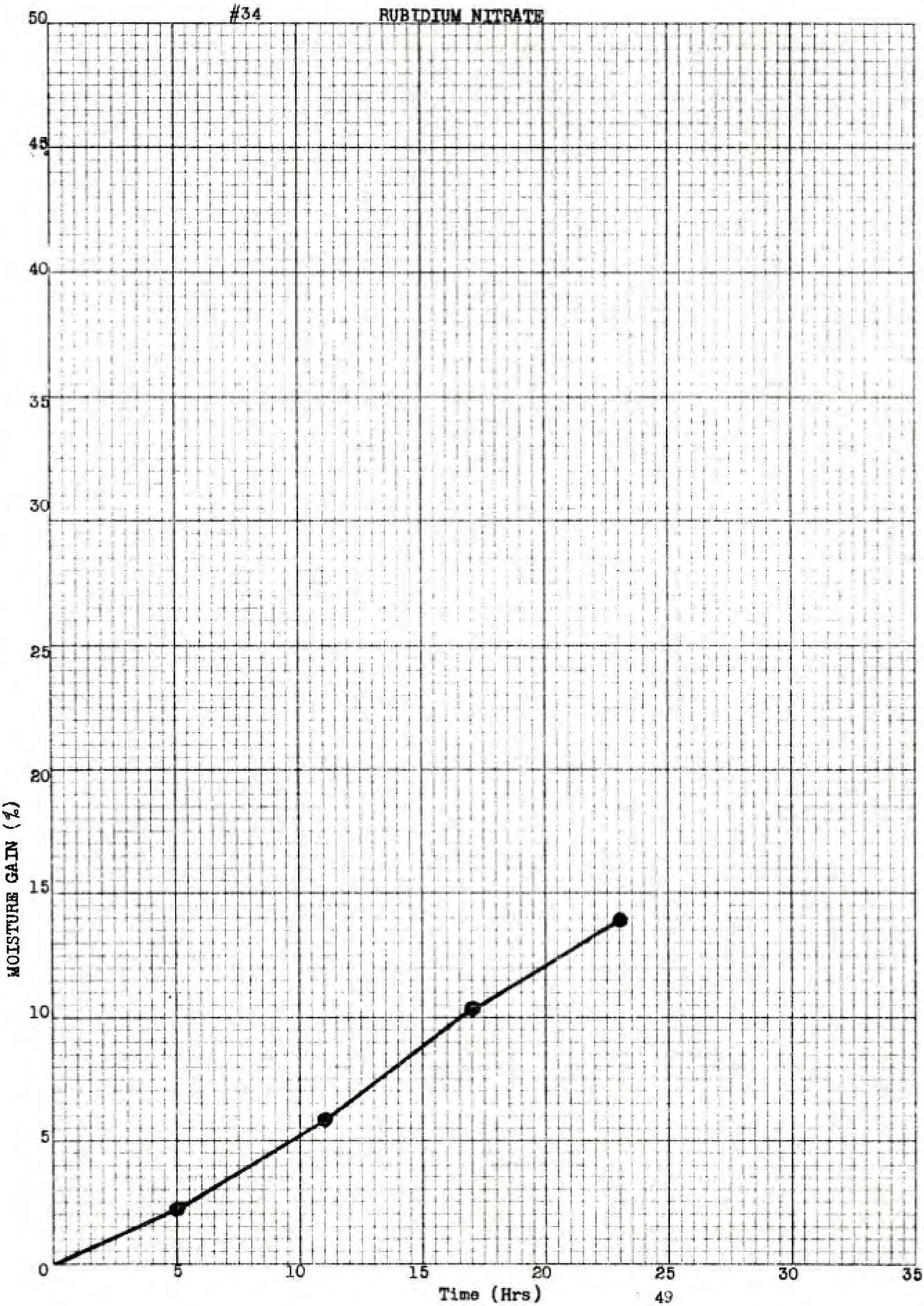
#31 PRAESODYMIUM SULFATE

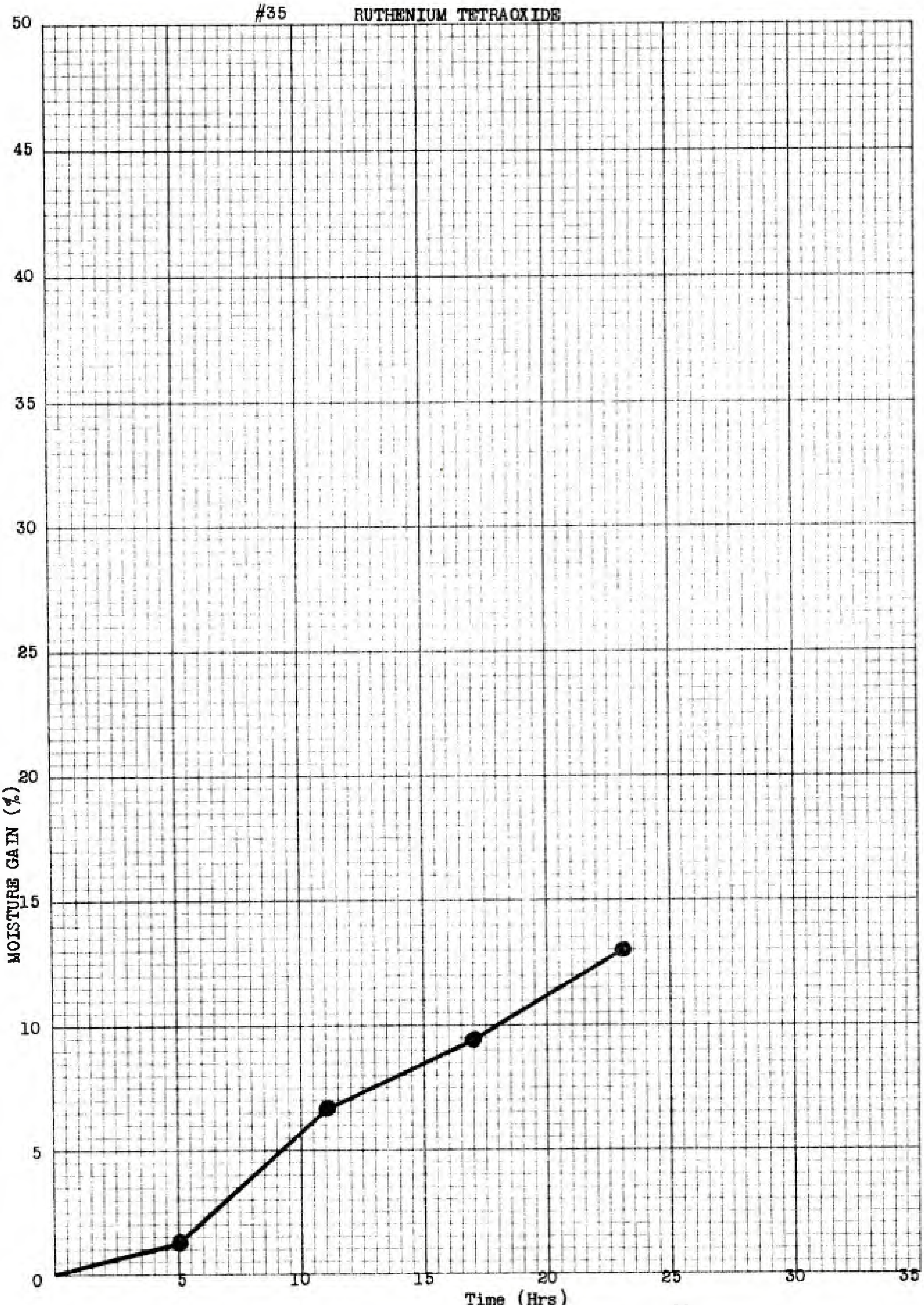


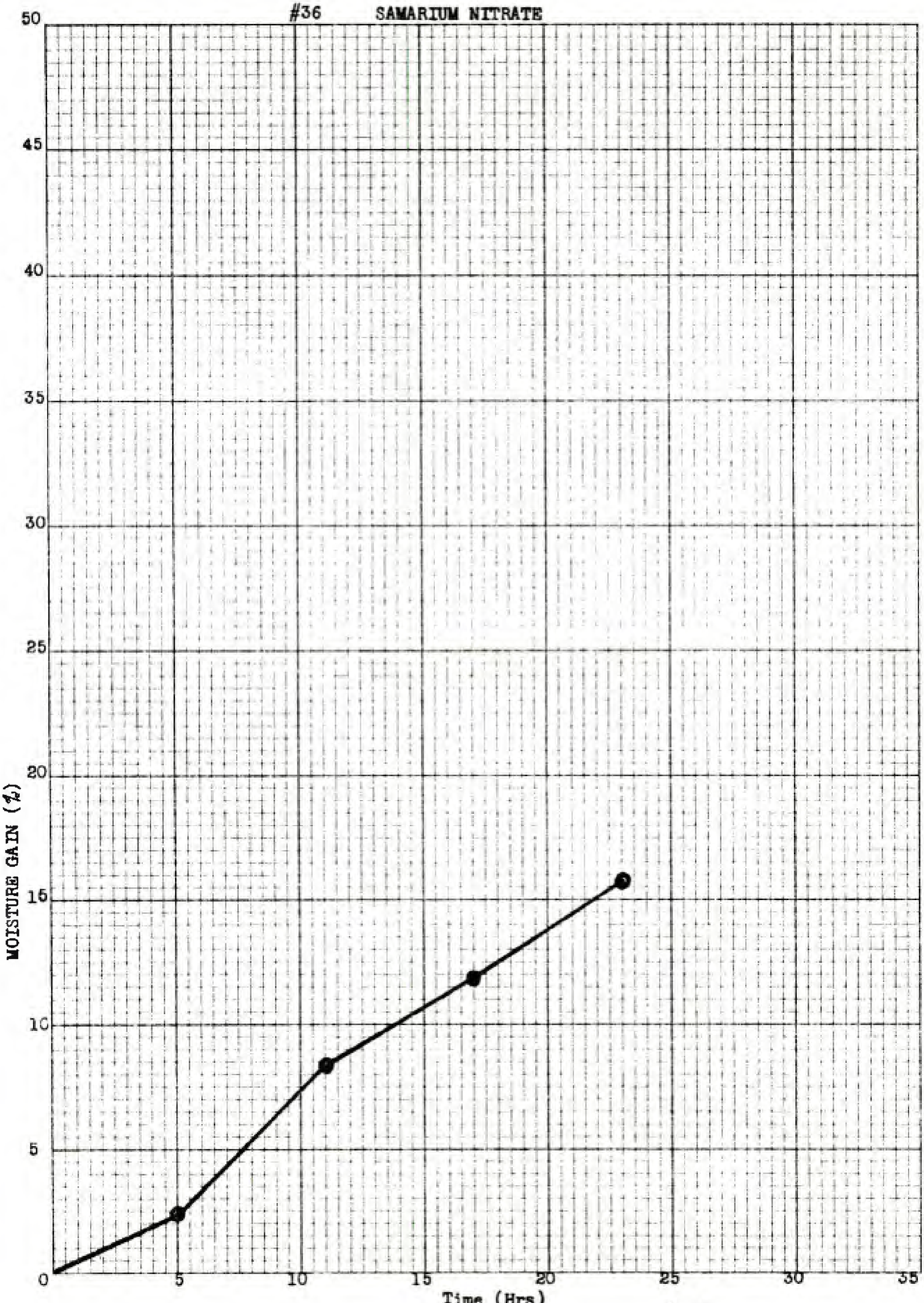

#32 RHENIUM TRICHLORIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



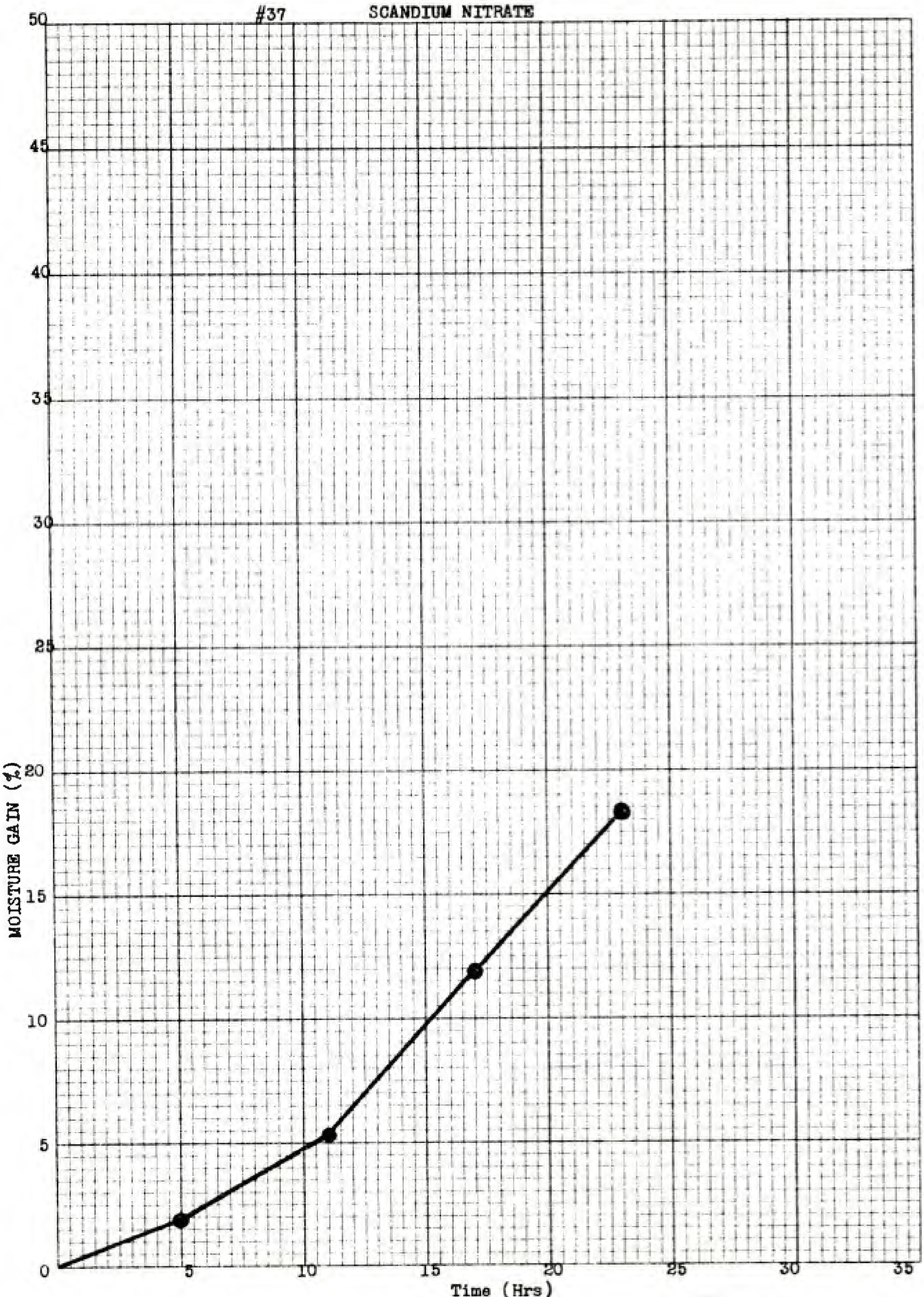
#33
RHODIUM NITRATE (Special Rerun)
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)

