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# A Study of Magnesium Silicate as a Base Matrix Material for Fluorescent Materials

John D. Hopperton

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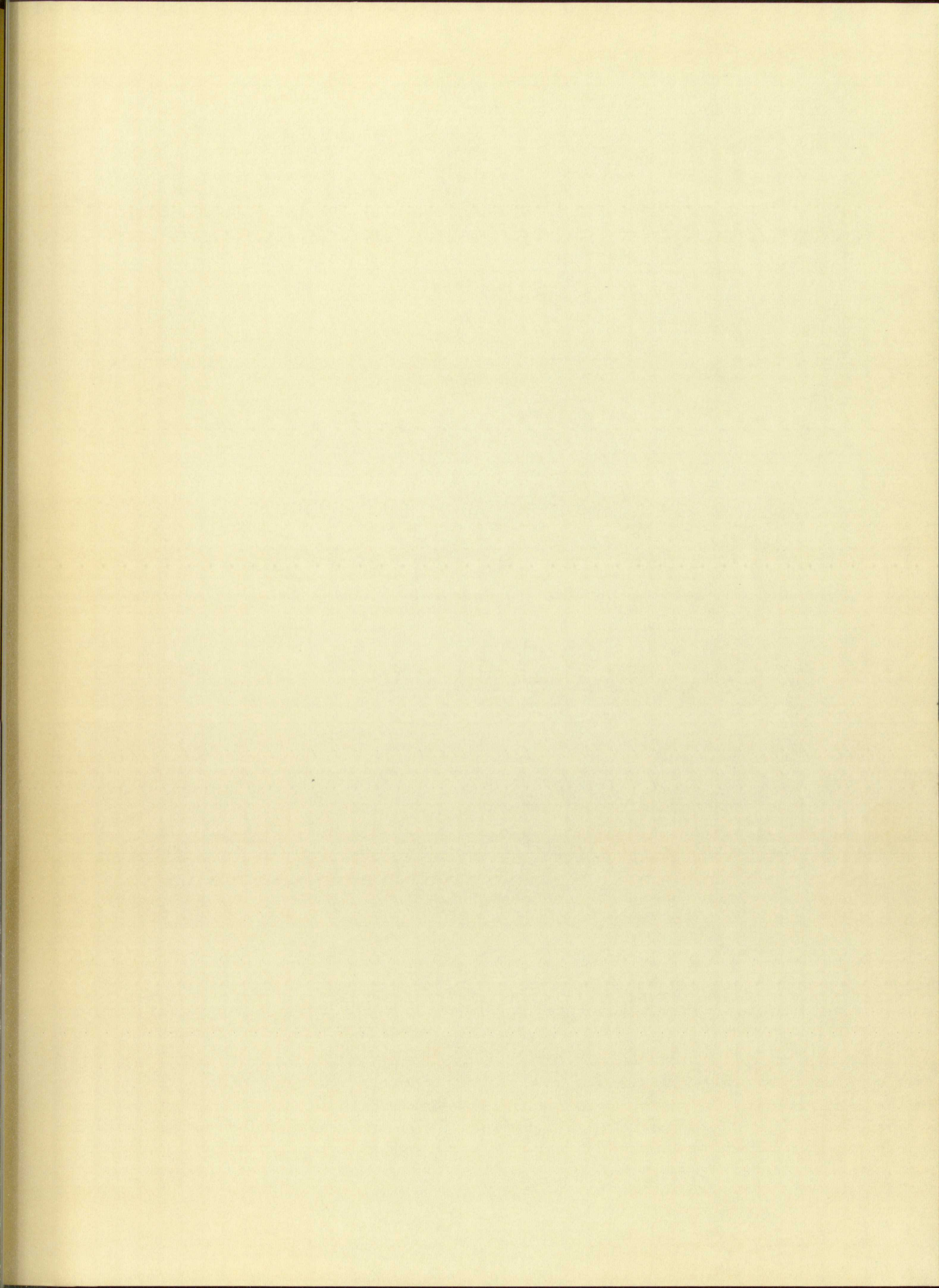






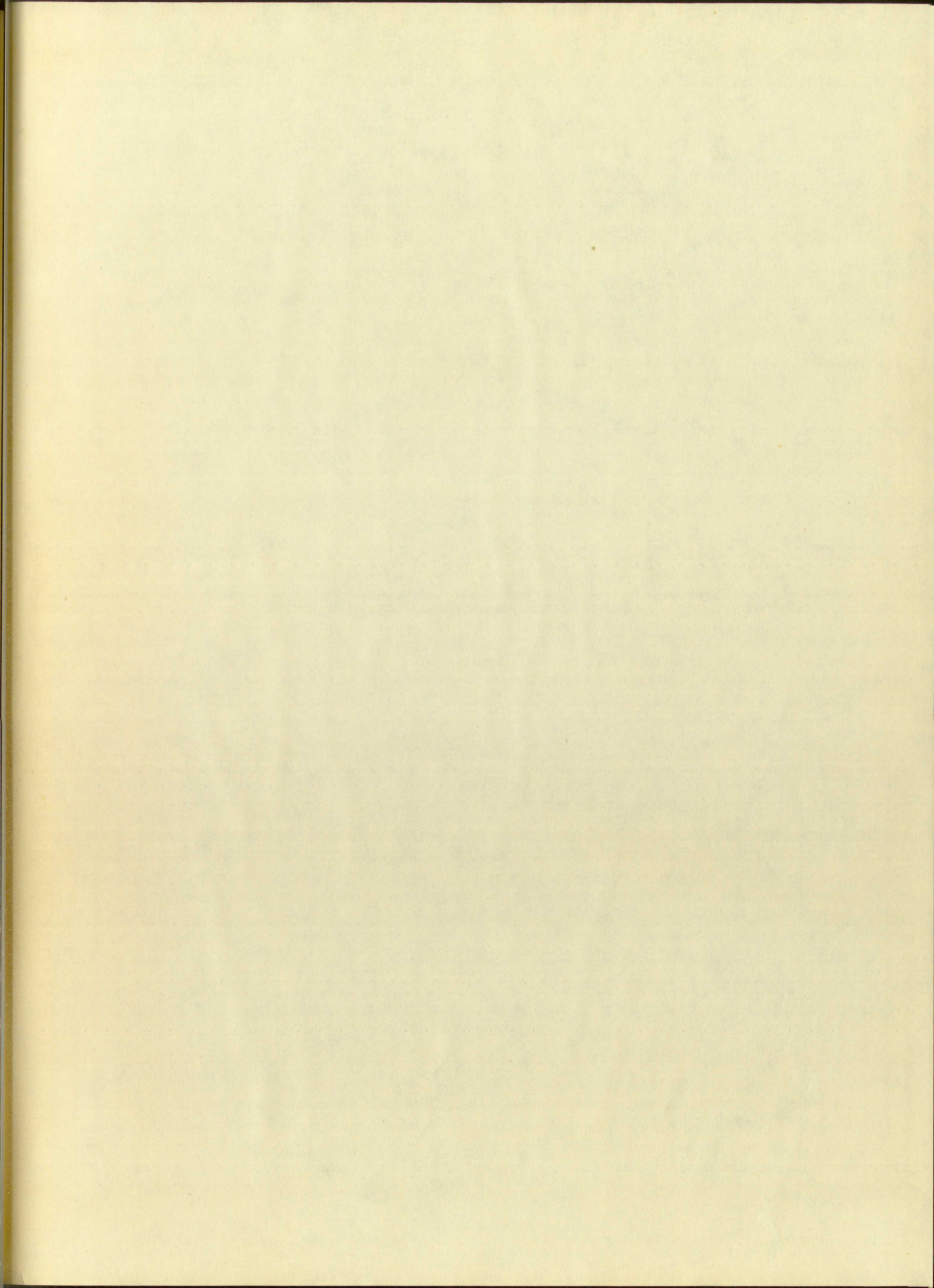


















A STUDY OF MAGNESIUM SILICATE AS A BASE MATRIX MATERIAL  
FOR FLUORESCENT MATERIALS

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A Thesis

Presented to

The Faculty of the Department of Chemistry  
University of New Mexico

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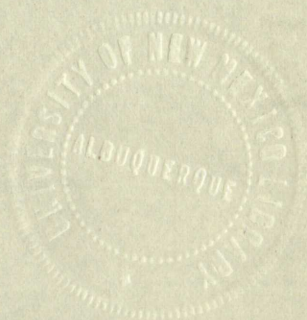
In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science

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by

John D. Hopperton

June 1949





A STUDY OF HANDBOOKS IN A NEW METHOD

FOR THE STUDENT



A STUDY

OF HANDBOOKS

IN THE DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NEW YORK

IN THE DEPARTMENT OF CHEMISTRY

OF THE UNIVERSITY OF NEW YORK

BY

JOHN D. HOPKINSON

1900



This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

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DATE

A STUDY OF MAGNESIUM SILICATE AS A BASE MATRIX MATERIAL  
FOR FLUORESCENT MATERIALS

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FOR FLUORESCENT MATERIALS

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## HISTORICAL INTRODUCTION

Luminescent materials have come into wide and important use within the past ten years in such equipments as the fluorescent lamp, and the cathode ray television tube. Because of this wide interest and usage, there has been made a concentrated search for ever brighter luminescent materials. It has also been of importance to produce and investigate materials which would produce as wide a range of colors under excitation as possible.

Luminescent materials are in general divided into two distinct classes: fluorescent compounds, and phosphorescent compounds. The first of these classes comprises those materials that produce light<sup>a</sup> when under excitation by a source of shorter wave length. The second class of materials also produces light when excited, but in contrast to the first class, continues to produce light after the cessation of the excitation. These materials are said to phosphoresce, or glow.