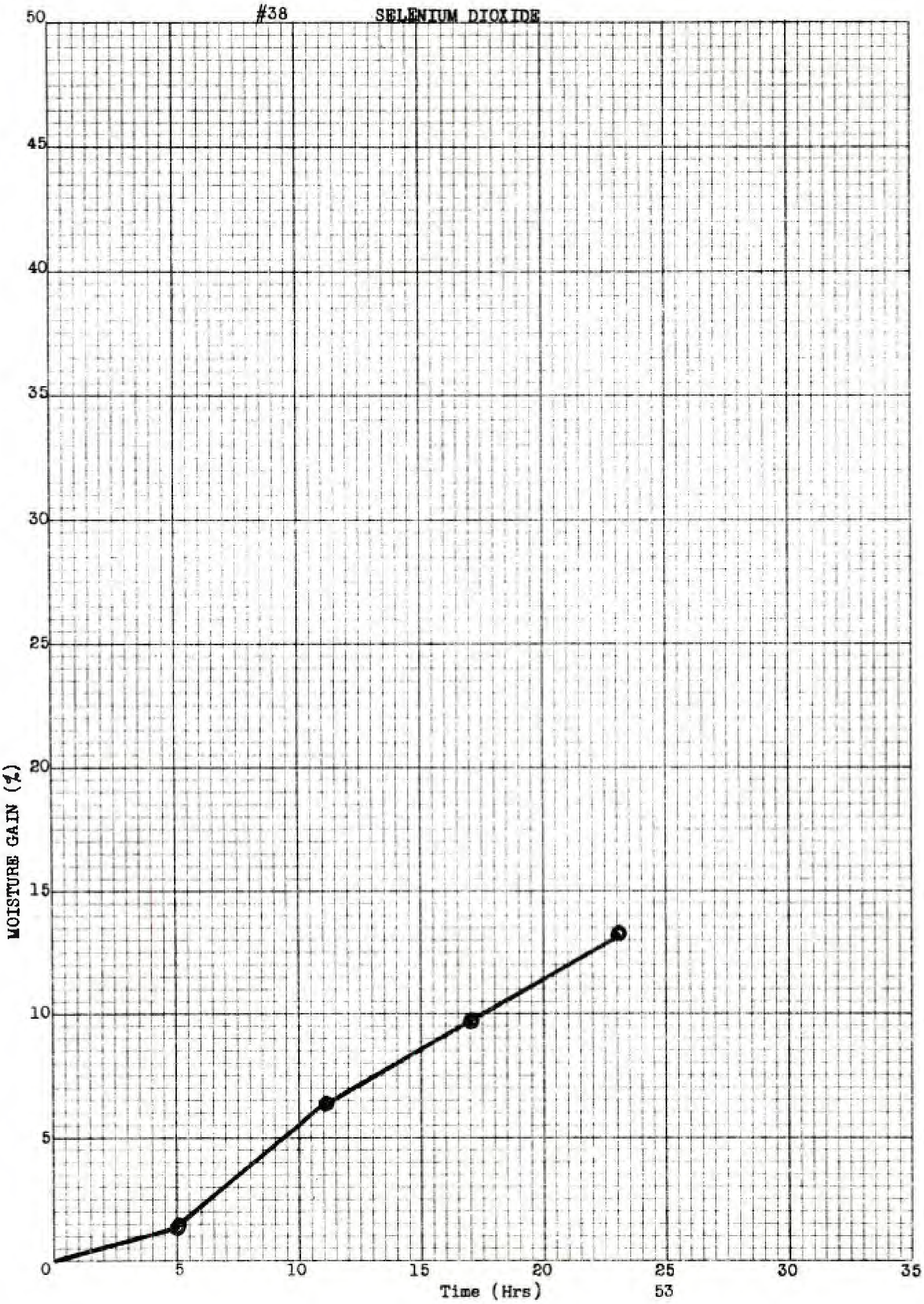

#34
RUBIDIUM NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

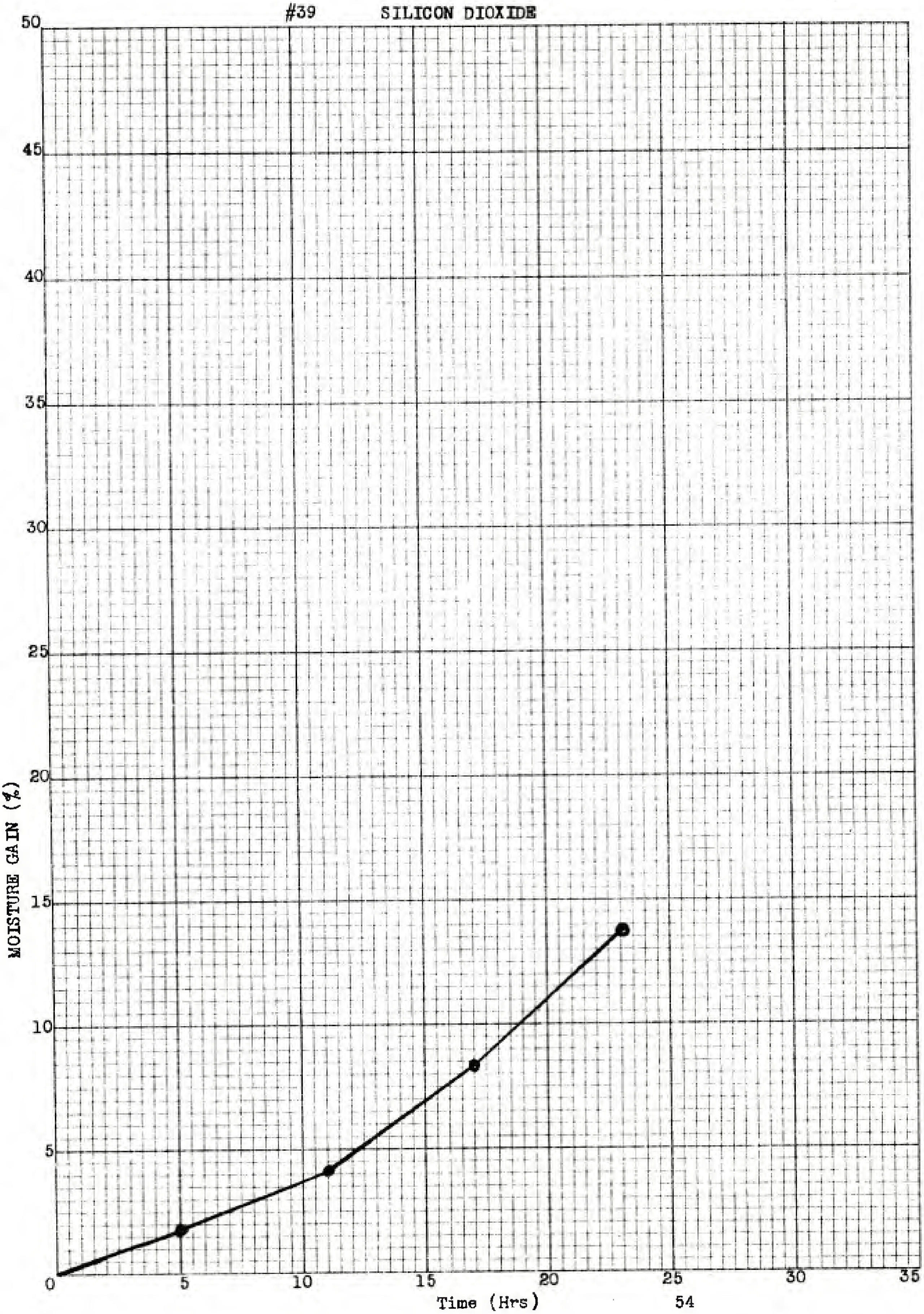

#35 RUTHENIUM TETRAOXIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35

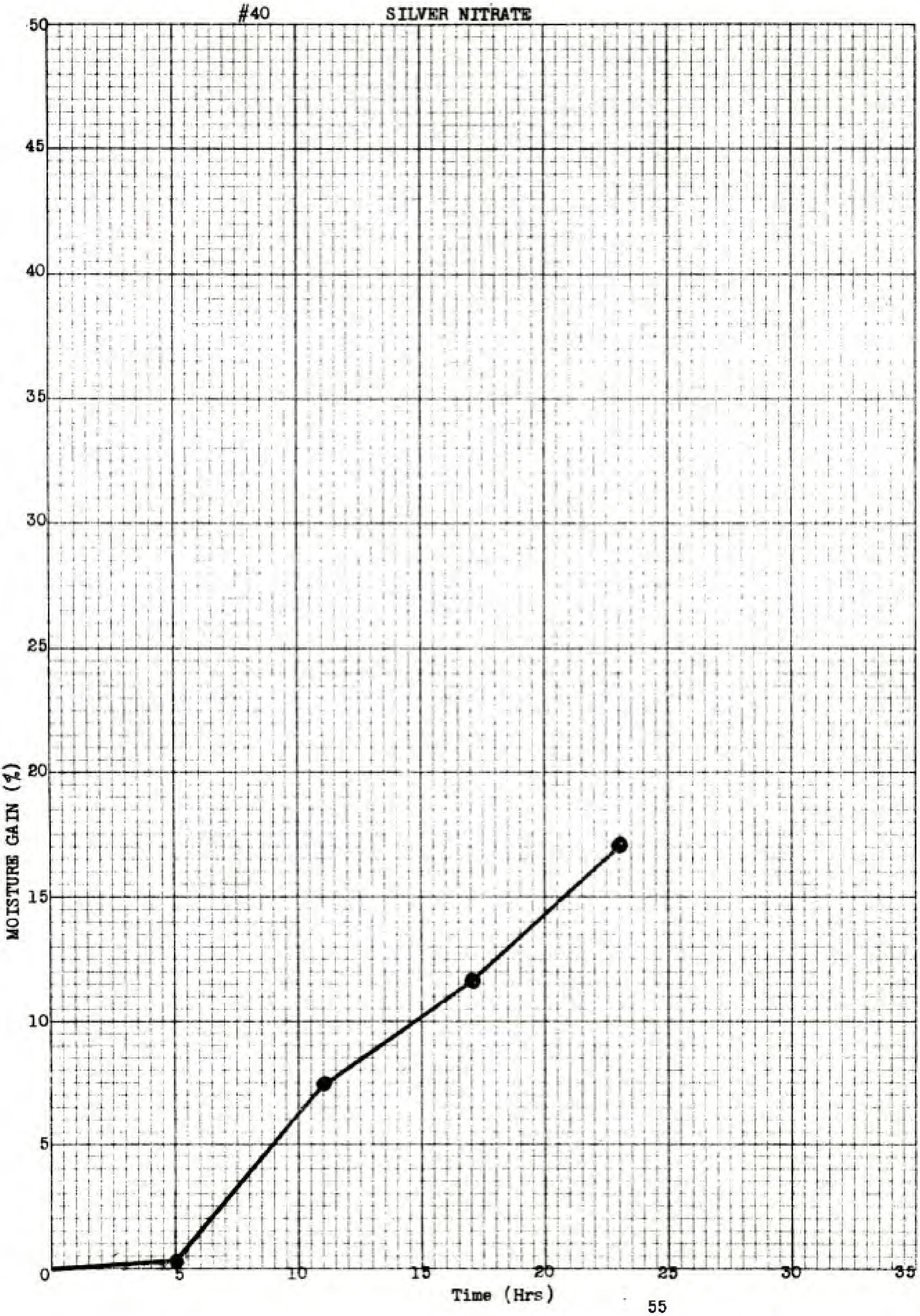


#36 SAMARIUM NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

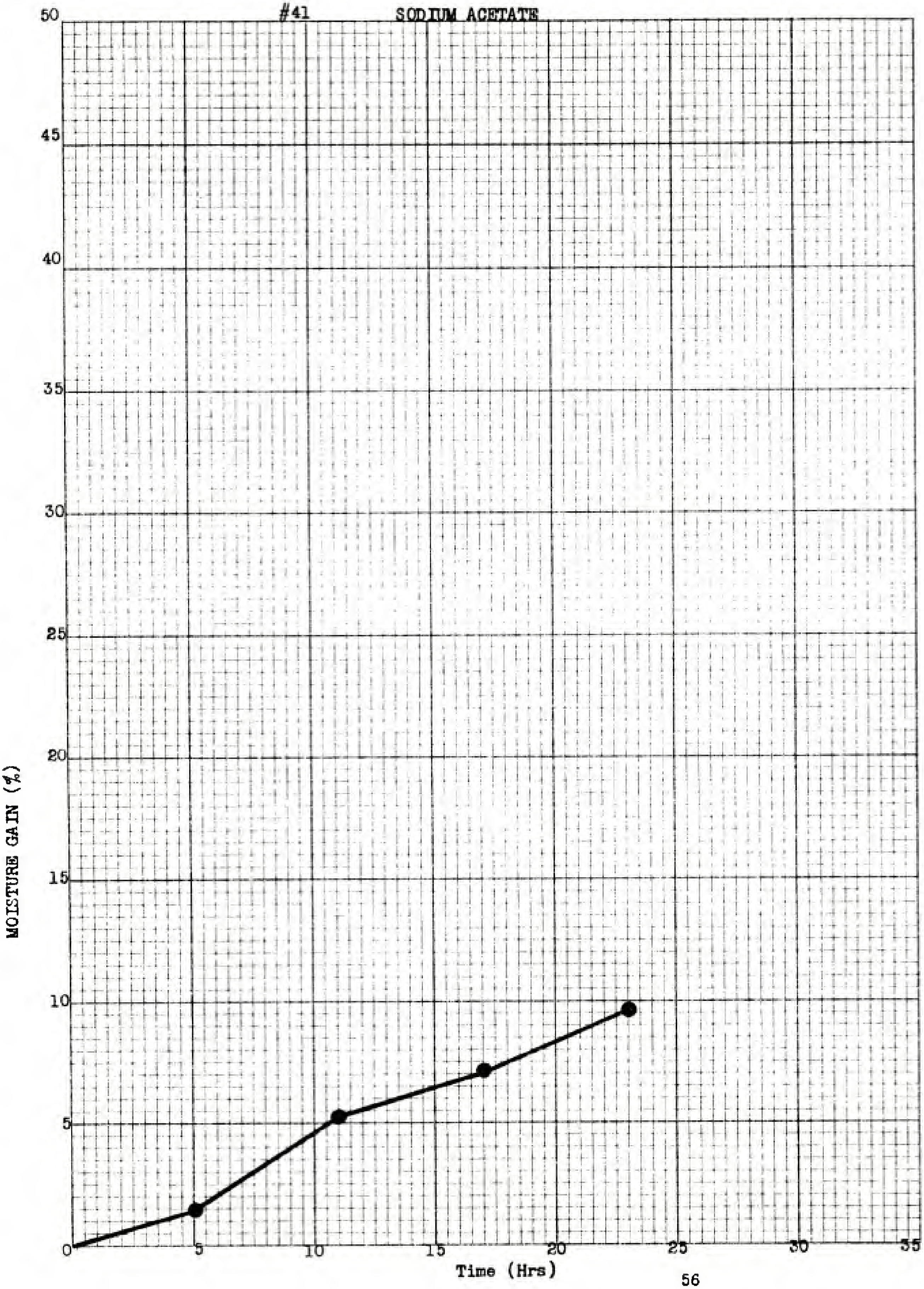

#37 SCANDIUM NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50


#38 SELENIUM DIOXIDE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs)
0
5
10
15
20
25
30
35


#39 SILICON DIOXIDE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs)
0
5
10
15
20
25
30
35

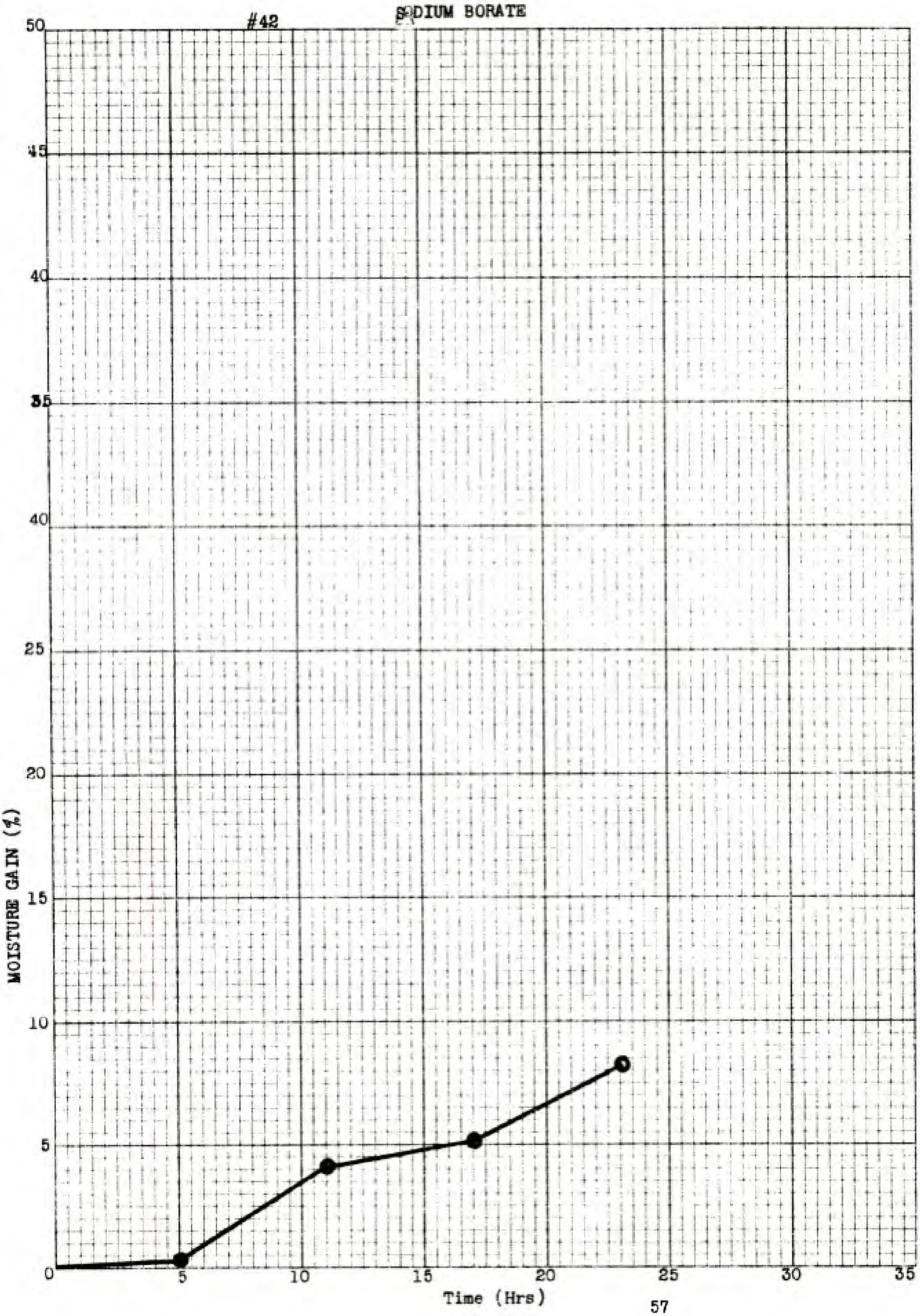


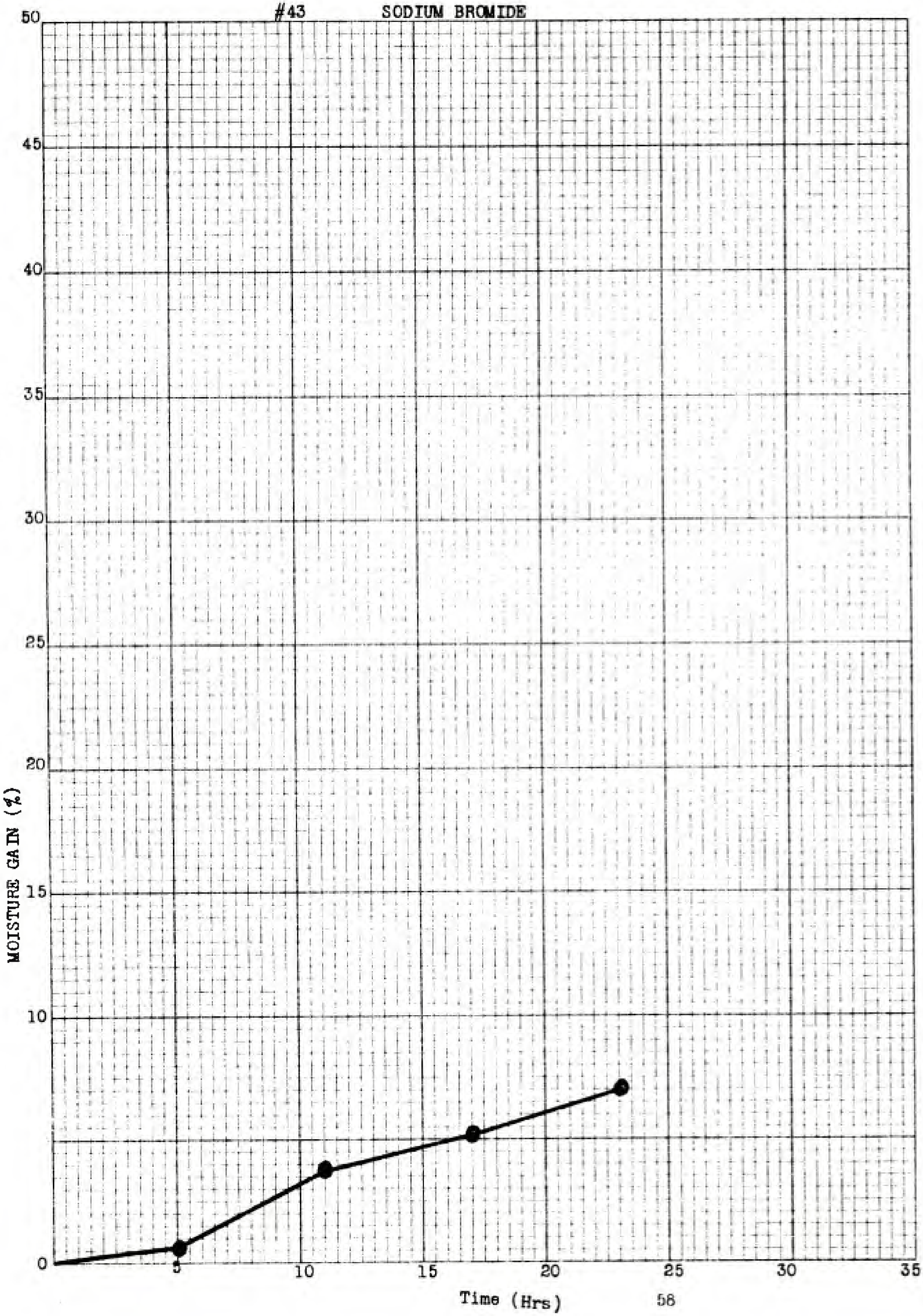
#40
SILVER NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

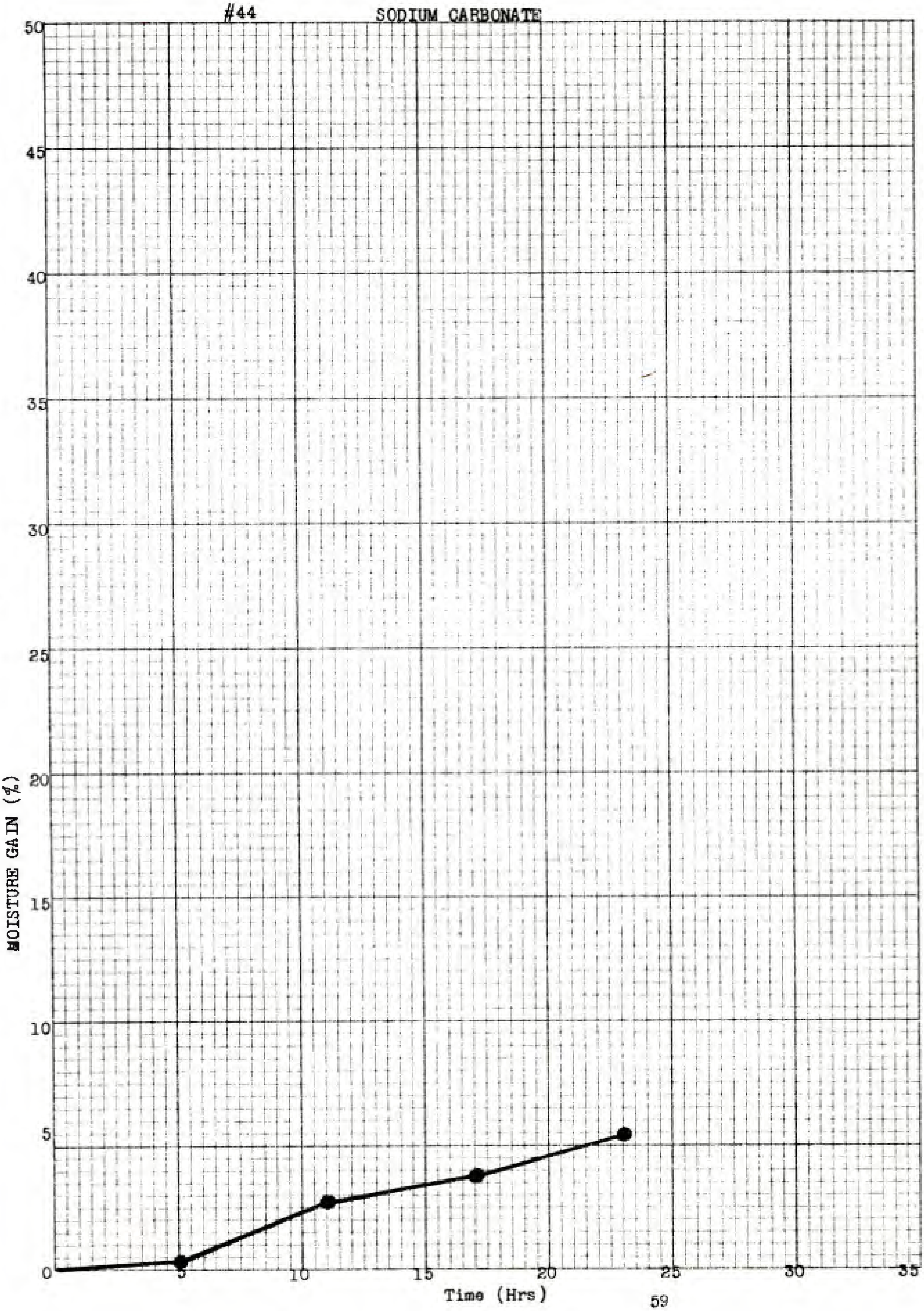


#41 SODIUM ACETATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

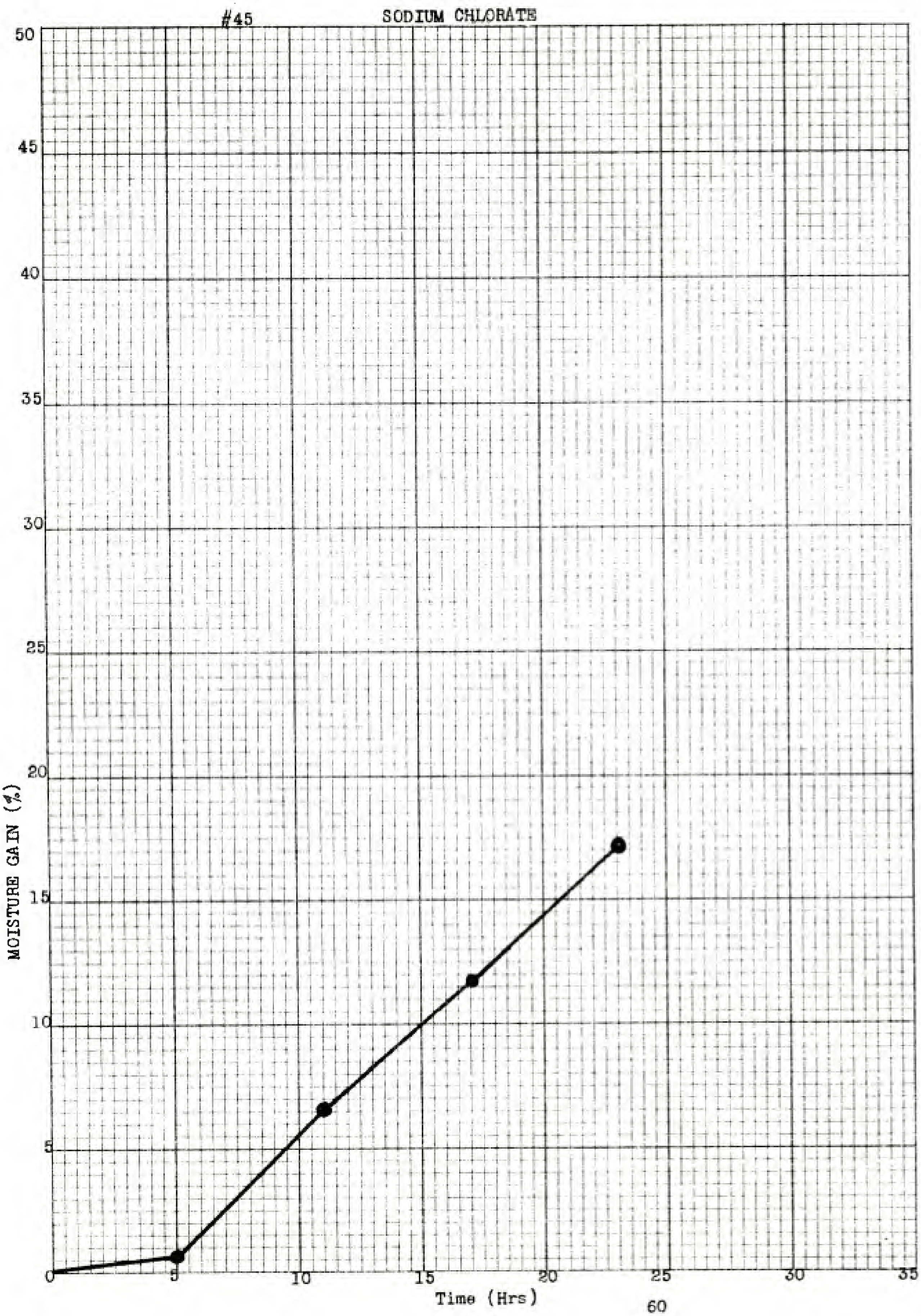
#42

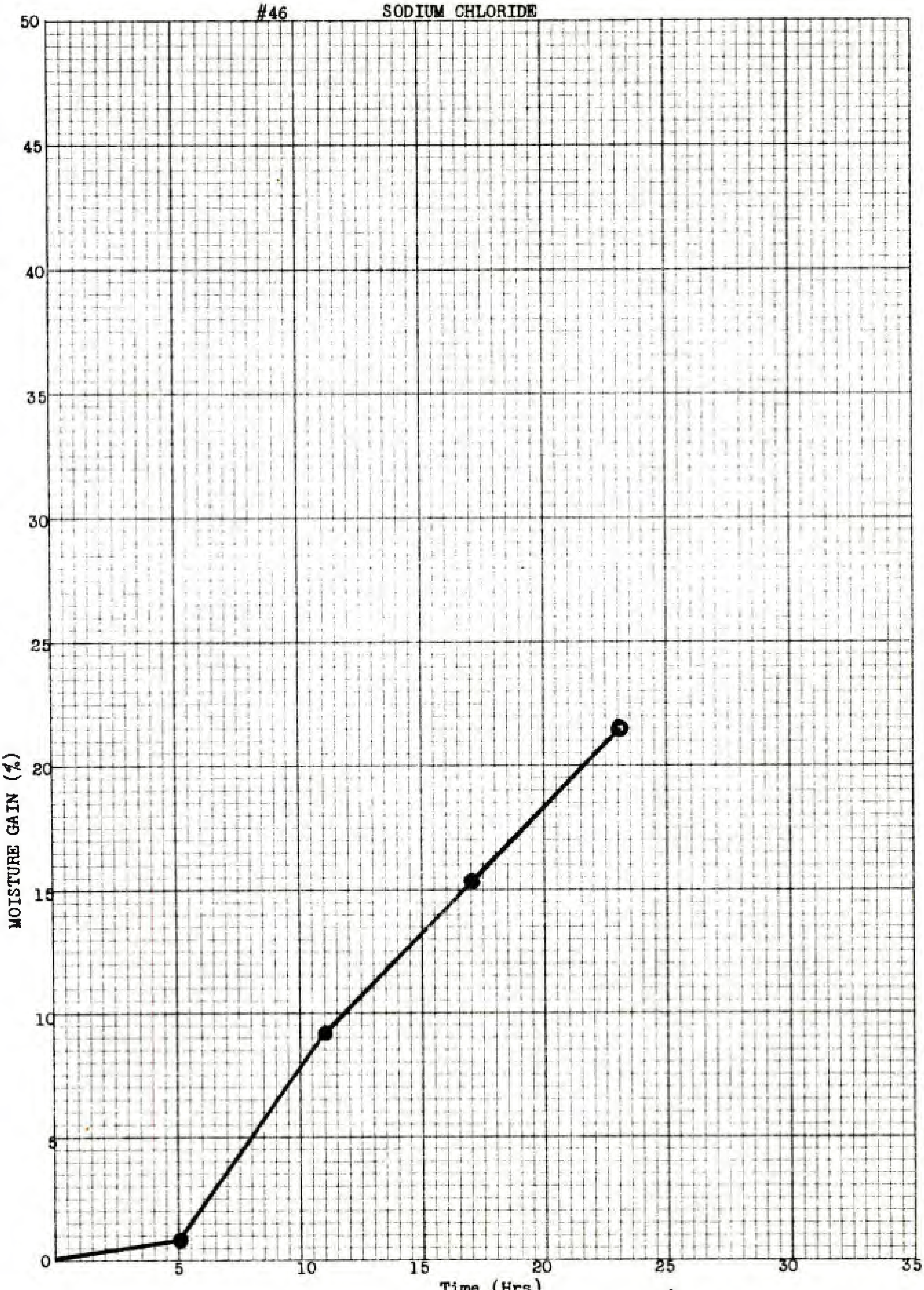

SODIUM BORATE
MOISTURE GAIN (%)
Time (Hrs)
50
45
40
35
40
25
20
15
10
5
0
5
10
15
20
25
30
35

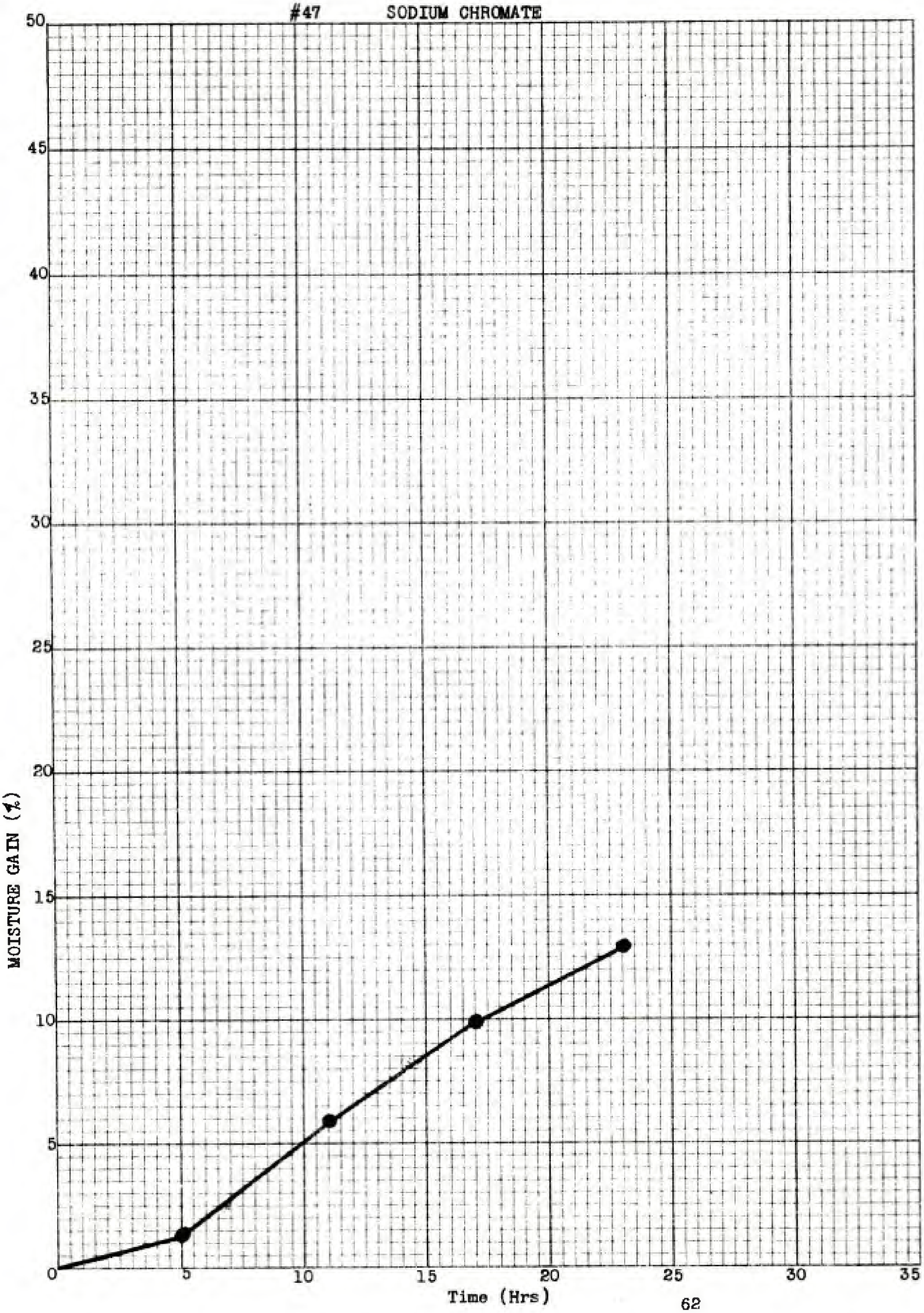

#43 SODIUM BROMIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



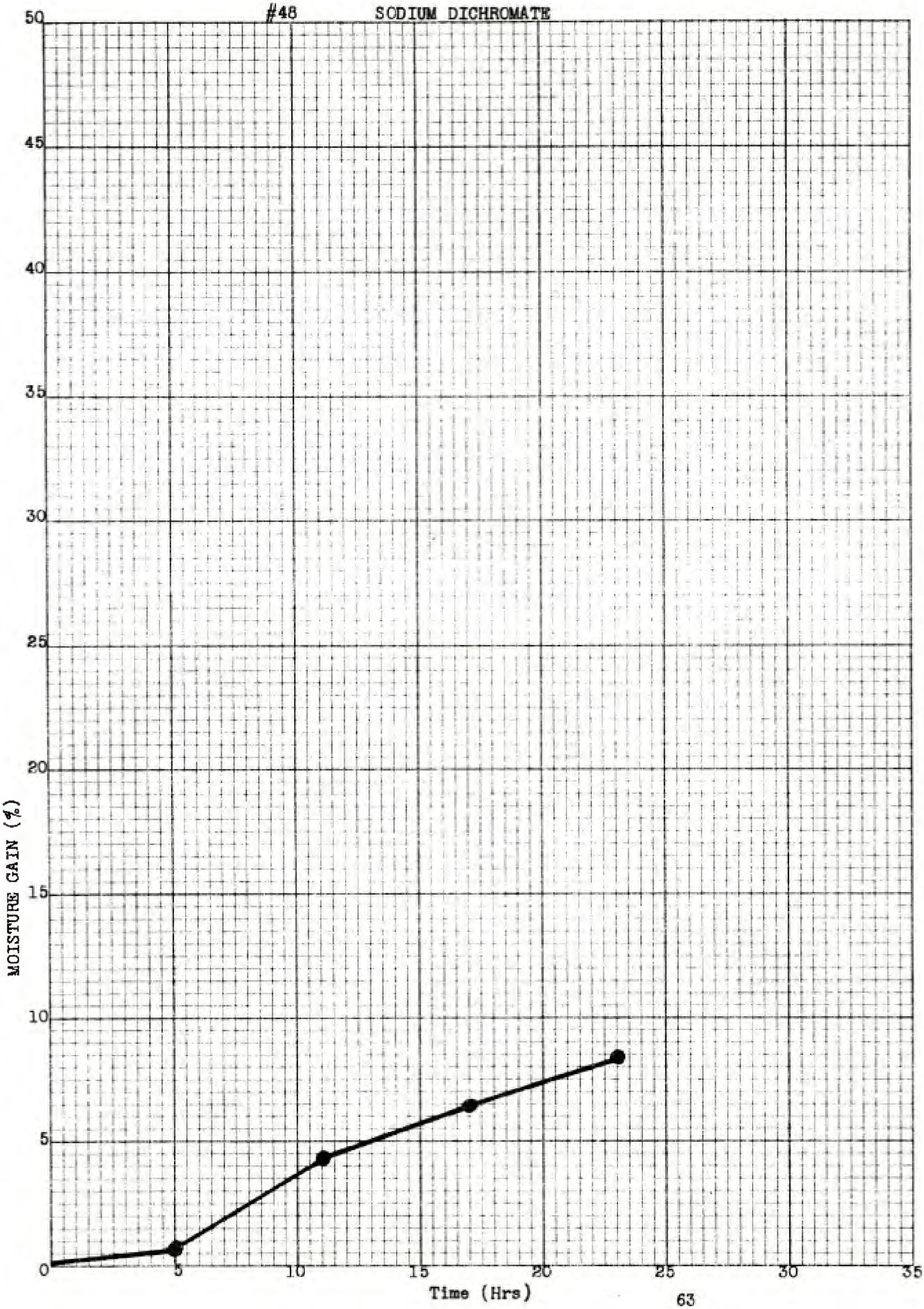
#44
SODIUM CARBONATE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs)


#45
SODIUM CHLORATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

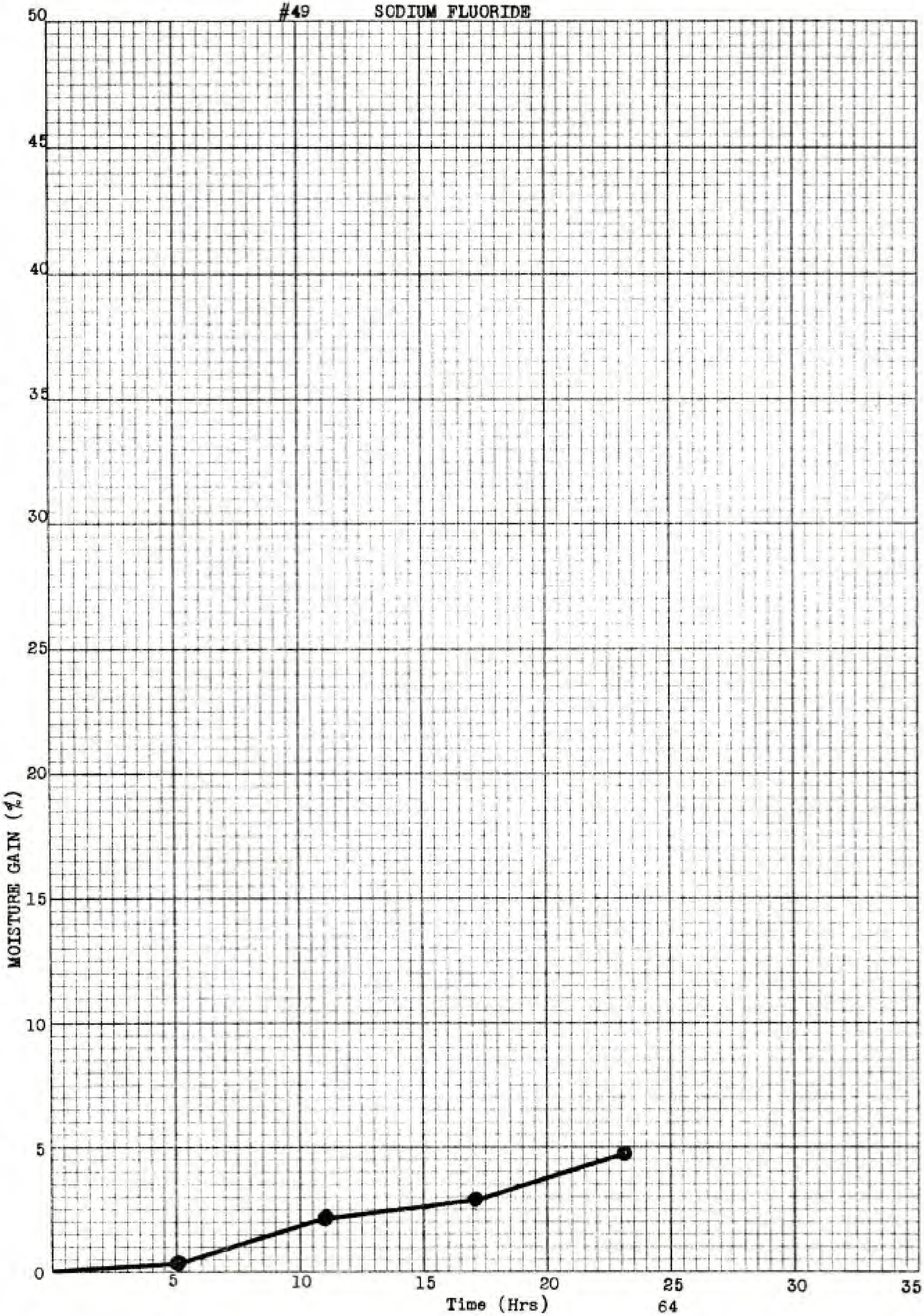

#46 SODIUM CHLORIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
30
35

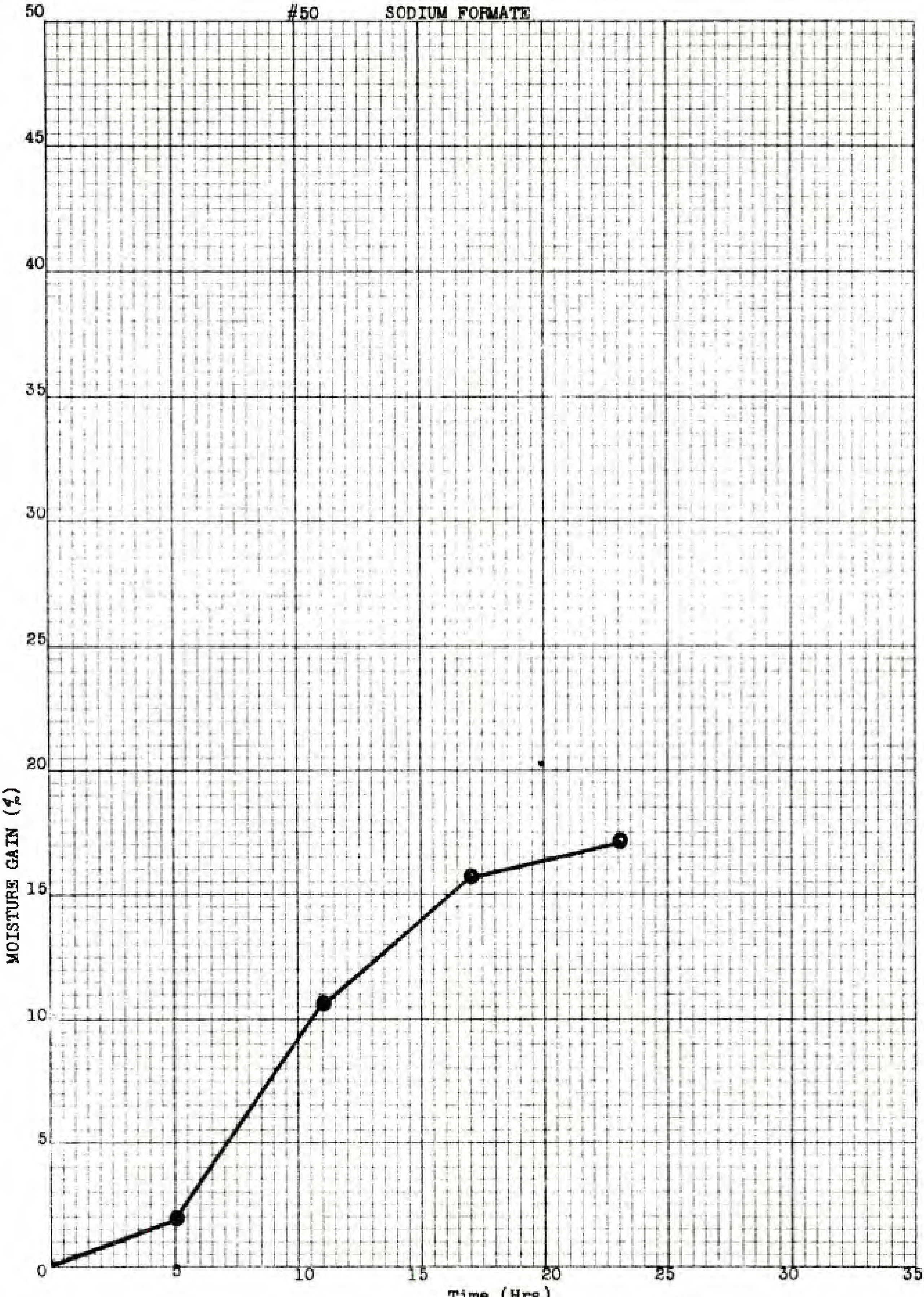


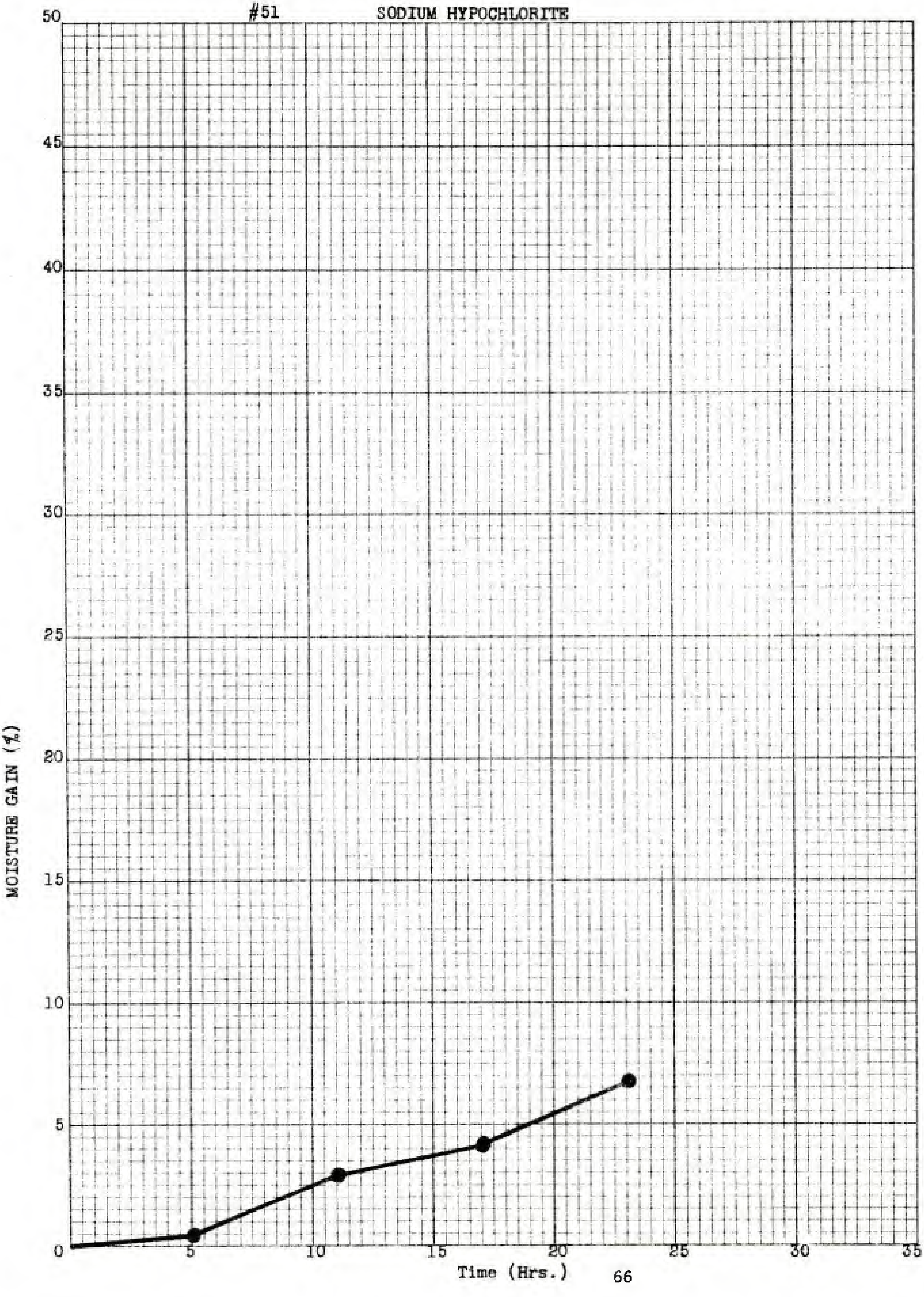
#47 SODIUM CHROMATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



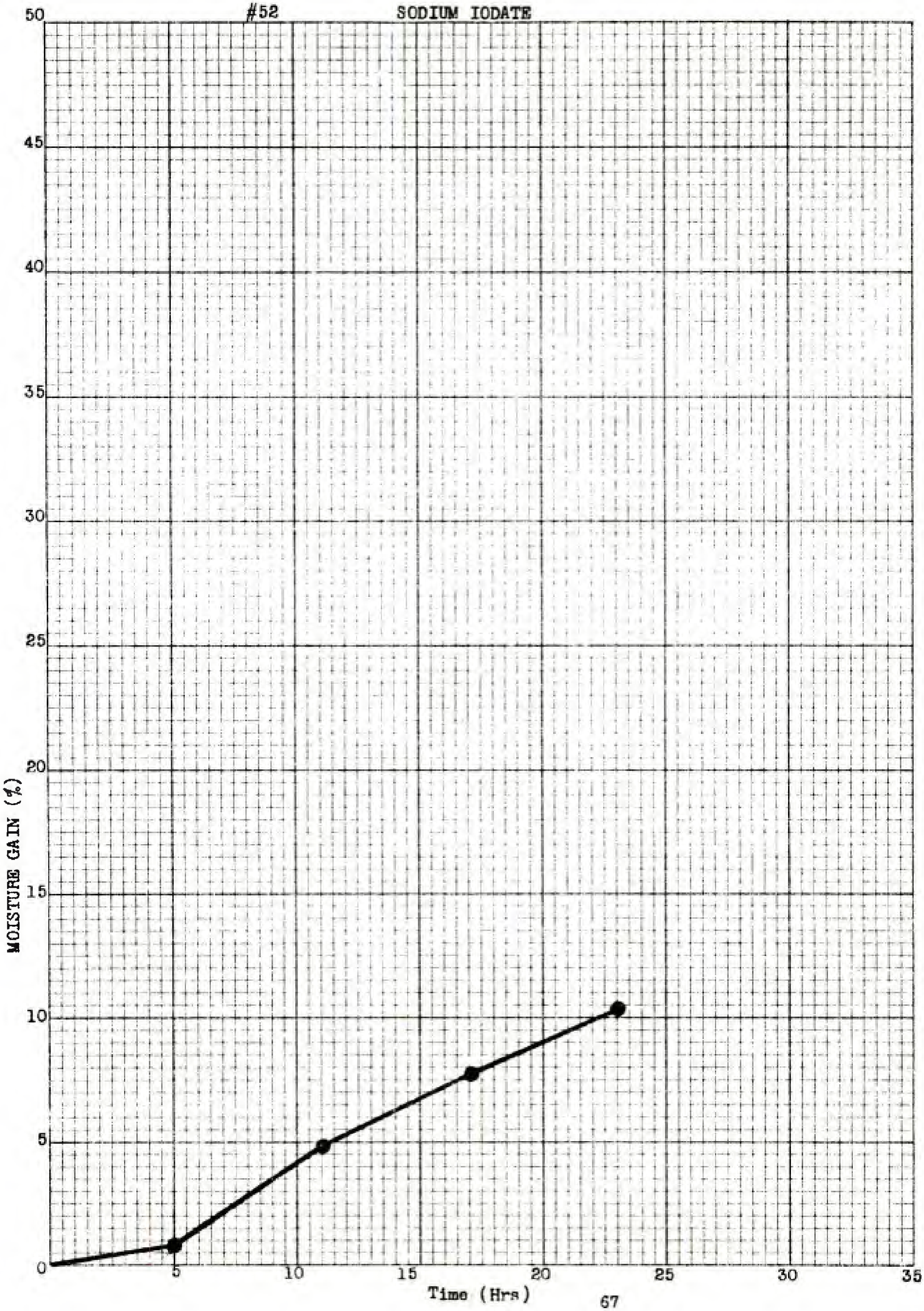
#48
SODIUM DICHROMATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

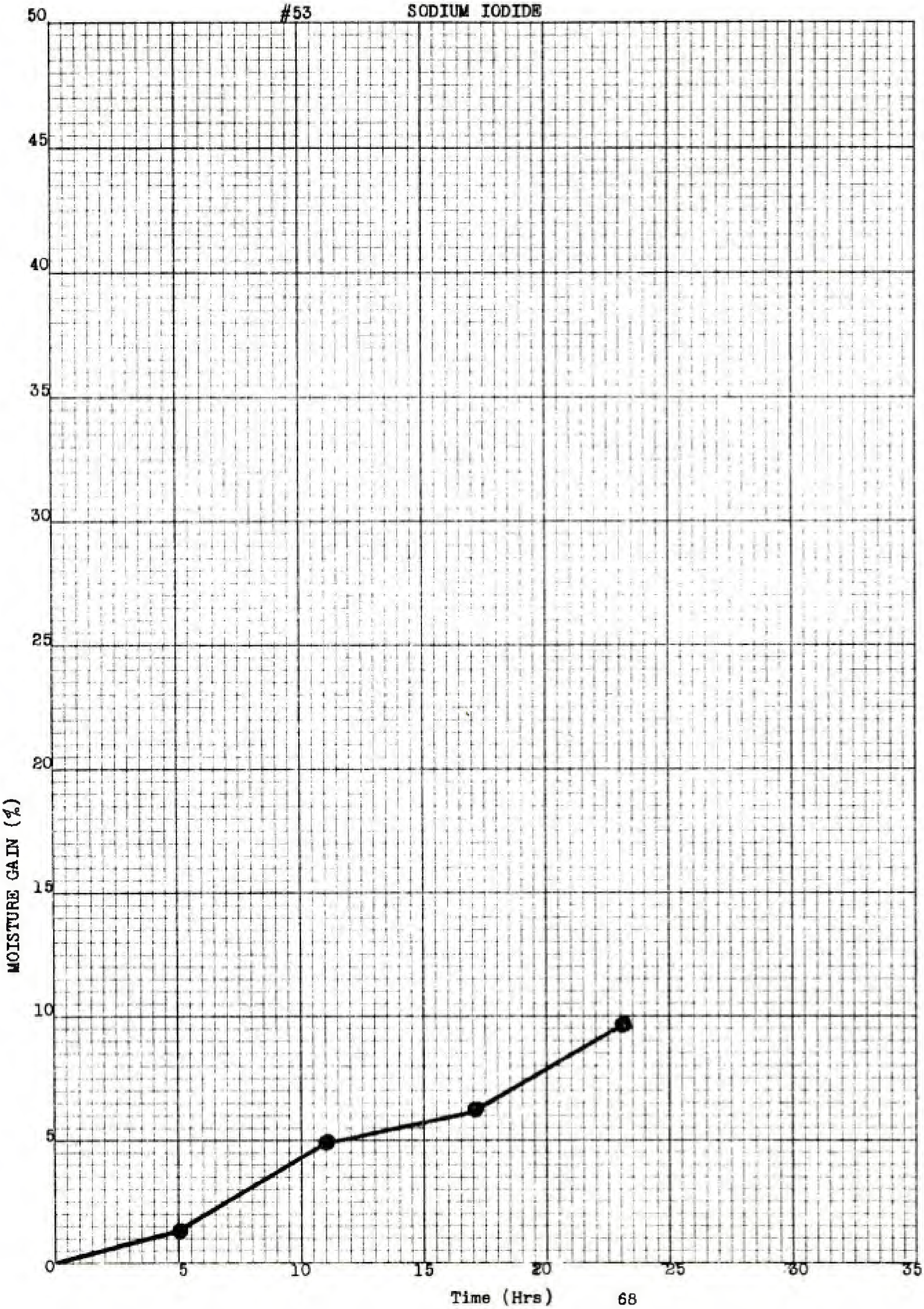

#49 SODIUM FLUORIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35

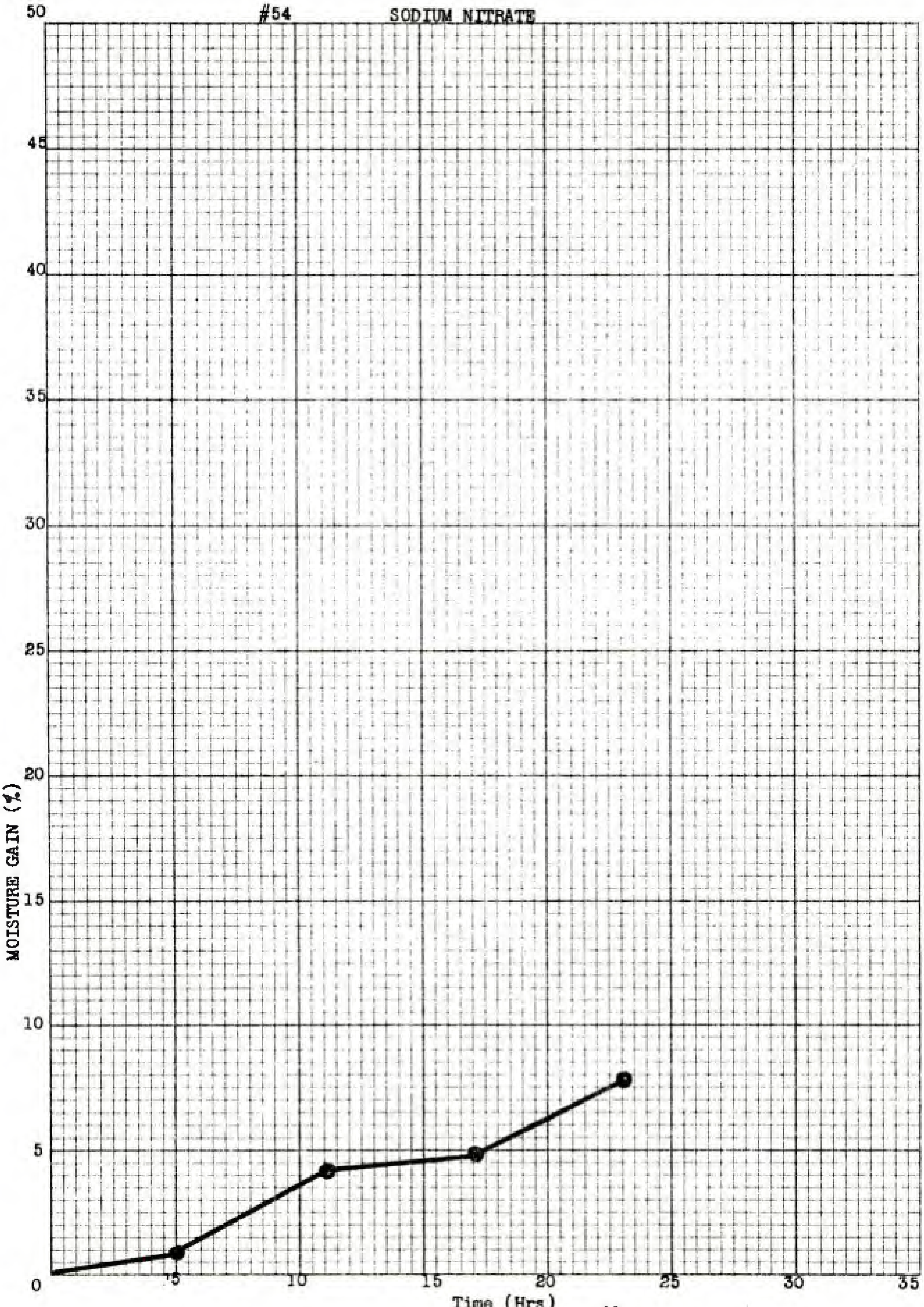

#50 SODIUM FORMATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
30
35



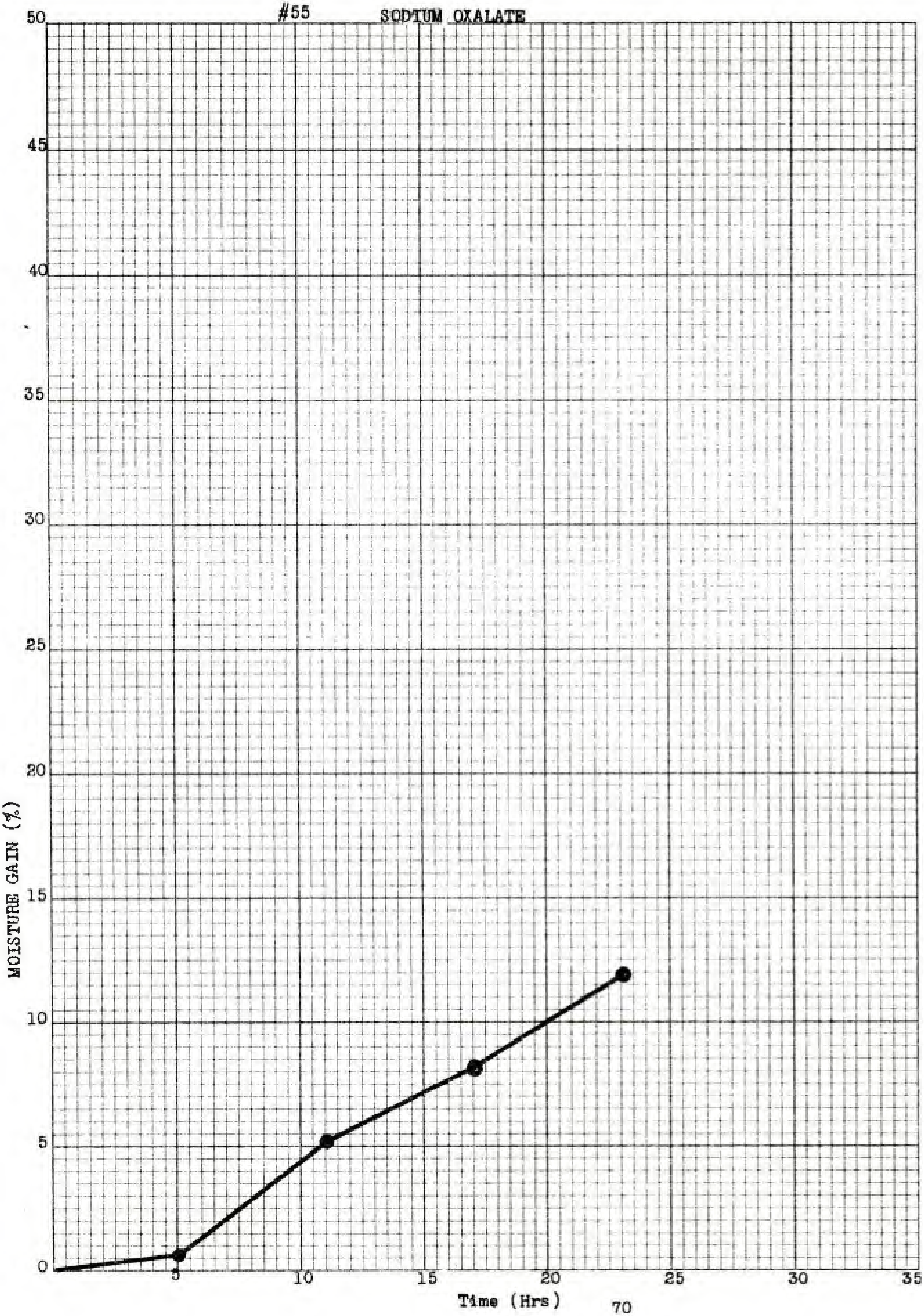
#51 SODIUM HYPOCHLORITE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs.)

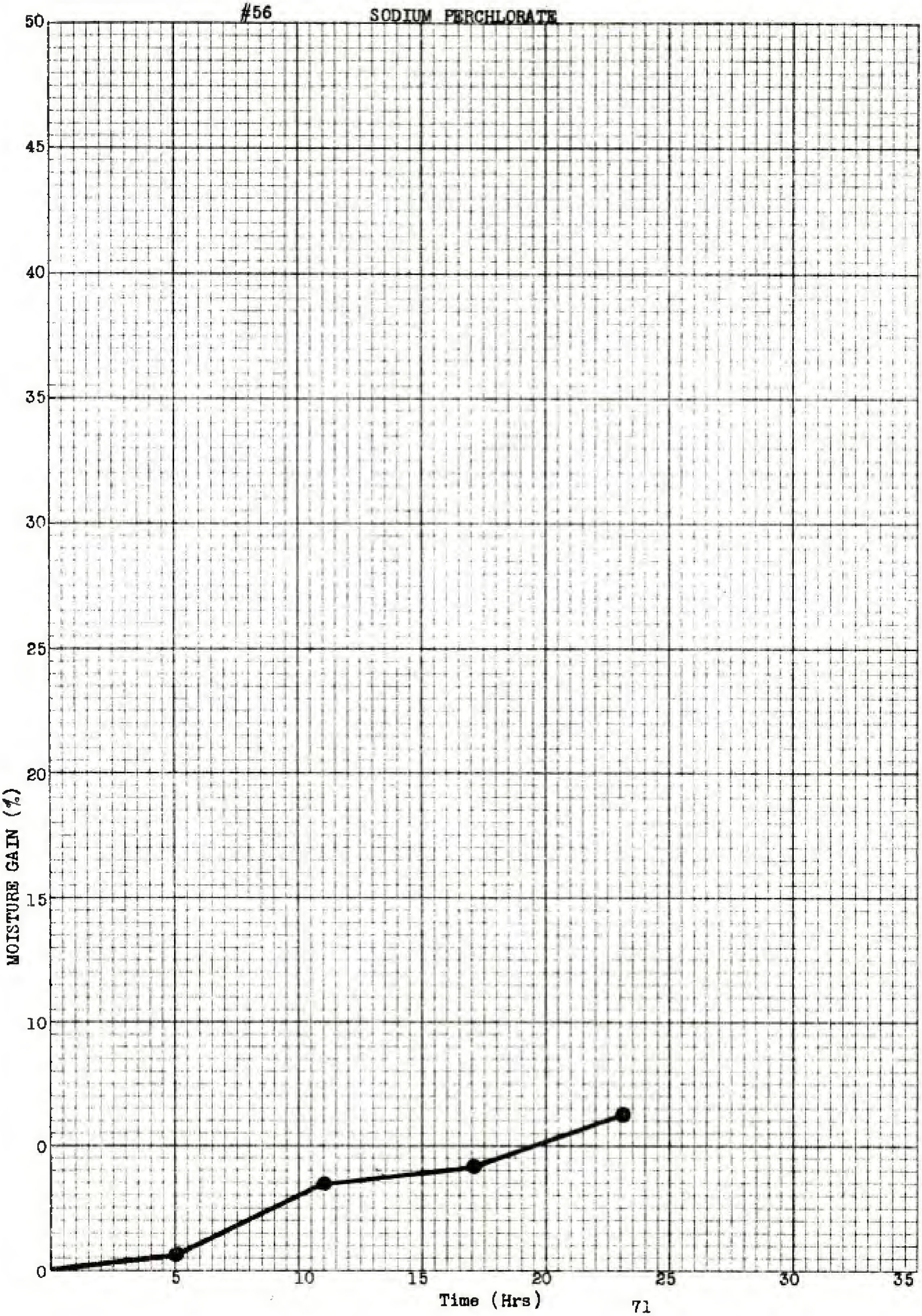

#52
SODIUM IODATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

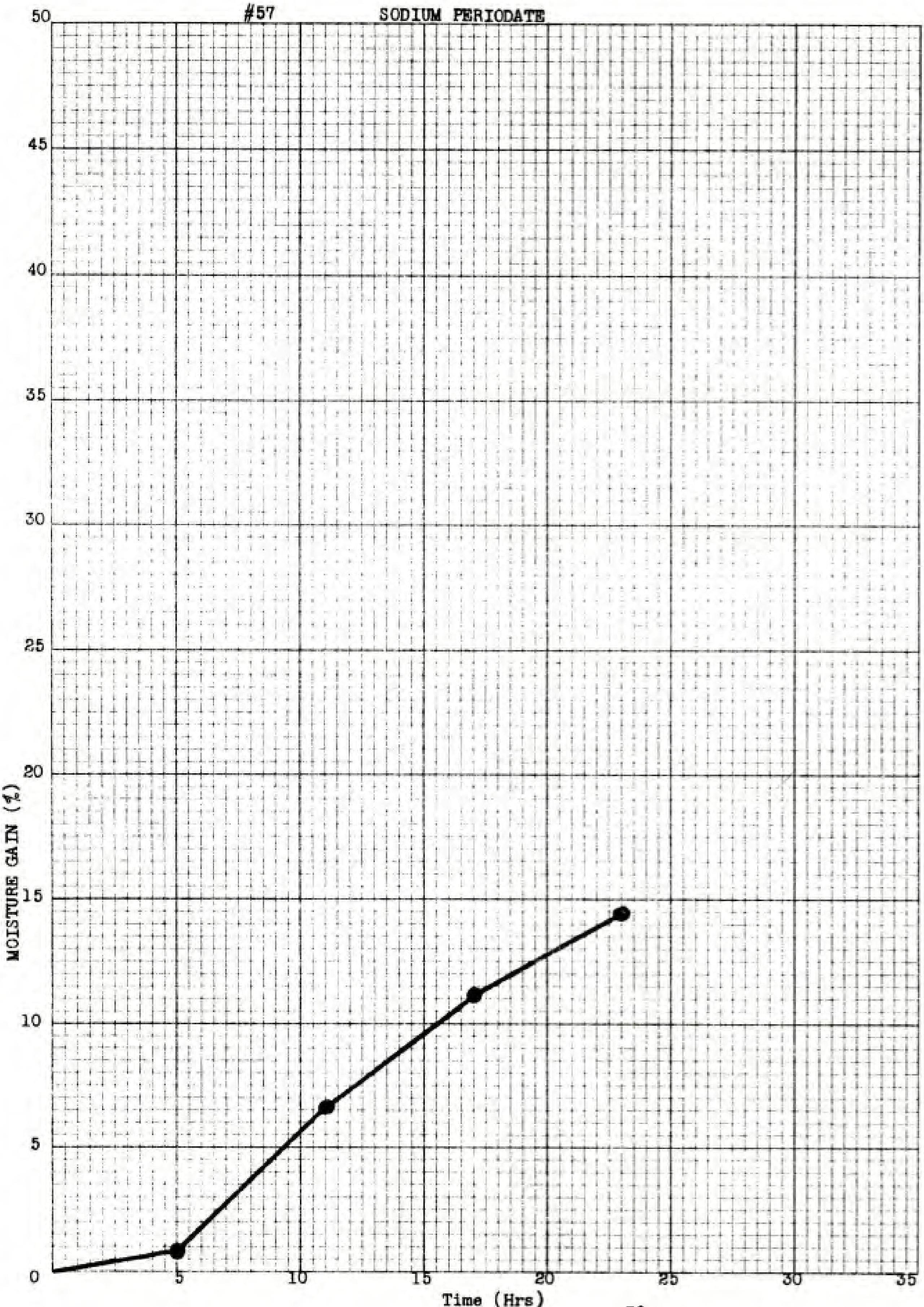

#53
SODIUM IODIDE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)



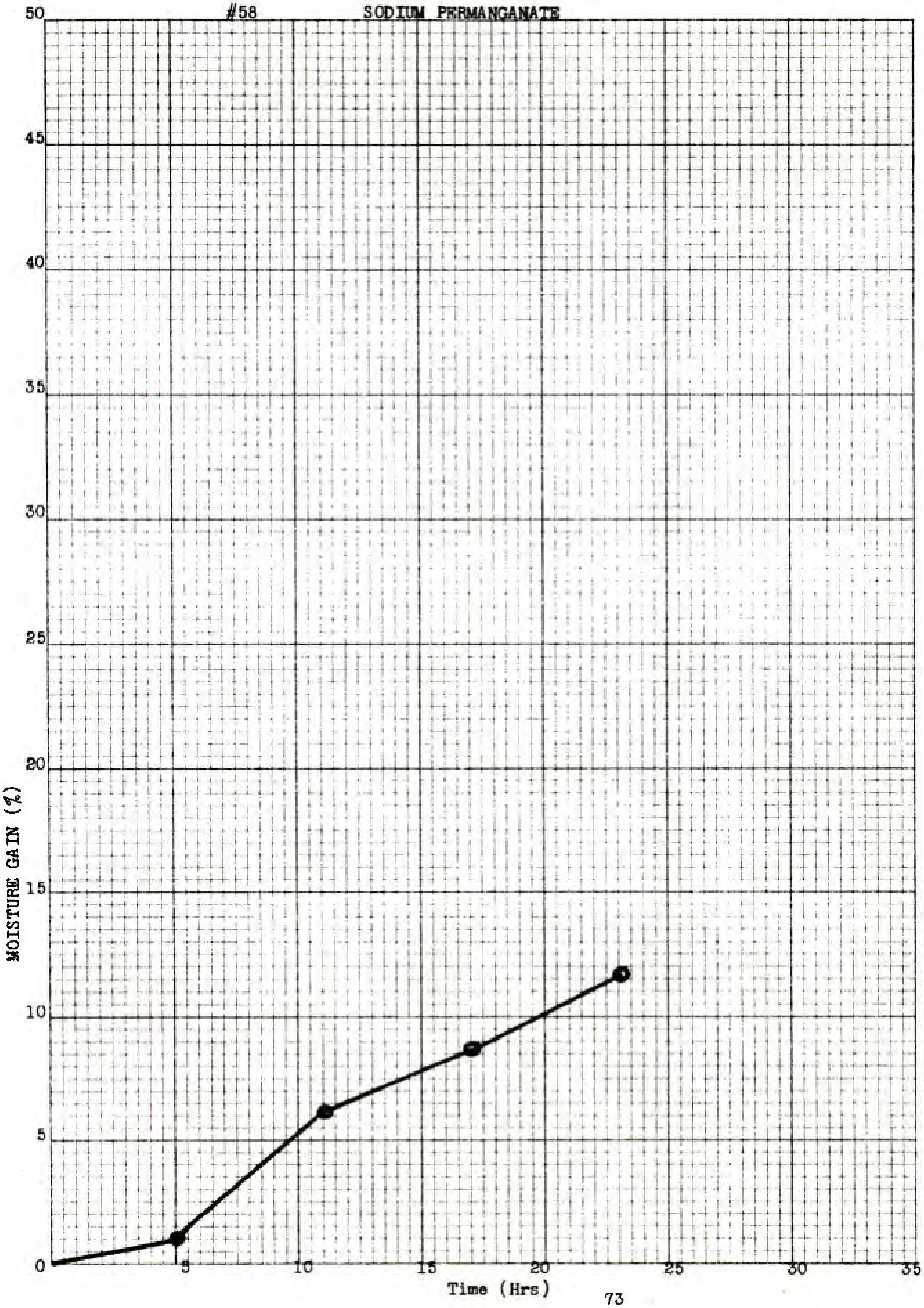
#54
SODIUM NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

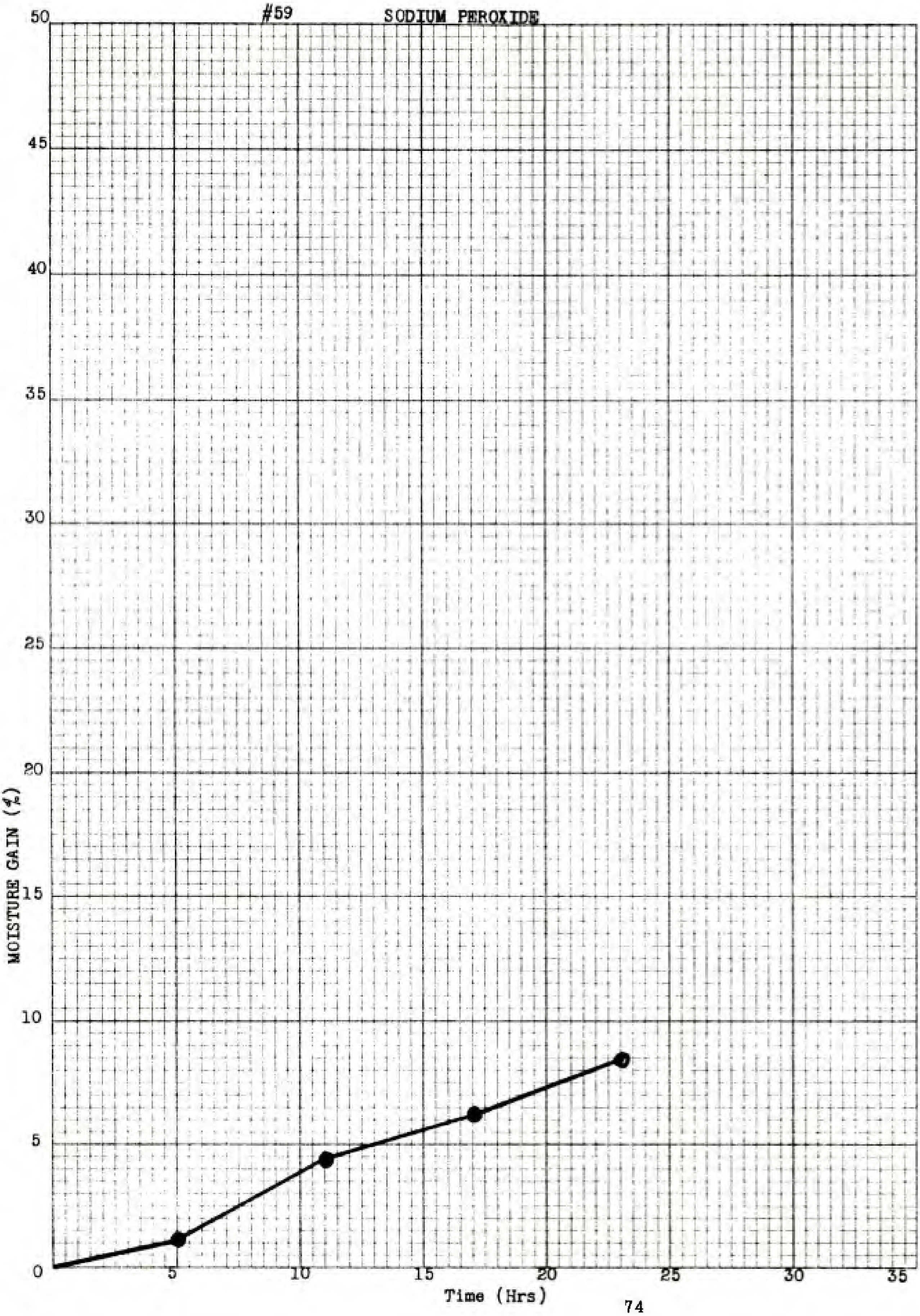

#55 SODIUM OXALATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50


#56
SODIUM PERCHLORATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

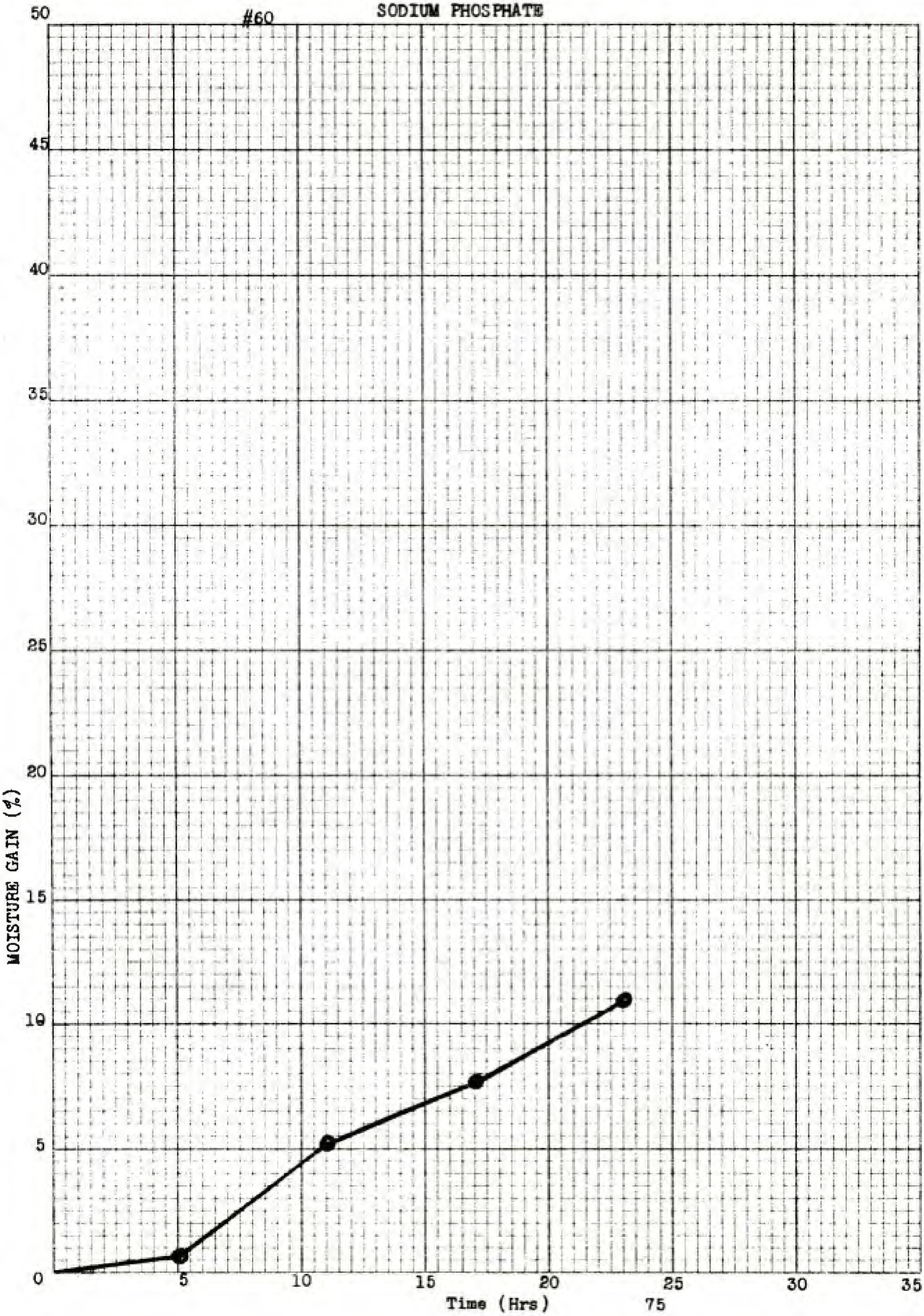

#57
SODIUM PERIODATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35

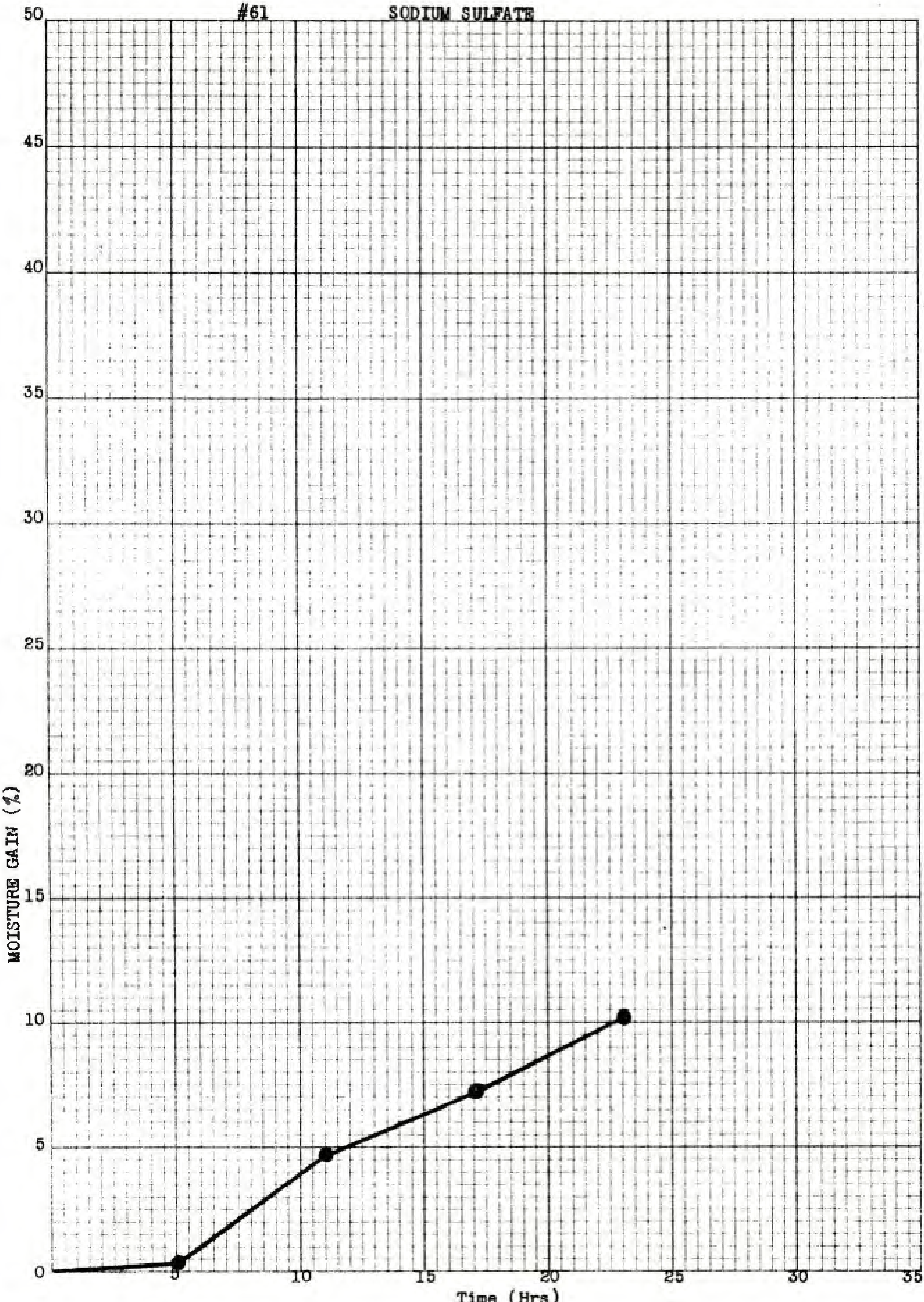
#58 SODIUM PERMANGANATE



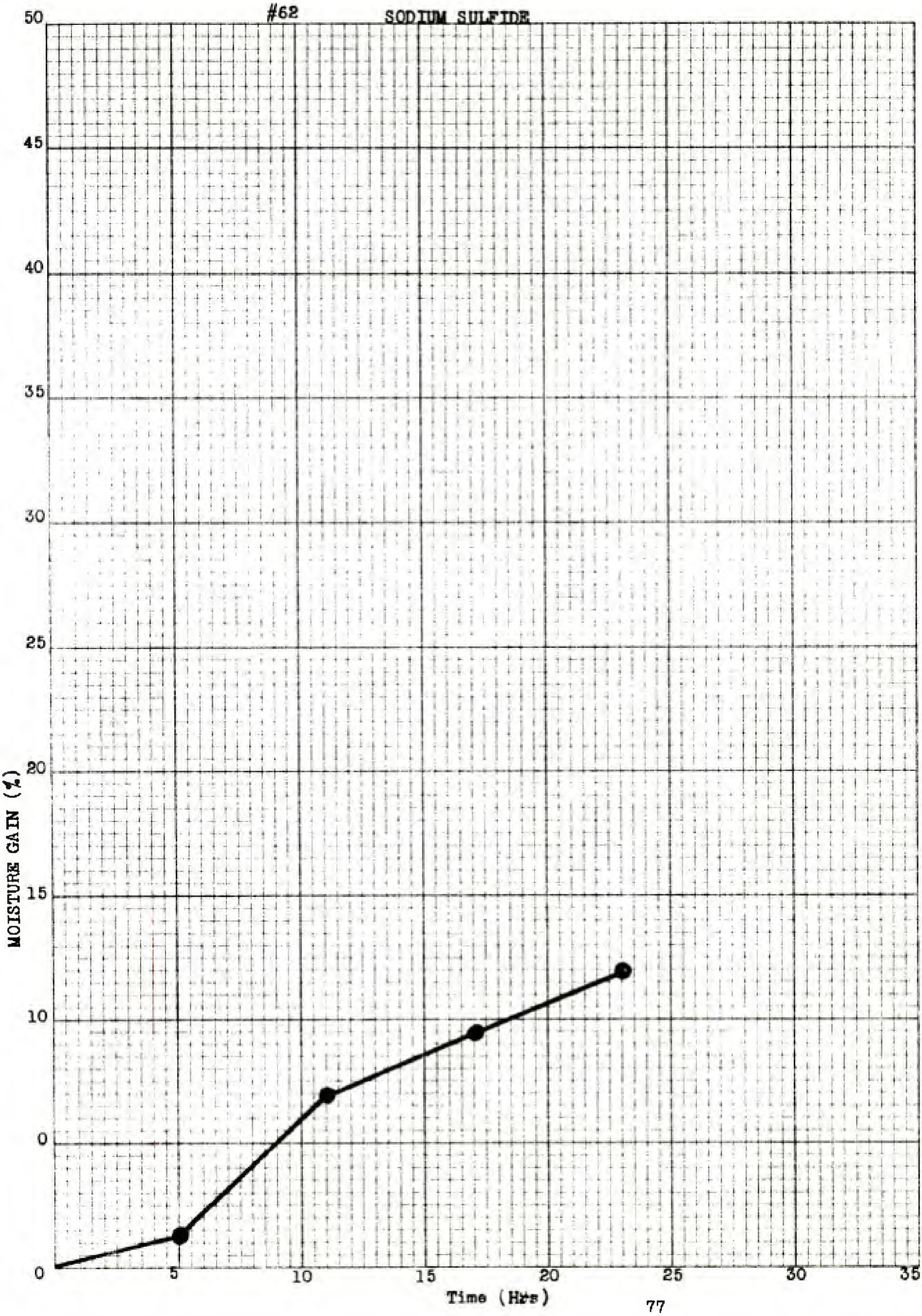


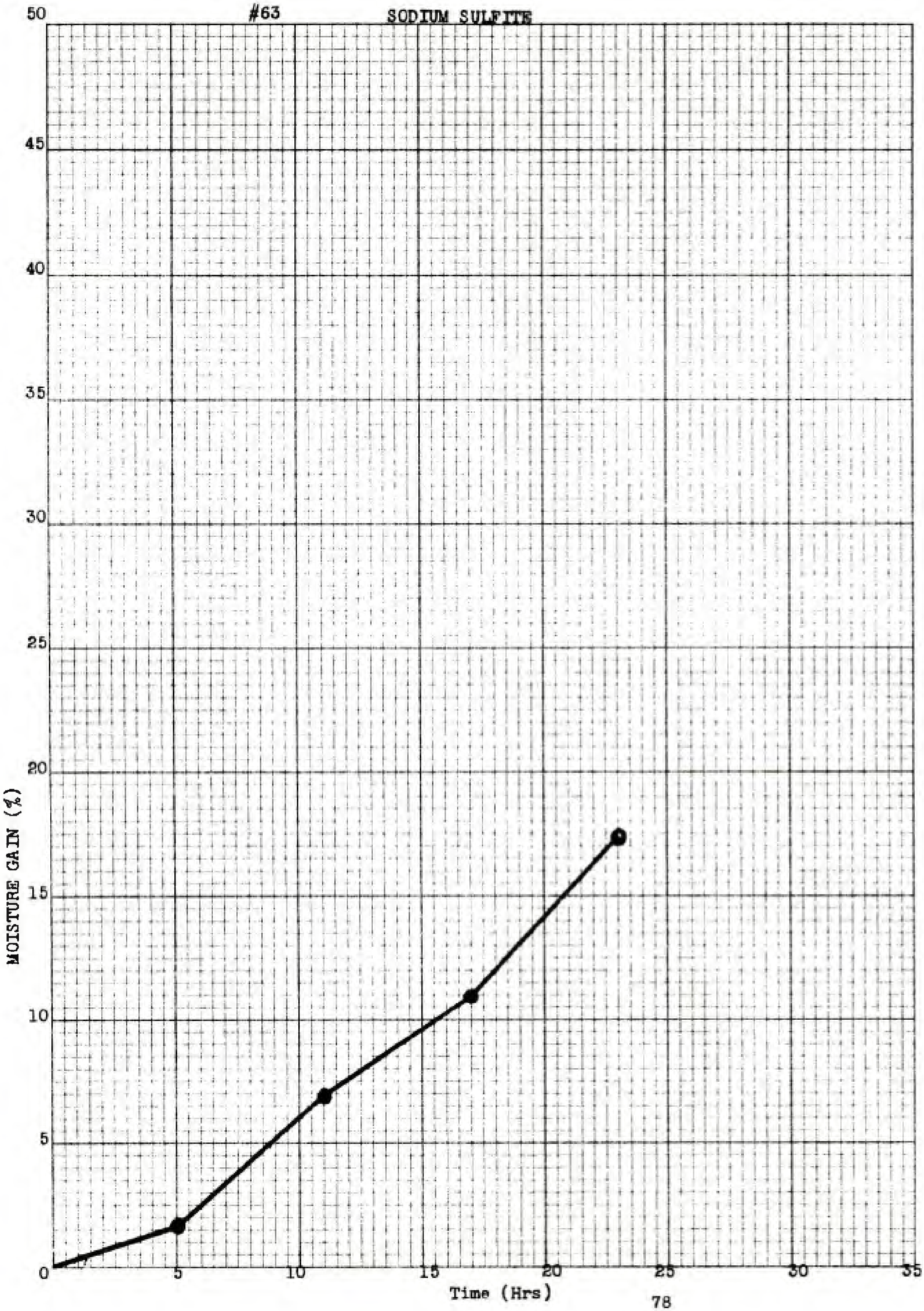
#59
SODIUM PEROXIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

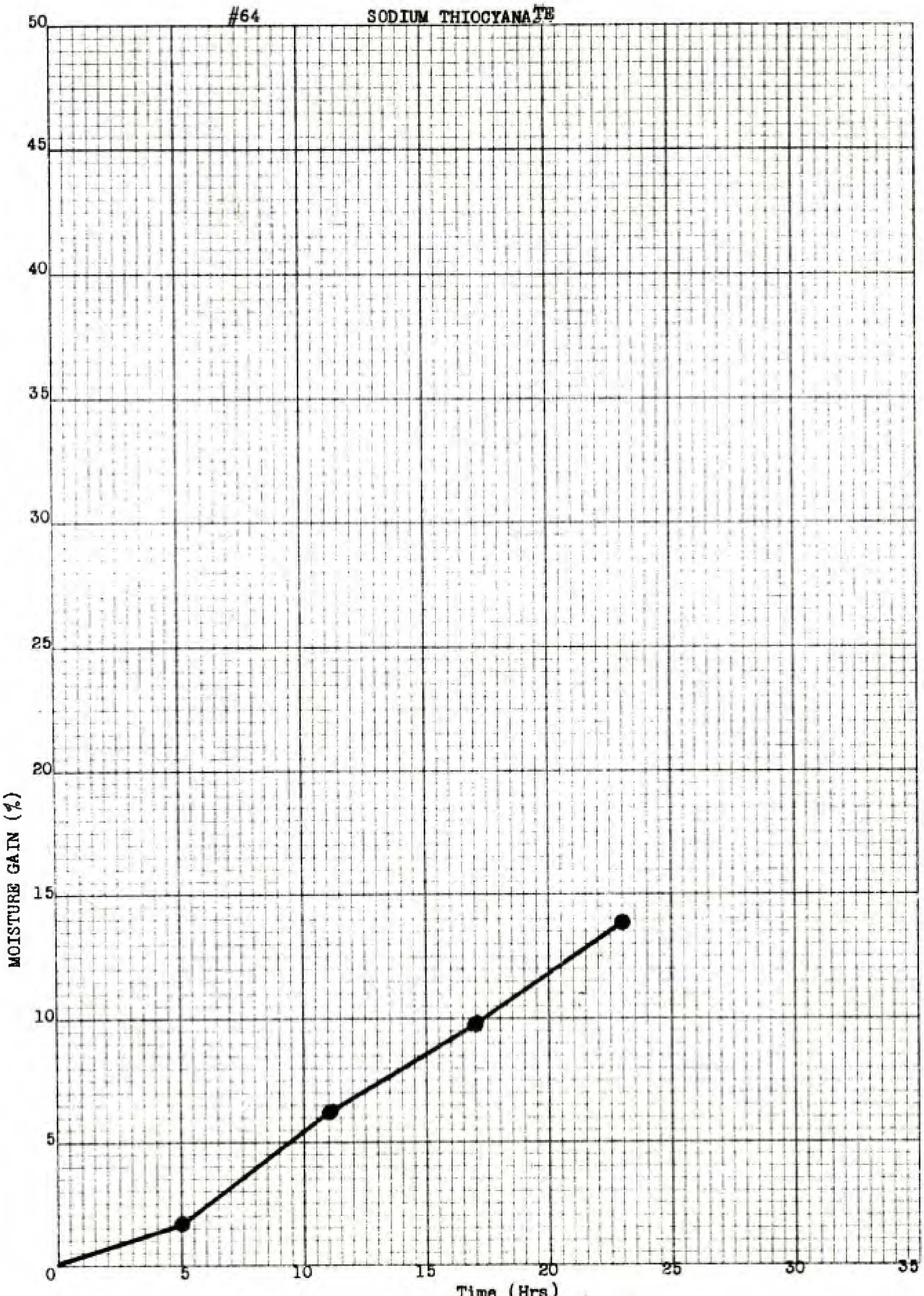

SODIUM PHOSPHATE
#60
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)

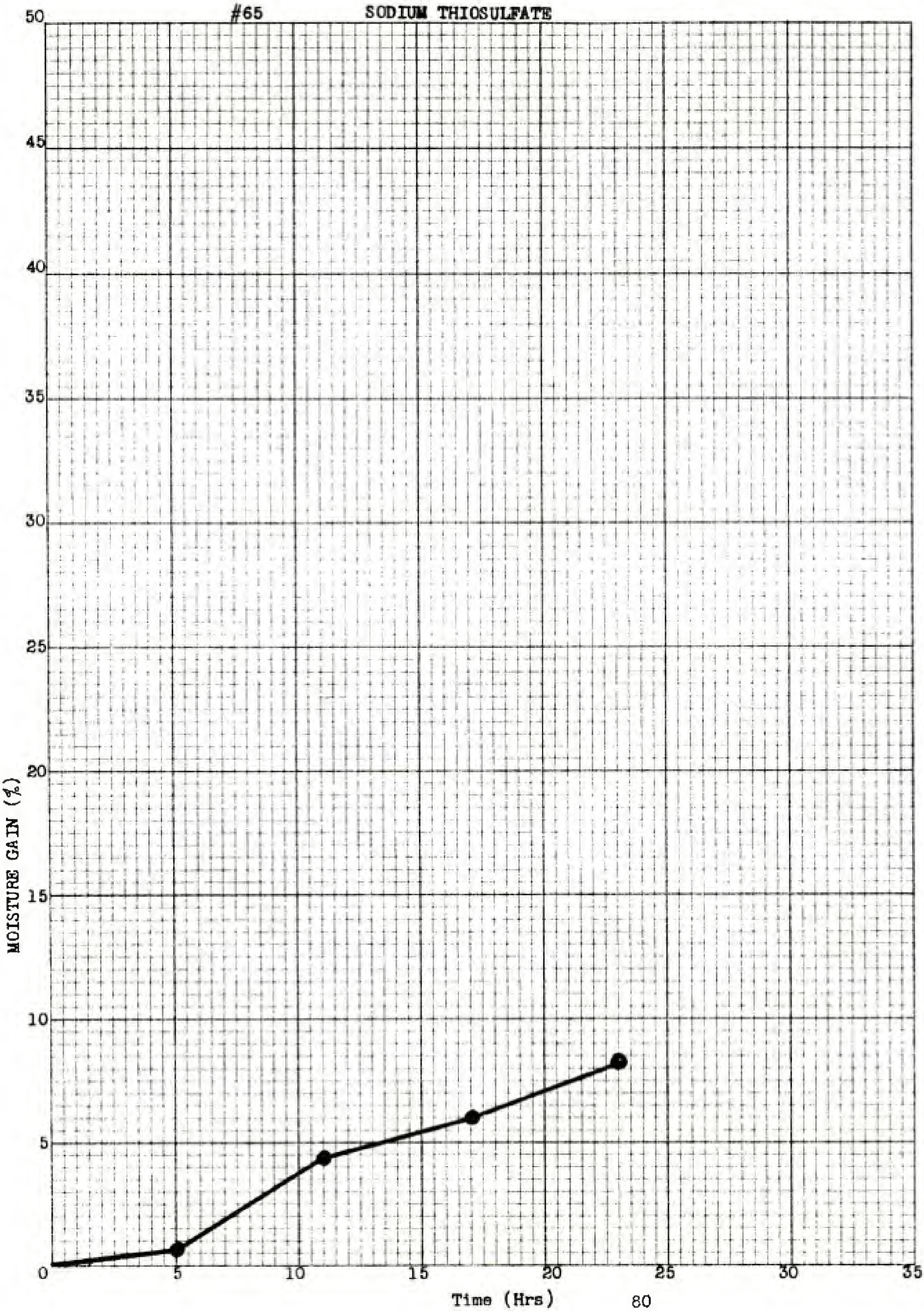


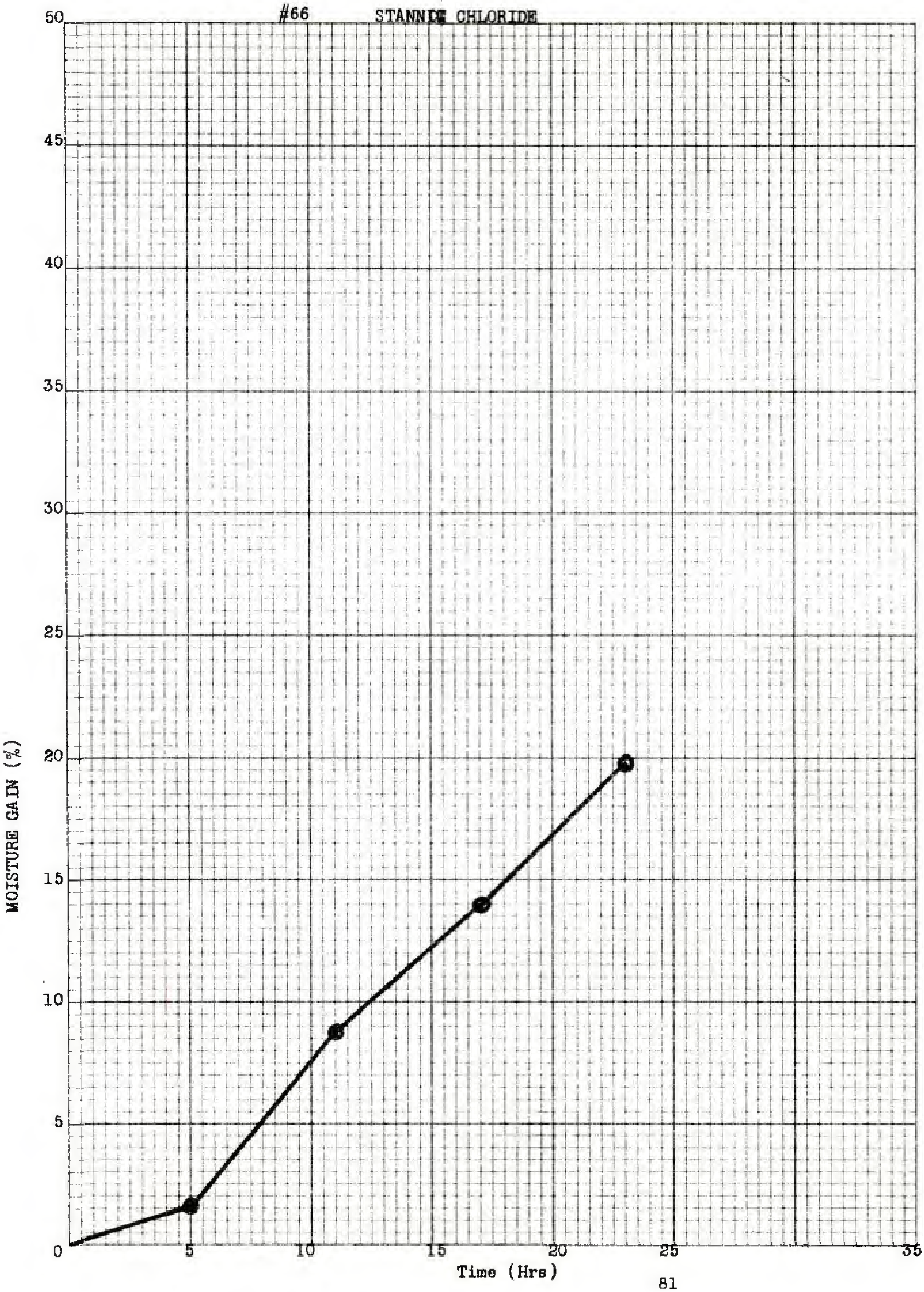
#61
SODIUM SULFATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50


#62
SODIUM SULFIDE
MOISTURE GAIN (%)
Time (Hrs)
50
45
40
35
30
25
20
15
10
0
0
5
10
15
20
25
30
35

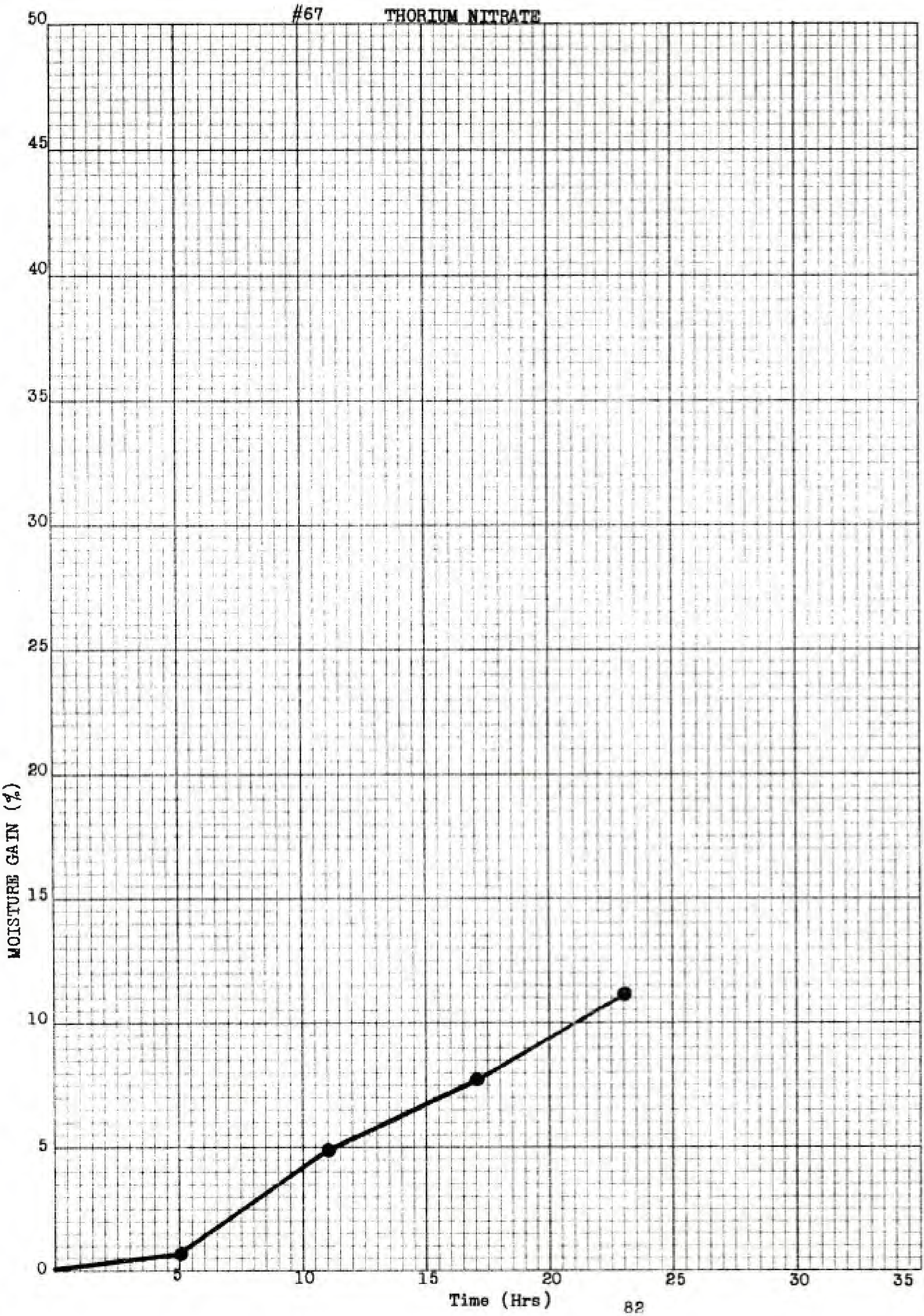

#63
SODIUM SULFITE
MOISTURE GAIN (%)
0
5
10
15
20
25
30
35
40
45
50
Time (Hrs)
0
5
10
15
20
25
30
35

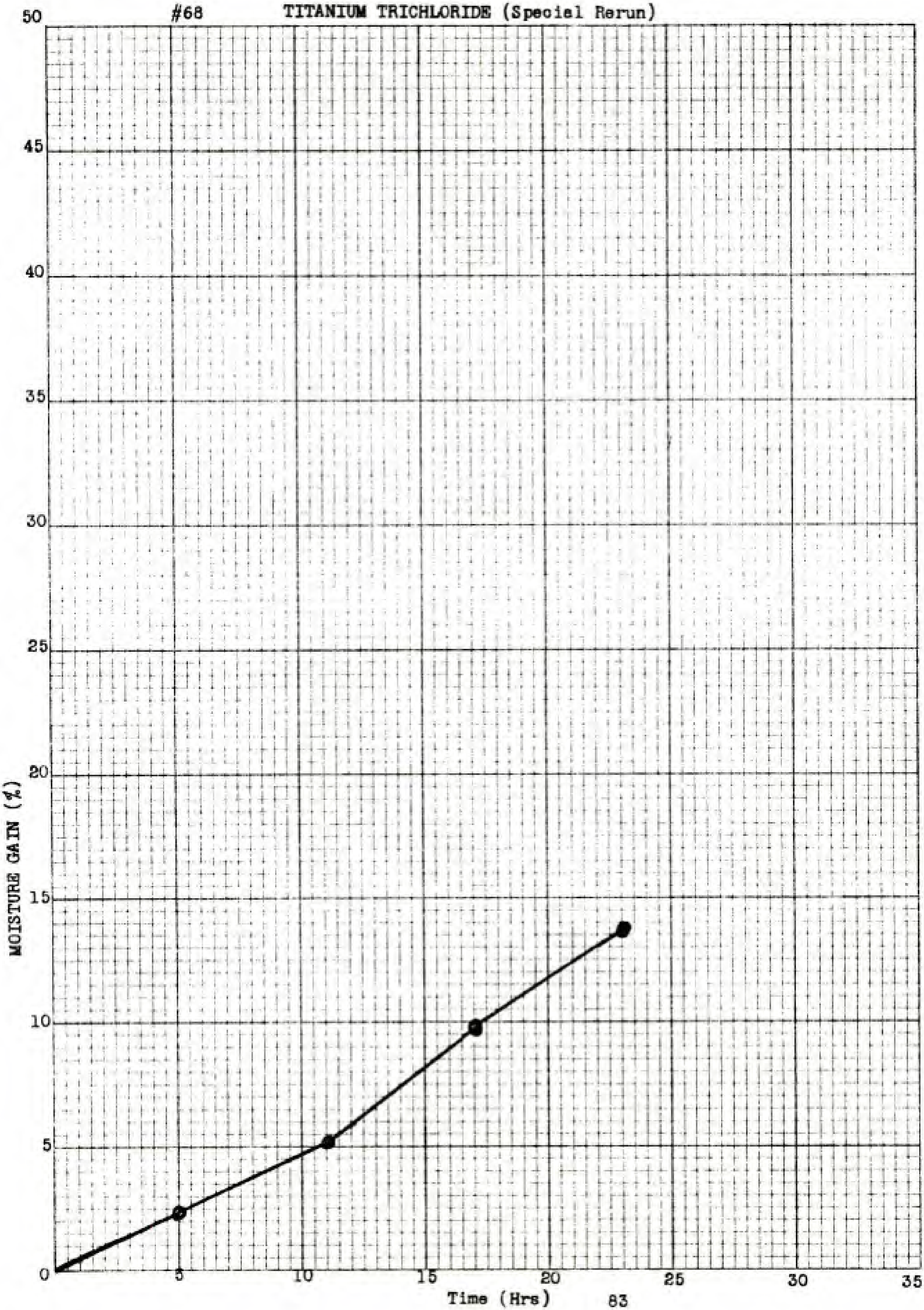

#64
SODIUM THIOCYANATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

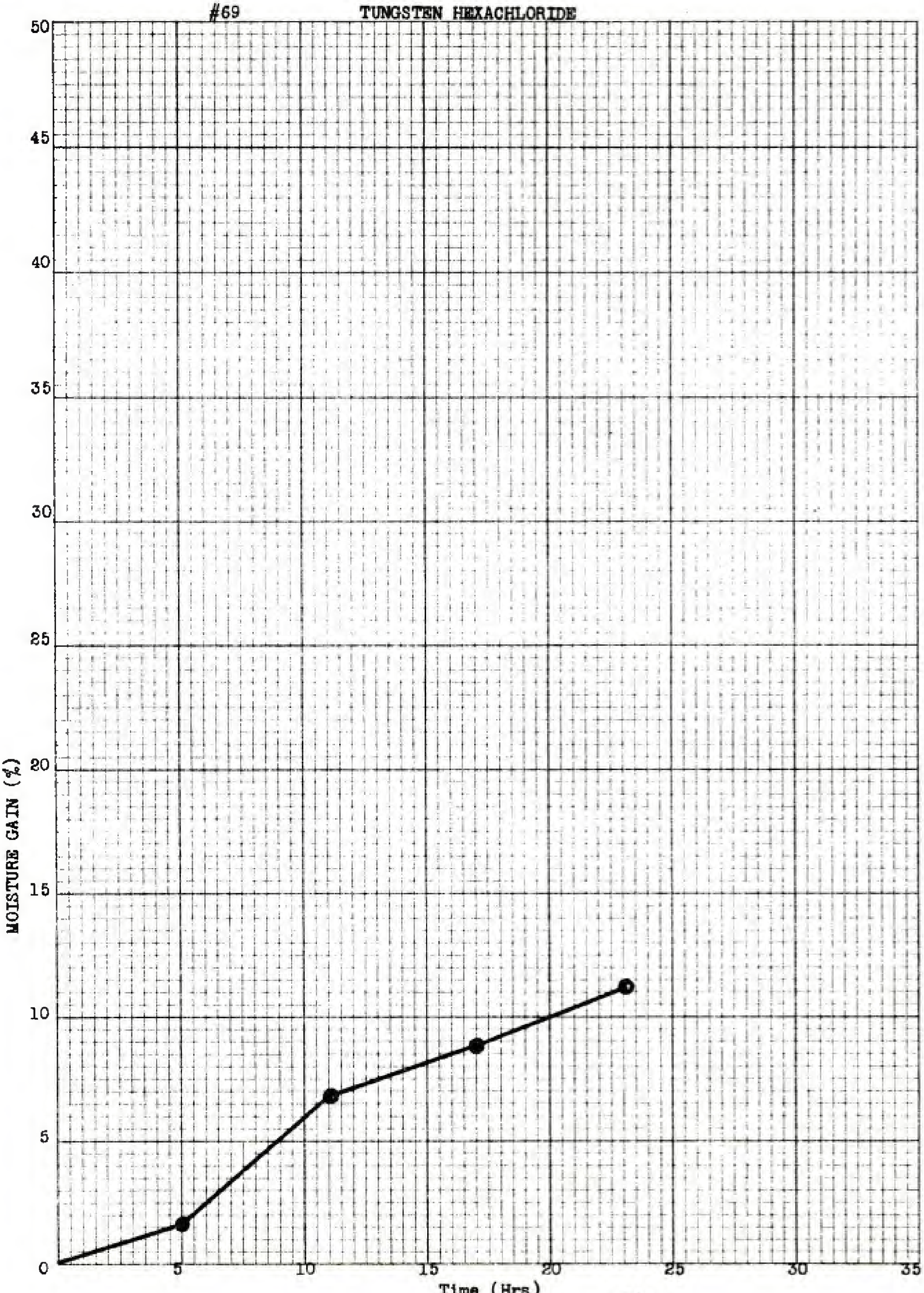

#65
SODIUM THIOSULFATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)


#66 STANNIC CHLORIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
35

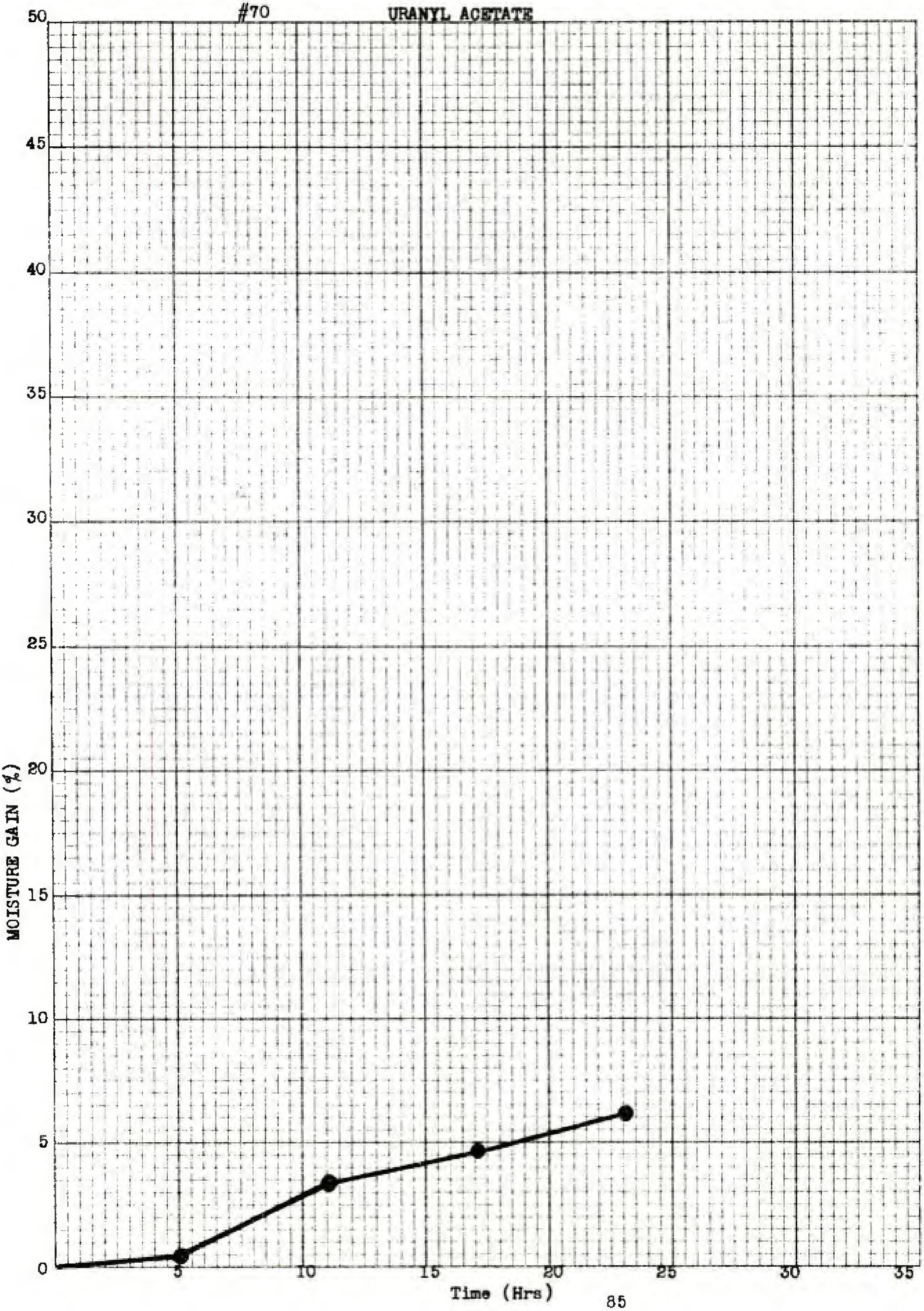
#67 THORIUM NITRATE

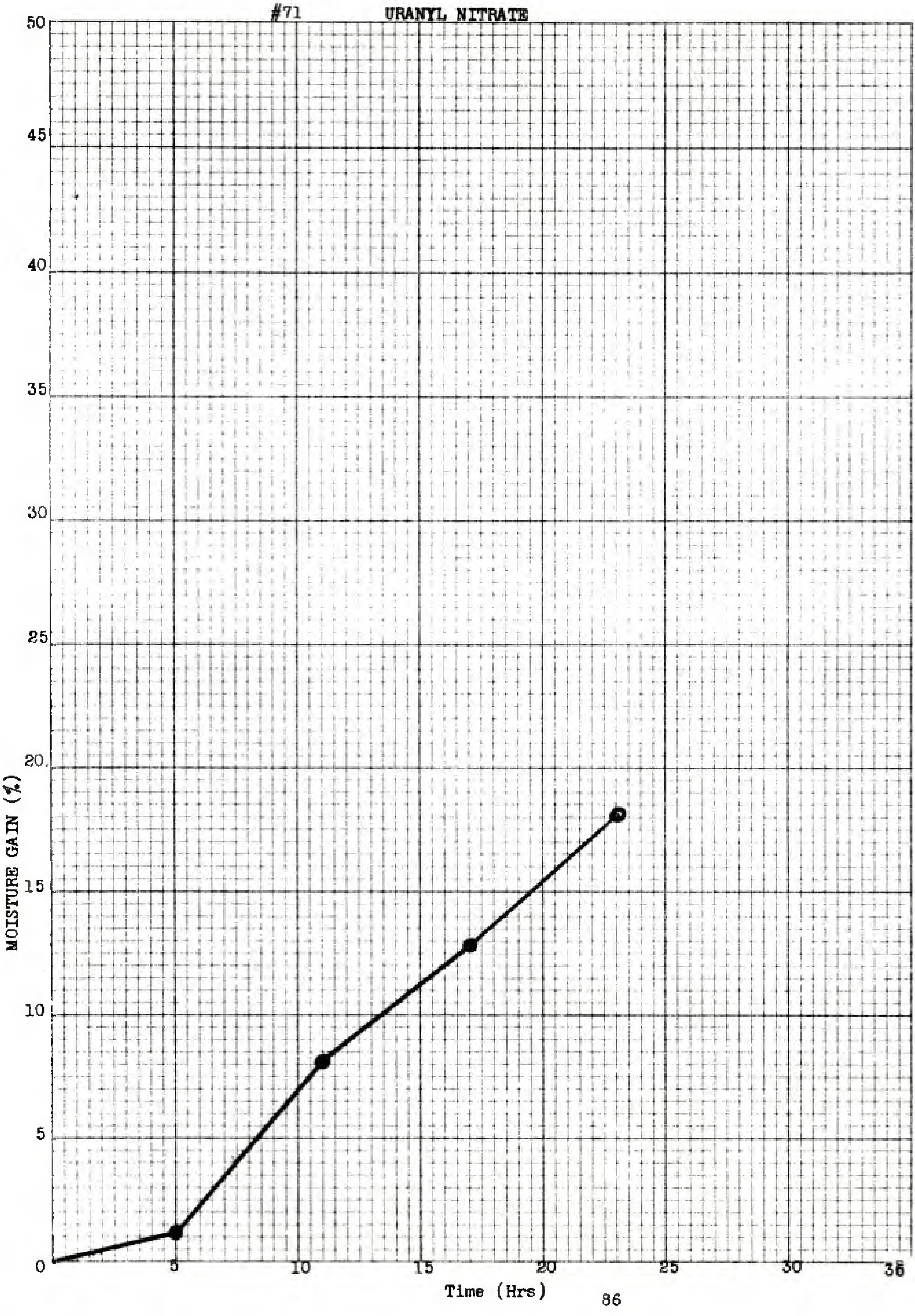


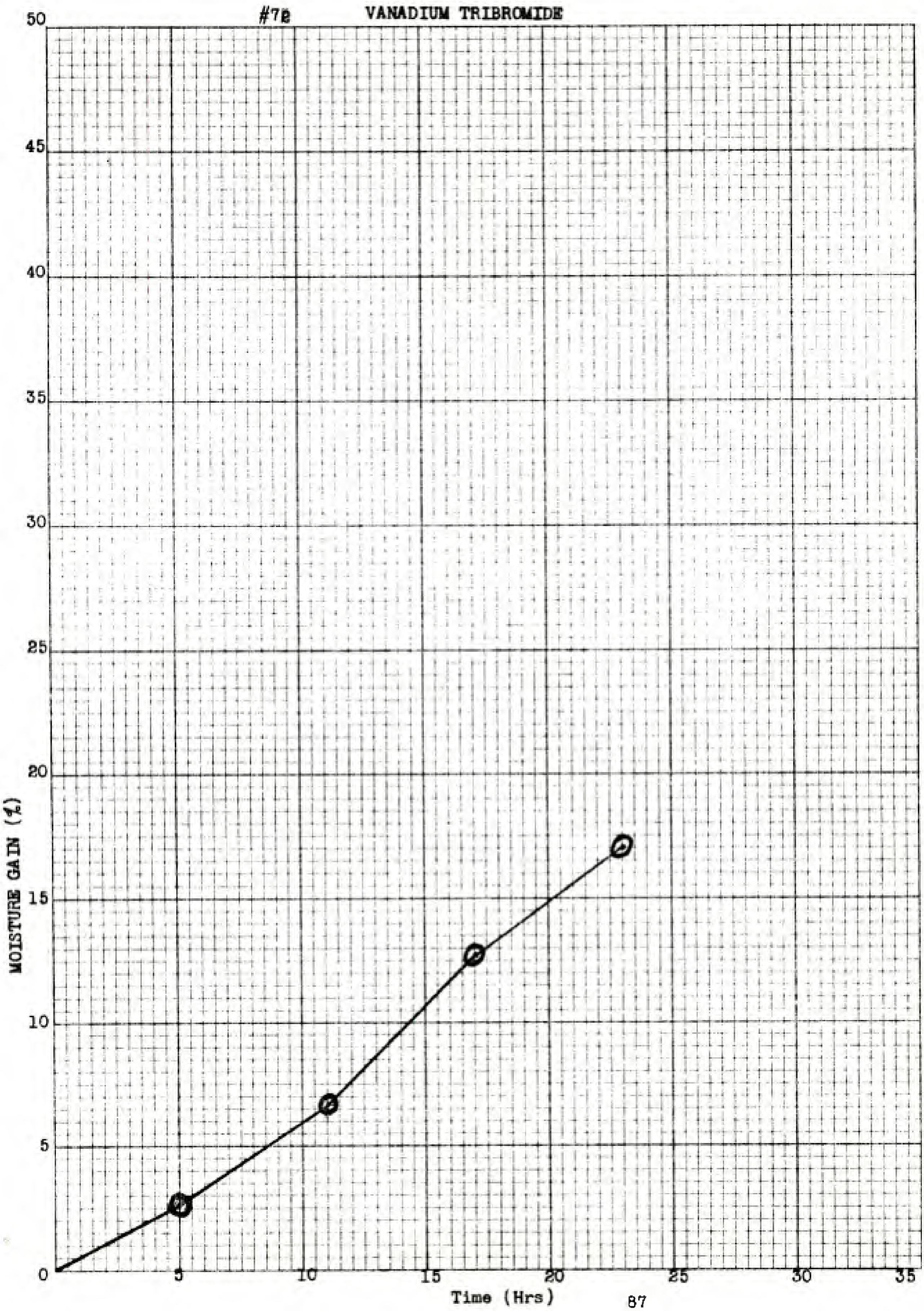

#68
TITANIUM TRICHLORIDE (Special Rerun)
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

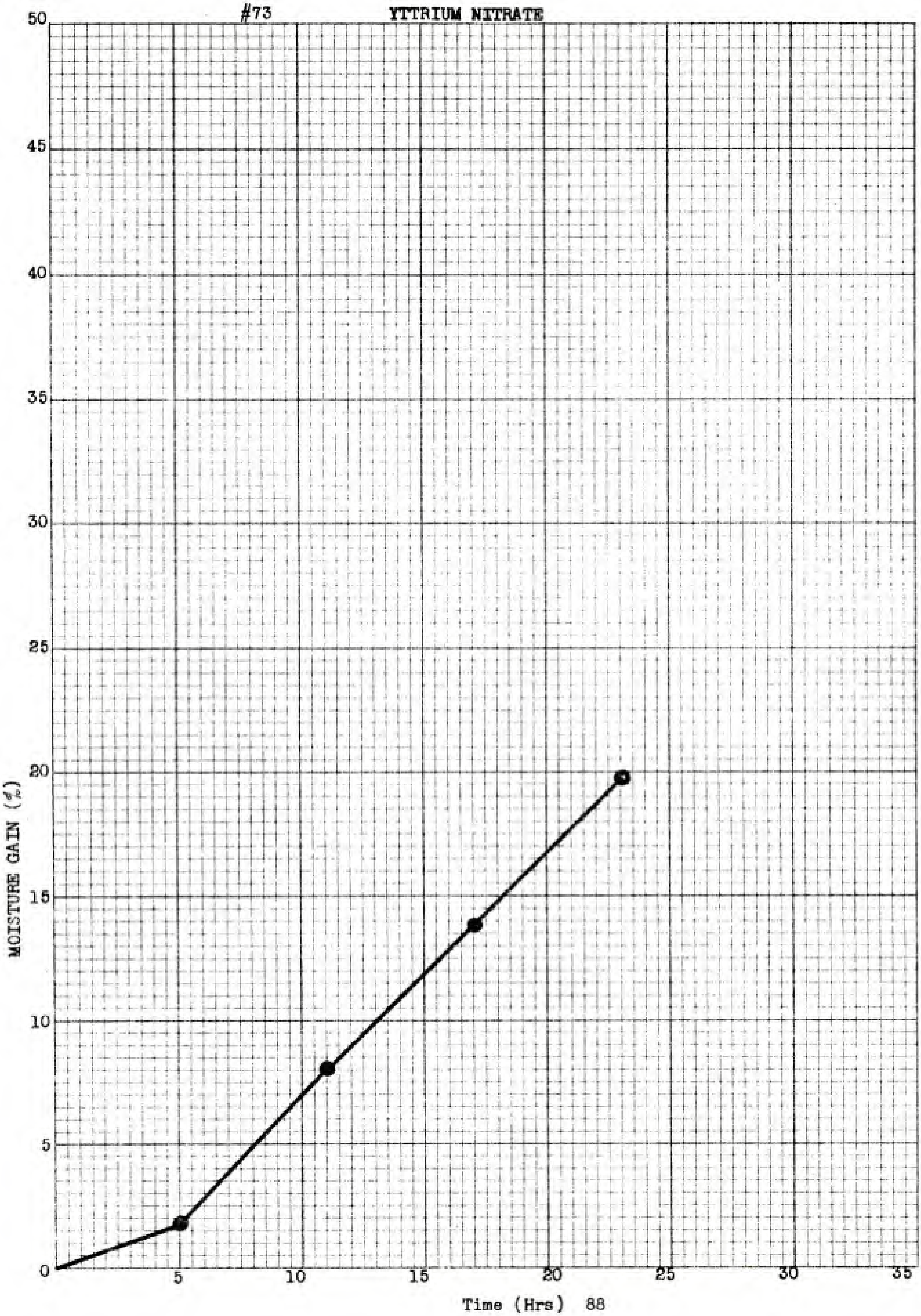


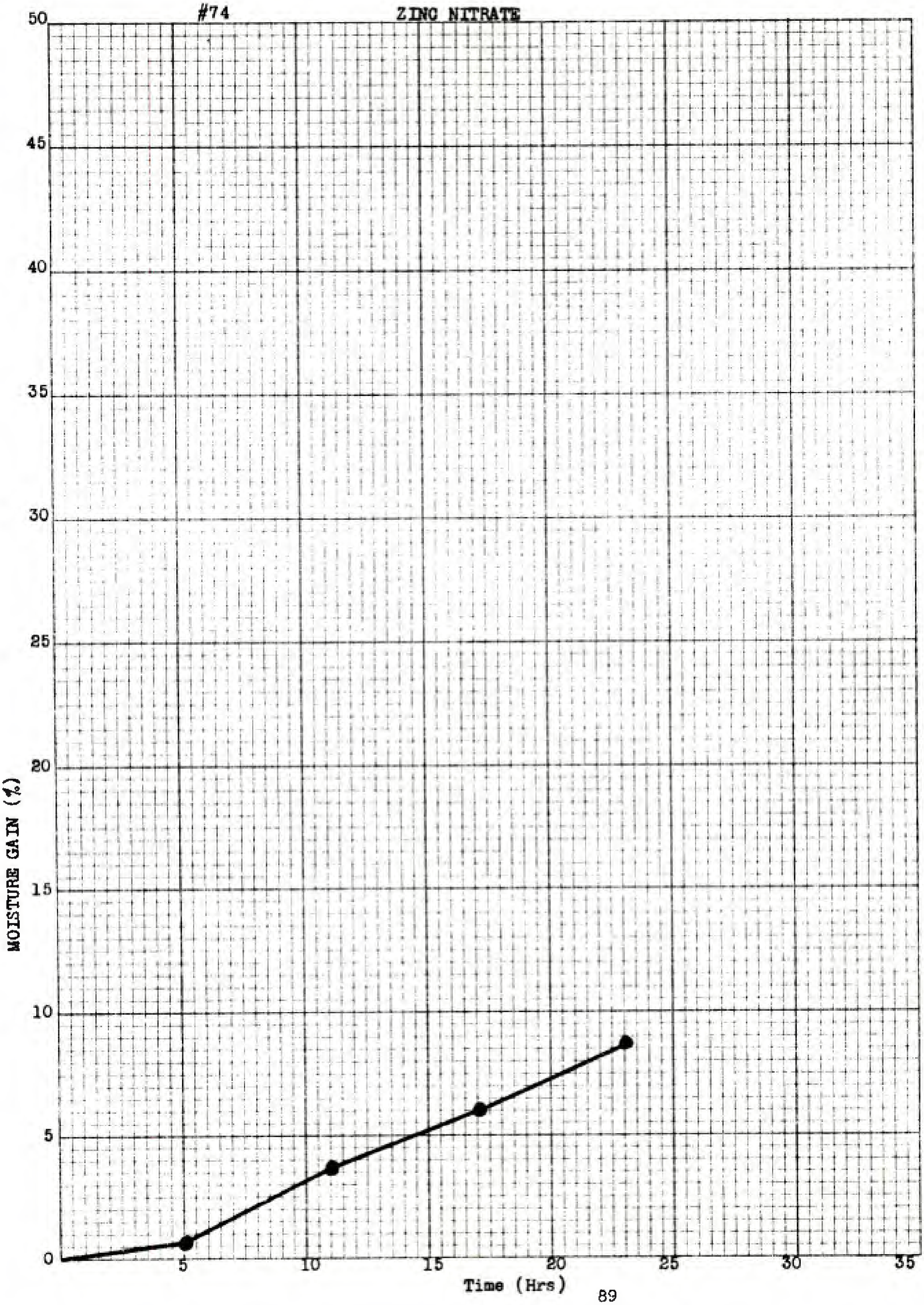
#69
TUNGSTEN HEXACHLORIDE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)


#70
URANYL ACETATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)

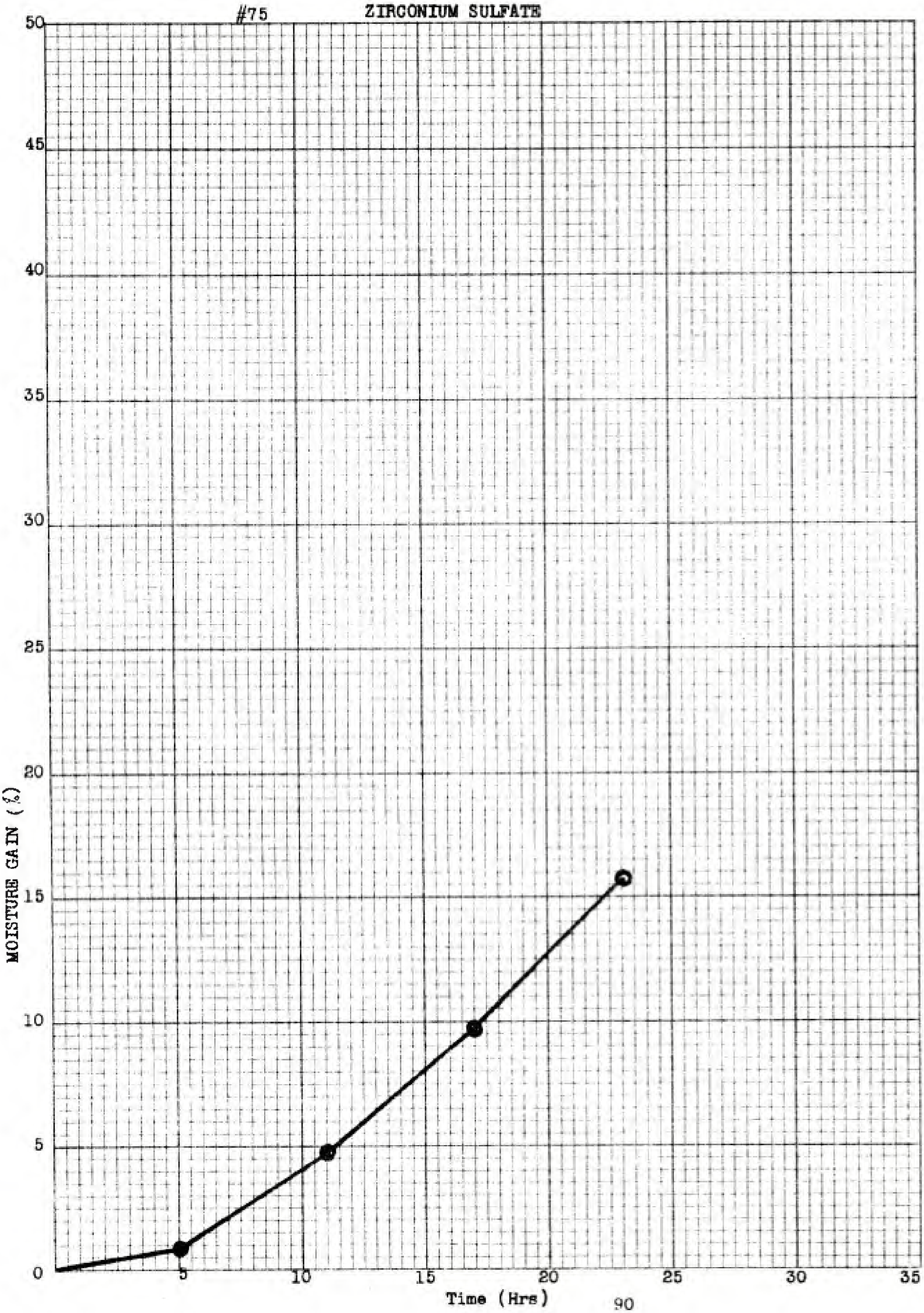

#71 URANYL NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

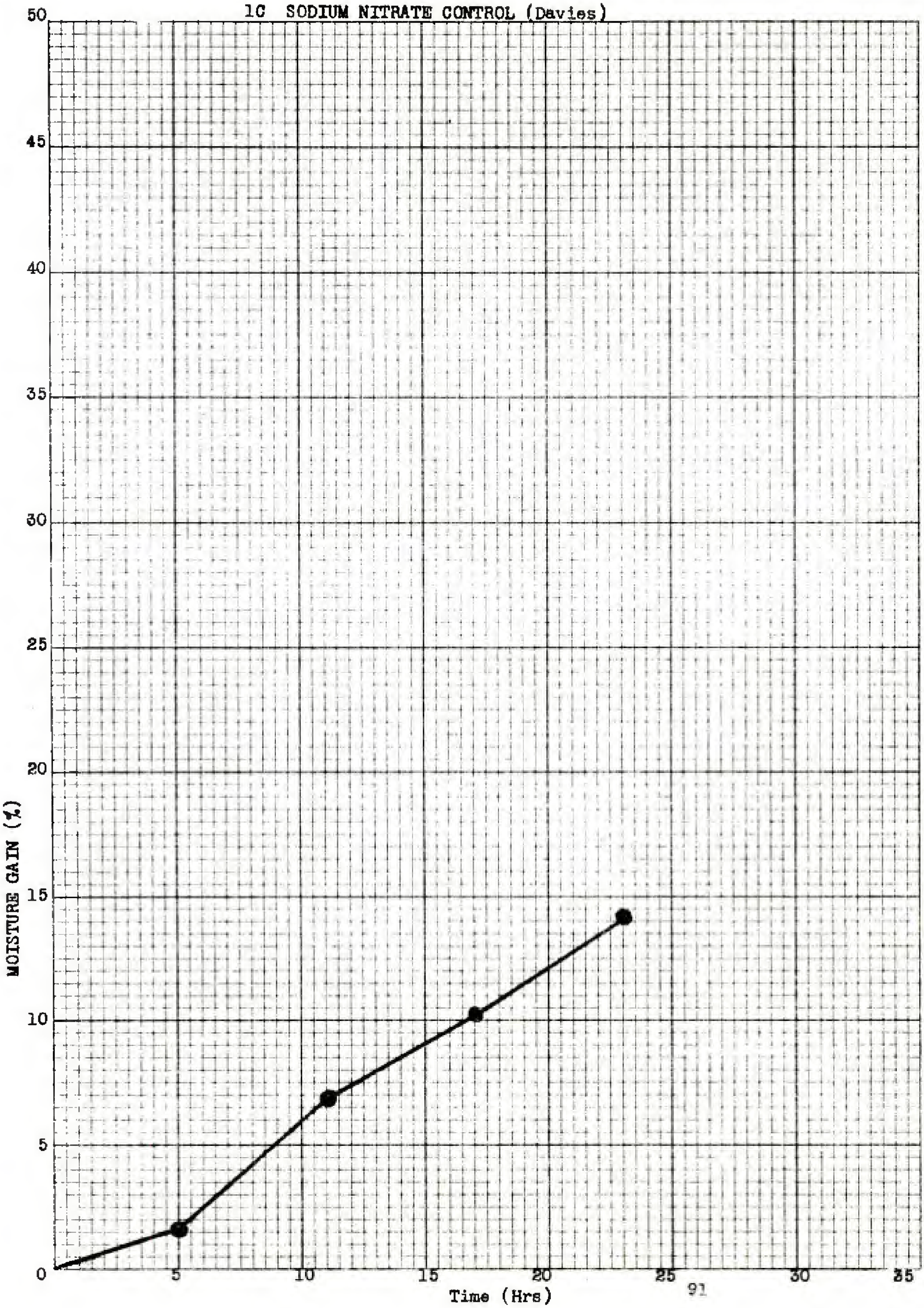

#72 VANADIUM TRIBROMIDE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

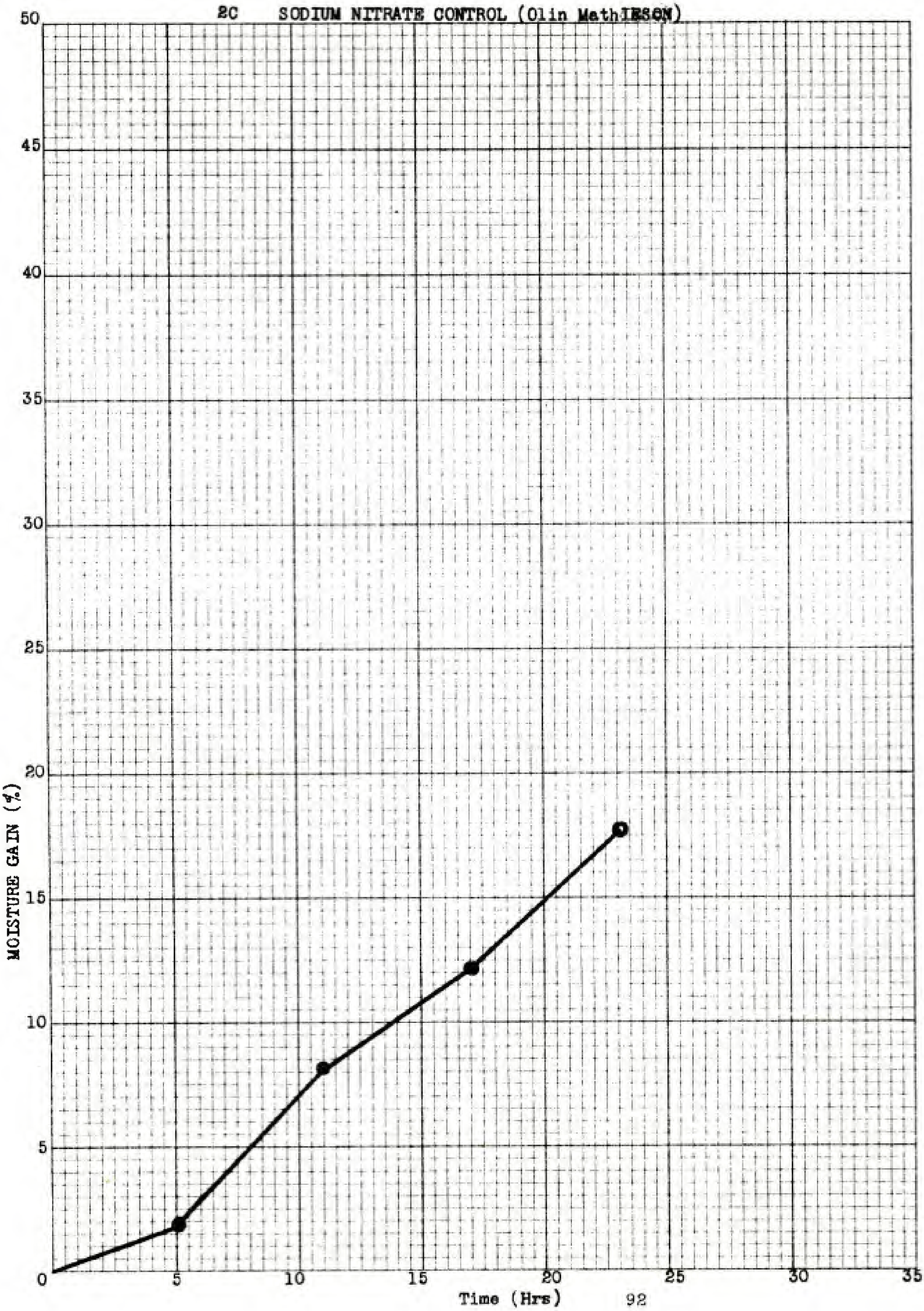

#73
YTTRIUM NITRATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50



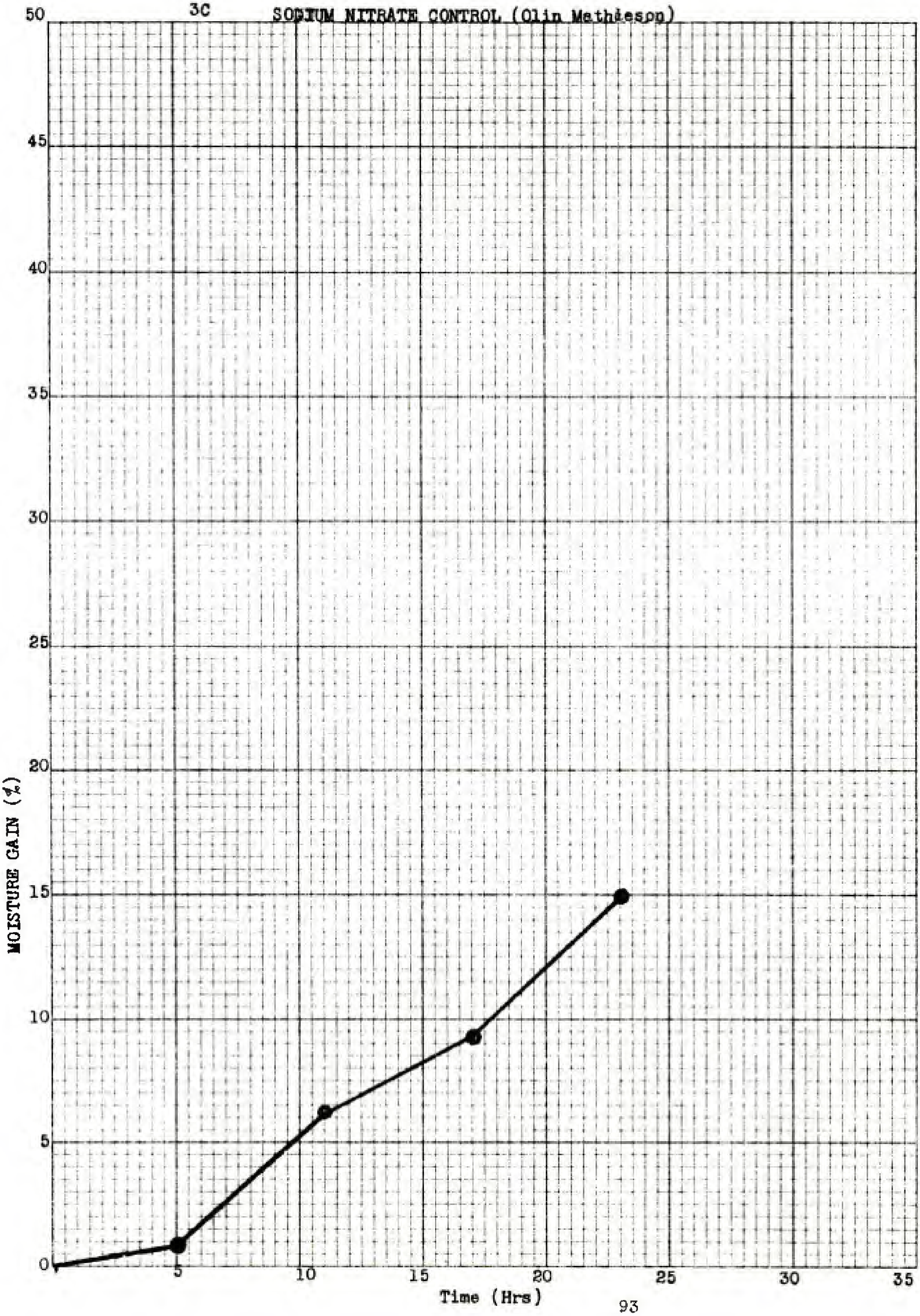
#74
ZINC NITRATE
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)


#75
ZIRCONIUM SULFATE
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35

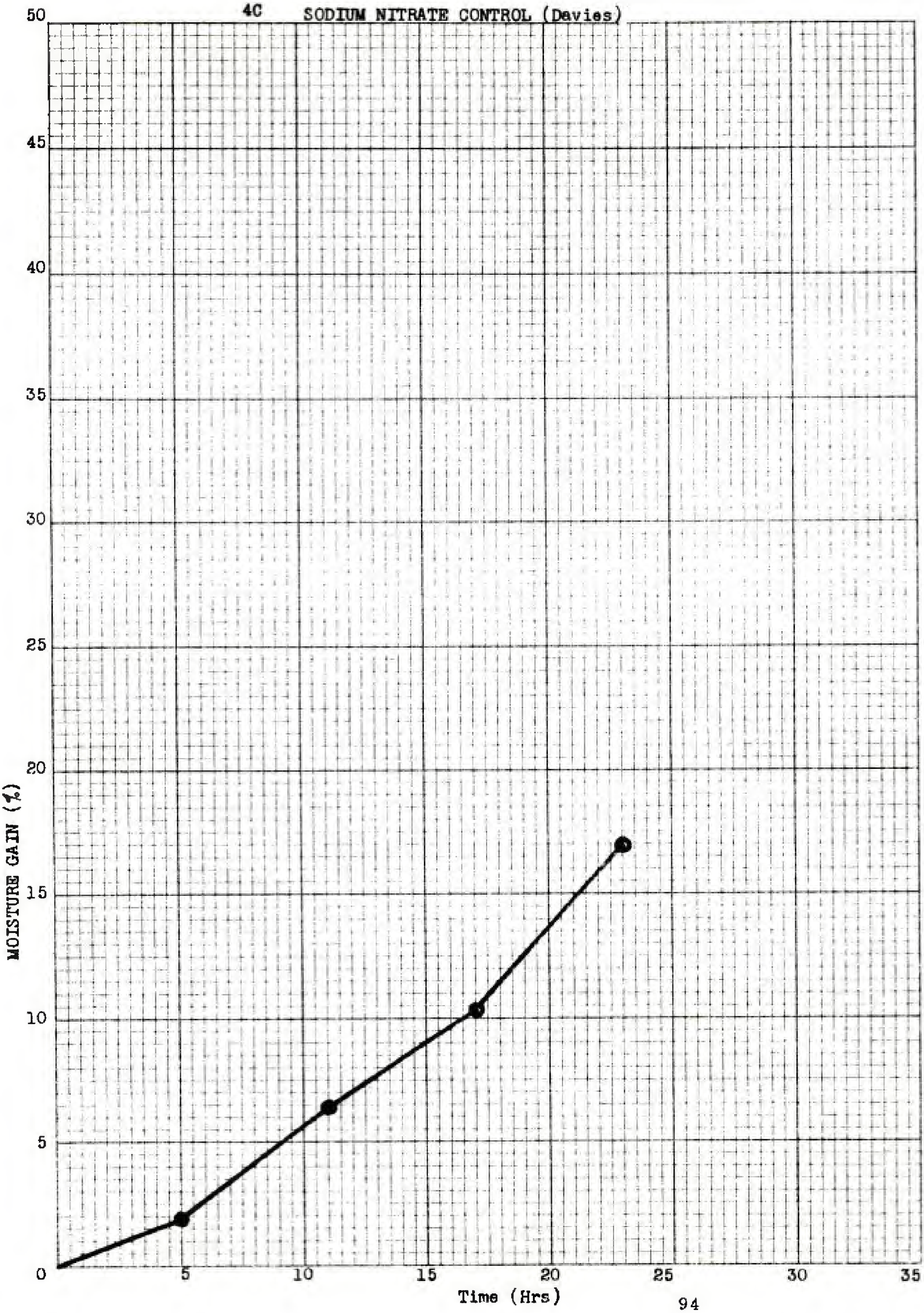

1C SODIUM NITRATE CONTROL (Davies)
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35

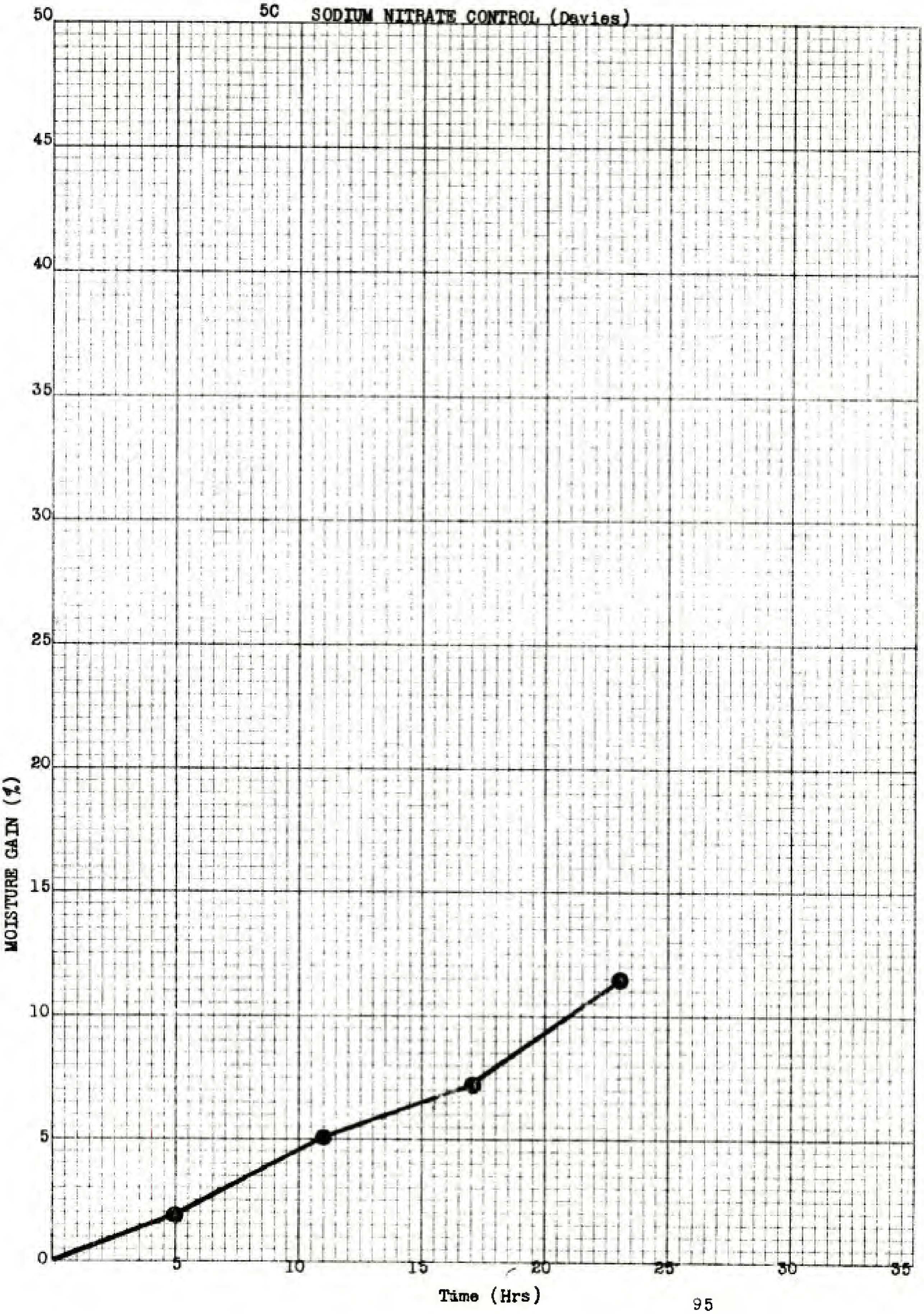

2C SODIUM NITRATE CONTROL (Olin Mathieson)
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50

3C

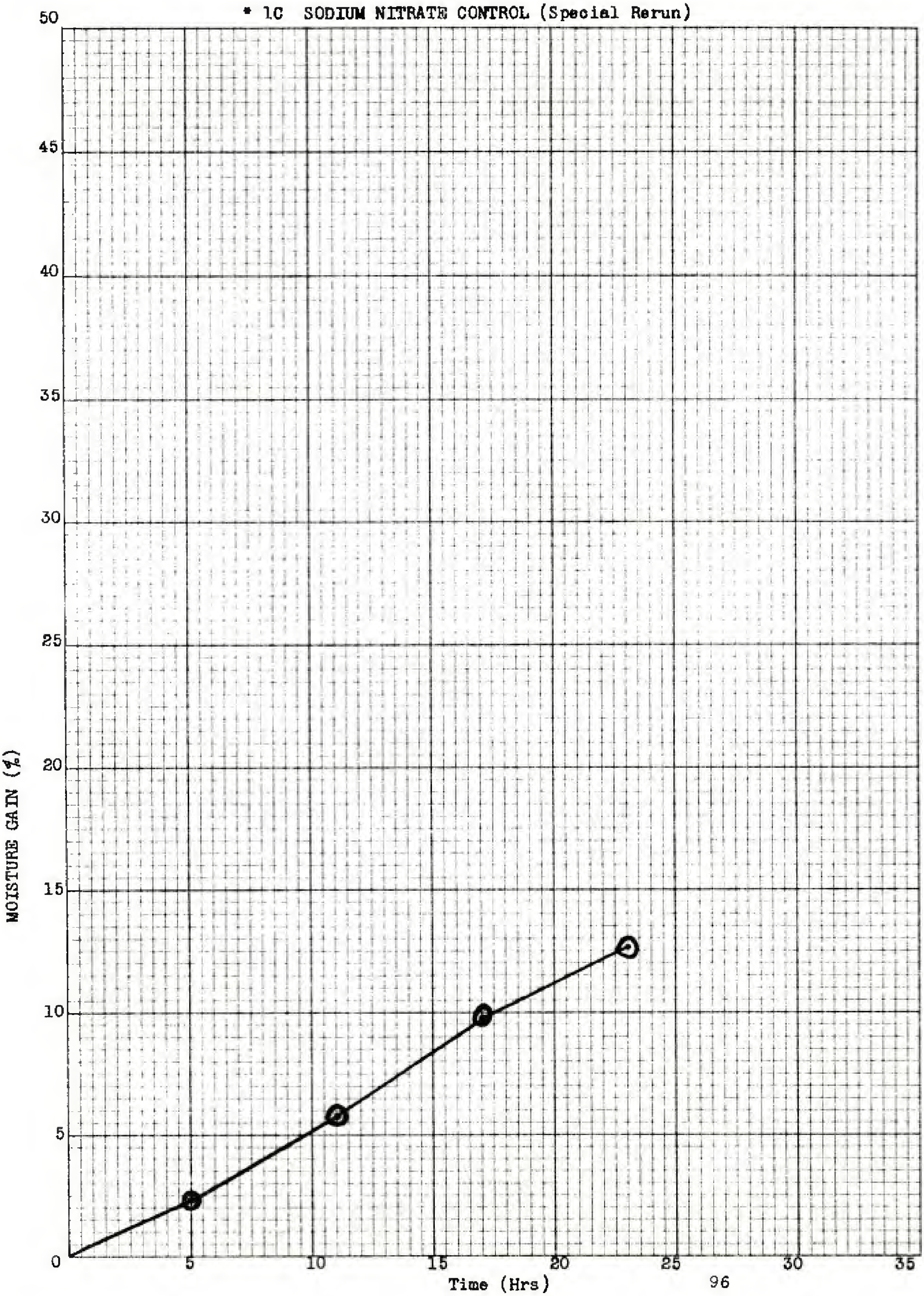


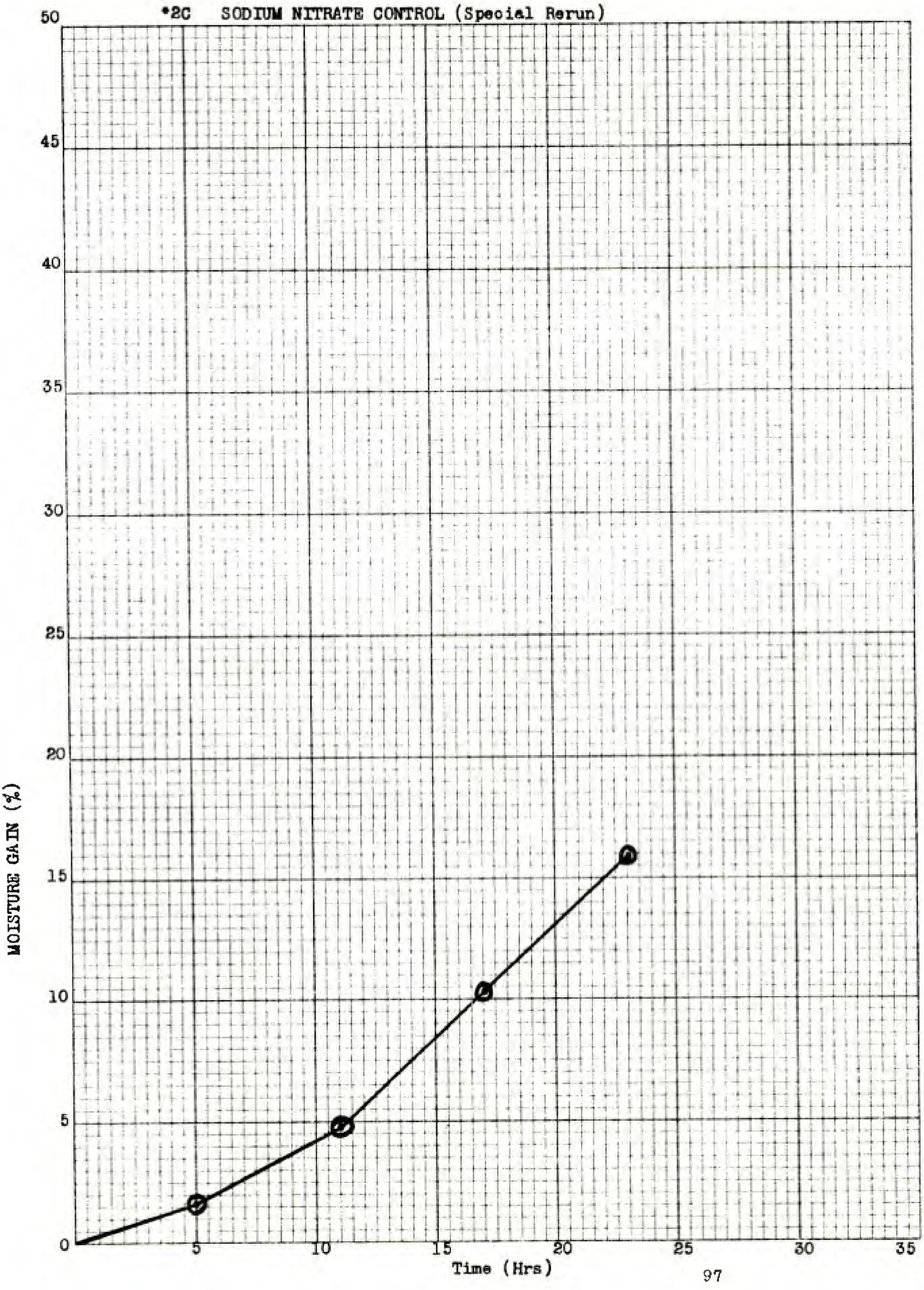
SODIUM NITRATE CONTROL (Olin Mathieson)
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50


4C SODIUM NITRATE CONTROL (Davies)
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)



5C SODIUM NITRATE CONTROL (Davies)
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50


* 1C SODIUM NITRATE CONTROL (Special Rerun)
MOISTURE GAIN (%)
50
45
40
35
30
25
20
15
10
5
0
5
10
15
20
25
30
35
Time (Hrs)


*2C SODIUM NITRATE CONTROL (Special Rerun)
MOISTURE GAIN (%)
Time (Hrs)
0
5
10
15
20
25
30
35
40
45
50
5
10
15
20
25
30
35

APPENDIX II

TABLE I

Effects of Contaminants on Crystallization and Yield of Sodium Nitrate

Sample No.	Contaminant	Rough Yield %	Remarks
1	Aluminum Nitrate	43.6	Slow to crystallize from solution.
2.	Ammonium Nitrate	47.0	Crumbly, easy to crush.
3.	Antimony Trichloride	45.0	Crystal was difficult to crush; dried powder free-flowing.
4	Arsenic Trioxide	58.0	Does not of course dissolve in $NaNO_3$.
5	Barium Nitrate	29.5	
6	Bismuth Nitrate	60.8	
7	Boric Acid	10.0	Crystallization in cold bath very slow; very low yield.
8	Cadmium Nitrate	52.3	
9	Calcium Nitrate	-	Special rerun.
10	Cerium Nitrate	43.7	Faint Yellow Crystals.
11	Chromium Nitrate	69.5	Gray-green in crystals.
12	Cobalt Nitrate	55.0	Pink crystals

Sample No.	Contaminant	Rough Yield %	Remarks
13	Dysprosium Nitrate	52.8	
14	Erbium Sulfate	58.6	
15	Ferric Nitrate	53.9	Light orange crystals.
16	Gadolinium Nitrate	37.8	
17	Gallium Nitrate	46.0	Crumbly, easily crushed.
18	Germmium Diiodide	23.6	0.5% solution.
19	Gold Chloride	29.8	0.5% solution.
20	Indium Nitrate	48.7	Extremely fine crystals formed; very hard cake on drying.
21	Iridium Triiodide	28.6	0.5% solution.
22	Lead Nitrate	59.7	
23	Lithium Nitrate	57.8	
24	Magnesium Nitrate	51.6	
25	Manganese Nitrate	60.0	Brown crystals.
26	Mercuric Nitrate	49.0	Yellow crystals.
27	Nickel Nitrate	68.0	Light green crystals.
28	Osmium Trichloride	53.3	0.5% Solution; decomposes producing chlorine gas, NO_2(?). Grey crystals
29	Platinic Chloride	17.7	0.5% Solution.

Sample No.	Contaminant	Rough Yield %	Remarks
30	Potassium Nitrate	-	Special rerun
31	Praesodymium Nitrate	54.7	
32	Rhenium Trichloride	51.5	0.5% Solution: reacts with sodium solution.
33	Rhodium Nitrate	24.5	0.5% Solution: decomposes $NANO_3$
34	Rubidium Nitrate	48.7	
35	Ruthenium Tetraoxide	28.6	0.5% Solution
36	Samarium Nitrate	42.0	
37	Scandium Nitrate	51.3	0.5% Solution
38	Selenium Dioxide	51.0	Crumbly; fluffy when dry
39	Silicon Dioxide	50.0	
40	Silver Nitrate	57.5	
41	Sodium Acetate	57.5	
42	Sodium Borate	54.0	
43	Sodium Bromide	48.0	
44	Sodium Carbonate	48.6	Anti-caking
45	Sodium Chlorate	52.0	Small crystals; difficult to dry; hard residue when dry
46	Sodium Chloride	53.0	
47	Sodium Chromate	46.2	Yellow crystals
48	Sodium Dichromate	56.0	Appears to increase solubility of $NANO_3$ when added

Sample No.	Contaminant	Rough Yield %	Remarks
49	Sodium Fluoride	54.5	Anticaking
50	Sodium Formate	48.6	
51	Sodium Hypochlorite	51.0	
52	Sodium Iodate	37.0	
53	Sodium Iodide	59.0	
54	Sodium Nitrite	48.0	
55	Sodium Oxalate	46.0	
56	Sodium Perchlorate	62.5	
57	Sodium Periodate	44.5	
58	Sodium Permanganate	41.0	Difficult to dry and process.
59	Sodium Peroxide	-	
60	Sodium Phosphate	62.0	
61	Sodium Sulfate	59.0	Anticaking
62	Sodium Sulfide	58.4	
63	Sodium Sulfite	48.7	
64	Sodium Thiosulfate	55.0	
65	Sodium Thiocyanate	50.0	Light yellow crystals.
66	Stannic Chloride	46.2	
67	Thorium Nitrate	55.4	
68	Titanium Trichloride	-	Special rerun; reacts with $NANO_3$ solution.

Sample No.	Contaminant	Rough Yield %	Remarks
69	Tungsten Hexachloride	26.4	Yellow; noncaking when dry.
70	Uranyl Acetate	52.7	Yellow crystals.
71	Uranyl Nitrate	53.5	Faint yellow crystals.
72	Vanadium Tribromide	22.2	Causes $NANO_3$ to decompose.
73	Yttrium Nitrate	56.8	
74	Zinc Nitrate	46.0	
75	Zirconium Sulfate	53.6	Forms budlike crystal masses; dried sample fluffy, crumbles easily, and does not cake on standing.
1C	Control Sodium Nitrate	72.0	

TABLE II

Contaminated Sodium Nitrate Samples
After 23 Hours In Humidity Chamber

Sample No.	Contaminant	Total Water Adsorbed, %
25	Manganese Nitrate	4.61
26	Mercuric Nitrate	4.62
49	Sodium Fluoride	4.73
12	Cobalt Nitrate	5.06
44	Sodium Carbonate	5.40
27	Nickel Nitrate	5.88
70	Uranyl Acetate	6.07
56	Sodium Perchlorate	6.27
11	Chromic Nitrate	6.54
1	Aluminum Nitrate	6.61
51	Sodium Hypochlorite	6.66
43	Sodium Bromide	7.00
5	Barium Nitrate	7.40
54	Sodium Nitrate	7.75
42	Sodium Borate	8.17
2	Ammonium Nitrate	8.27
64	Sodium Thiosulfate	8.27
48	Sodium Dichromate	8.33
59	Sodium Peroxide	8.45

Sample No.	Contaminant	Total Water Adsorbed, %
74	Zinc Nitrate	8.53
61	Bismuth Nitrate	8.61
24	Magnesium Nitrate	8.86
19	Gold Chloride	9.13
15	Ferric Nitrate	9.35
41	Sodium Acetate	9.53
53	Sodium Iodide	9.59
22	Lead Nitrate	10.01
61	Sodium Sulfate	10.01
7	Boric Acid	10.16
52	Sodium Iodate	10.35
60	Sodium Phosphate	10.87
16	Gadolinium Nitrate	10.95
67	Thorium Nitrate	11.01
23	Lithium Nitrate	11.01
69	Tungsten Hexachloride	11.19
28	Osmium Trichloride	11.22
3	Antimony Trichloride	11.33
5C	Control #5	11.40
58	Sodium Permanganate	11.54
32	Rhenium Trichloride	11.60
62	Sodium Sulfide	11.80

Sample No.	Contaminant	Total Water Adsorbed. %
55	Sodium Oxalate	11.94
32	* Rhodium Nitrate	12.40
	* Control #1	12.60
14	Erbium Sulfate	12.61
35	Ruthenium Tetraoxide	12.93
47	Sodium Chromate	12.94
13	Dysprosium Nitrate	13.02
9	* Calcium Nitrate	13.10
38	Selenium Dioxide	13.21
18	* Germanium Diiodide	13.40
17	Gallium Nitrate	13.50
68	* Titanium Trichloride	13.60
20	Indium Nitrate	13.79
39	* Silicon Dioxide	13.80
65	Sodium Thiocyanate	13.81
34	Rubidium Nitrate	13.91
10	Control #1	14.08
8	Cadmium Nitrate	14.34
57	Sodium Periodate	14.47
4	Arsenic Trioxide	14.54
30	Control #3	14.93
21	Iridium Triiodide	15.33

Sample No.	Contaminant	Total Water Adsorbed %
31	Praseodymium Sulfate	15.44
75	Zirconium Sulfate	15.60
36	Samarium Nitrate	15.66
	* Control #2	15.80
30	* Potassium Nitrate	16.30
40	Control #4	16.93
40	Silver Nitrate	17.0
72	* Vanadium Tribromide	17.0
50	Sodium Formate	17.08
45	Sodium Chlorate	17.13
20	Control #2	17.67
71	Uranyl Nitrate	18.07
37	Scandium Nitrate	18.27
66	Stannic Chloride	19.66
73	Vittrium Nitrate	19.74
10	Cerium Nitrate	21.01
46	Sodium Chloride	21.40
63	Sodium Sulfite	22.25
29	Platinum Chloride	No Data

* Special rerun, not in original group

TABLE III

Water Adsorbed by Contaminated Sodium Nitrate Samples
After First Five Hours in Humidity Chamber

Contaminant	Water Adsorbed, %
Cobalt Nitrate	0.20
Manganese Nitrate	0.27
Silver Nitrate	0.27
Sodium Borate	0.27
Sodium Carbonate	0.27
Sodium Sulfate	0.27
Lead Nitrate	0.33
Sodium Fluoride	0.33
Sodium Hypochlorite	0.40
Arsenic Trioxide	0.47
Mercuric Nitrate	0.47
Nickel Nitrate	0.47
Uranyl Acetate	0.47
Bismuth Nitrate	0.53
Sodium Oxalate	0.54
Aluminum Nitrate	0.60
Sodium Chlorate	0.60
Sodium Perchlorate	0.60
Sodium Phosphate	0.60

Contaminant	Water Adsorbed, %
Sodium Thiosulfate	0.60
Zinc Nitrate	0.60
Barium Nitrate	0.67
Ferric Nitrate	0.67
Sodium Bromide	0.67
Sodium Dichromate	0.67
Thorium Nitrate	0.67
Control #3	0.80
Cadmium Nitrate	0.80
Lithium Nitrate	0.80
Sodium Chloride	0.80
Sodium Periodate	0.80
Zirconium Sulfate	0.80
Sodium Iodate	0.81
Boric Acid	0.87
Sodium Nitrite	0.94
Ammonium Nitrate	1.00
Chromic Nitrate	1.00
Sodium Permanganate	1.00
Antimony Trichloride	1.07
Cerium Nitrate	1.07
Gallium Nitrate	1.08

Contaminant	Water Adsorbed, %
Matnesium Nitrate	1.13
Sodium Peroxide	1.13
Uranyl Nitrate	1.14
Gold Chloride	1.27
Sodium Sulfide	1.27
Ruthenium Tetraoxide	1.28
Sodium Iodide	1.33
Sodium Chromate	1.34
Sodium Acetate	1.40
Indium Nitrate	1.41
Iridium Triiodide	1.47
Selenium Dioxide	1.47
Sodium Sulfite	1.53
Sodium Thiocyanate	1.53
Stannic Clòride	1.53
Praesodymium Sulfate	1.54
Control #1	1.60
* Control #2	1.60
Erbium Nitrate	1.60
Tungsten Hexachloride	1.61
* Silicon Dioxide	1.70
Ittrium Nitrate	1.74
Dysprosium Nitrate	1.80

Contaminant	Water Adsorbed, %
Control #2	1.87
Control #4	1.93
Control #5	1.93
Rhenium Trichloride	1.93
Scandium Nitrate	1.93
*Rhodium Nitrate	2.00
Sodium Formate	2.00
Osmium Trichloride	2.01
*Potassium Nitrate	2.20
Rubidium Nitrate	2.20
*Control #1	2.30
Gadolinium Nitrate	2.33
Samarium Nitrate	2.33
*Titanium Trichloride	2.40
*Germanium Diiodide	2.70
*Vanadium Tribromide	2.70
*Calcium Nitrate	2.75

* Special Rerun

TABLE IV

Water Adsorbed by Contaminated Sodium Nitrate Samples
During Second Period of Exposure (6 Hours) in Humidity Chamber

Contaminant	Water Adsorbed, %
Sodium Fluoride	1.80
Cobalt Nitrate	2.13
Manganese Nitrate	2.13
Chromic Nitrate	2.33
Sodium Carbonate	2.40
Sodium Hypochlorite	2.40
Mercuric Nitrate	2.47
Nickel Nitrate	2.47
* Germanium Diiodide	2.50
* Silicon Dioxide	2.50
Ferric Nitrate	2.87
* Rhodium Nitrate	2.60
Sodium Perchlorate	2.87
* Titanium Trichloride	2.80
Uranyl Acetate	2.87
Bismuth Nitrate	2.93
Osmium Trichloride	2.94
Sodium Bromide	3.06
Zinc Nitrate	3.08

Contaminant	Water Adsorbed %
Ammonium Nitrate	3.07
Antimony Trichloride	3.13
Control #5	3.14
* Control #2	3.20
Rhenium Trichloride	3.20
Sodium Nitrite	3.20
* Calcium Nitrate	3.25
Barium Nitrate	3.26
Sodium Peroxide	3.32
Aluminum Nitrate	3.33
Gadolinium Nitrate	3.35
Scandium Nitrate	3.40
* Control #1	3.45
Rubidium Nitrate	3.60
Sodium Dichromate	3.60
Sodium Iodide	3.60
* Potassium Nitrate	3.70
Sodium Borate	3.76
Sodium Acetate	3.80
Sodium Thiosulfate	3.80
Magnesium Nitrate	3.87
Sodium Iodate	4.00
* Vanadium Tribromide	4.00

Contaminant	Water Adsorbed, %
Zirconium Sulfate	4.00
Thorium Nitrate	4.00
Gold Chloride	4.33
Lead Nitrate	4.34
Sodium Sulfate	4.40
Cadmium Nitrate	4.47
Control #4	4.47
Erbium Nitrate	4.47
Sodium Phosphate	4.53
Lithium Nitrate	4.60
Sodium Chromate	4.60
Sodium Oxalate	4.60
Boric Acid	4.69
Dysprosium Nitrate	4.69
Sodium Thiocyonate	4.69
Selenium Dioxide	4.87
Sodium Permanganate	5.13
Tungsten Hexachloride	5.17
Arsenic Trioxide	5.27
Control #1	5.27
Control #3	5.27
Gallium Nitrate	5.36

Contaminant	Water Adsorbed, %
Ruthenium Tetraoxide	5.37
Iridium Nitrate	5.45
Sodium Sulfite	5.45
Praesodymium Sulfate	5.46
Sodium Sulfide	5.67
Sodium Periodate	5.74
Sodium Chlorate	5.93
Samarium Nitrate	6.07
Control #2	6.20
Iridium Triiodide	6.20
Yttrium Nitrate	6.27
Uranyl Nitrate	6.93
Silver Nitrate	7.20
Stannic Chloride	7.20
Cerium Nitrate	7.87
Sodium Chloride	8.33
Sodium Formate	8.55

TABLE V

Chemical Requirements of Sodium Nitrate by Military Specification Mil-S-322B

Property	Grade A		Grade B_1	
	Percentage		Percentage	
	Maximum	Minimum	Maximum	Minimum
Moisture	0.75	...	0.5	...
Insoluble Matter	0.5	...	0.1	...
Alkalinity (as Na_2O)	0.05	...	None	...
Nitrates (as $NaNO_3$)	...	97.0	...	99.5
Chlorates (as $KClO_3$)	0.06	...	None	...
Calcium (as CaO)	0.30	...	0.1	...
Magnesium (as MgO)	0.15	...	0.06	...
Sulfates (as Na_2SO_4)	0.5	...	0.2	...
Chlorides (as NaCl)	...	...	0.15	...

The percentages indicated, except the percent of moisture, are to be obtained in the sodium nitrate after the sample has been dried to constant weight at 302 ± 5°F(150±3°C).

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13. ABSTRACT

A preliminary screen is made of the effects of 75 contaminants on the hygroscopicity of sodium nitrate. Results indicate that contaminants exert a significant effect both in increasing and in decreasing hygroscopicity. Various side effects are noted, for example the pronounced anticaking effect of zirconium sulfate and other compounds.

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14 KEY WORDS	LINK A		LINK B		LINK C	
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Contaminants						
Crystallization						
Humidity Chamber						
Hygroscopicity						
Sodium Nitrate						

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