Fluorescent materials can be further subdivided into two classes by nature of their chemical composition; i.e. organic compounds, and inorganic compounds. The first materials to attain wide importance were the inorganic materials, or phosphors. At the present time these materials are still the most widely used.

Phosphors are composed of three parts: the base matrix, the matrix modifier, and the activator. In general the base matrix constitutes the bulk of the phosphor, from 70 to 99 per cent. of the material. The matrix

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<sup>a</sup> Light: Radiant energy in the wavelength band between 4000 and 7500 Angstrom units.







modifier may be present in small amounts, of the order of 5 to 15 per cent. The activator is present in extremely small amounts: the order of  $10^{-6}$  to 1 per cent. Thus it can be seen that, for the production of a phosphor with the desired luminescent properties, there are three chemical variables. There are also a few physical variables which have an effect upon the luminescent properties of a phosphor. These will be discussed later.

Many phosphors are found in nature in such a form that they will luminesce when excited by ultra-violet light of the proper energy content. Such materials are willemite ( $\text{ZnSiO}_4\text{-Mn}$ ) and Calcite ( $\text{CaCO}_3\text{-Mn}$ ). The first applications of fluorescence were through the use of these materials. The minerals were ground to the proper fineness and applied to the device in which a fluorescent or phosphorescent screen was desired. There were many difficulties with this process, and very soon after the demonstration by men at the Radio Corporation of America and the General Electric Company that luminescent materials had commercial possibilities, research was started to produce these luminescent materials synthetically.

The first man to produce a synthetic willemite was Dr. H. W. Leverenz<sup>1</sup> at the RCA Laboratories in Harrison, New Jersey. With his discovery of some of the basic tenets for the production of a satisfactory phosphor, the work progressed with great speed. By 1940 there were known several systems that would produce satisfactory phosphors. Some of these

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<sup>1</sup> Leverenz, H. W., Private communication to author (1945).







systems were the zinc, beryllium silicate-manganese system, and the zinc-cadmium sulfide system.

It became evident early in fluorescent research that phosphors would have to be made specifically to fit particular applications. Phosphors appeared to fall into three classifications, depending upon the energy of the exciting radiation to which they were most sensitive. Because of the availability of certain fixed frequencies in the ultra-violet ( $3650 \text{ \AA}$ , and  $2537 \text{ \AA}$ , which are prominent lines in the mercury arc discharge spectrum) and of the broadness of the cathode ray spectrum, these three classes were defined as follows: (1) the long ultra-violet, or  $3650 \text{ \AA}$  class, (2) the short ultra-violet, or  $2537 \text{ \AA}$  class, and (3) the cathode ray class. While it was found that many materials would fluoresce to all three of these radiations, there was always one wavelength which gave a far greater efficiency. This class was then defined as the primary radiation class for the material. The other classes in which response was found were classified as secondary classes. Many materials show fluorescence to only one class, and are completely inactive under excitation of other types.

A typical material with class (1) as its primary class is zinc sulfide. This material fluoresces a brilliant blue under  $3650 \text{ \AA}$  radiation. It is completely inert to  $2537 \text{ \AA}$  excitation, but shows good fluorescence under cathode rays. Zinc silicate is very weak under  $3650 \text{ \AA}$  but glows brilliantly when excited with  $2537 \text{ \AA}$  radiation, or with cathode rays. Certain other of the silicates show no activity when exposed to ultra-violet



systems were the same, containing all the same elements, and the same amount of energy was being supplied to each of the systems.

It became evident that the systems were not identical.

It would have to be made a study of the systems to see if they were identical.

It was found that the systems were not identical.

The energy of the exciting radiation was found to be the same.

The cause of the availability of energy was found to be the same.

The energy of the exciting radiation was found to be the same.

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The energy of the exciting radiation was found to be the same.



radiation of any wavelength, but are quite active under X-ray or cathode ray excitation.

Since the silicates and the sulfides appeared to be desirable base materials at the very beginning, much of the work to date has used these materials as bases. They were desirable for a number of reasons. First, they were stable compounds which did not decompose on heating. Second, they were comparatively easy to obtain in the pure state, and finally, they were inexpensive chemical materials. Of these two classes, the silicates fulfilled the above mentioned requirements the best, but since the silicates were inert to long ultra-violet excitation, it was necessary to use sulfides in many cases.

The sulfide system (zinc, cadmium sulfide-manganese) is capable of fluorescence emission throughout the visible spectrum. Pure zinc sulfide-manganese fluoresces blue. The fluorescence becomes more red as more cadmium is added to the phosphor. In the silicate phosphors, pure zinc silicate-manganese is green, but the emission color of the phosphor shifts toward the red as more beryllium is added to the phosphor.

With either of the materials mentioned above, the efficiency of the production of fluorescent light decreases with the shift of the radiation toward the red end of the spectrum, for two reasons. First, the quanta of the emitted light,  $h$  becomes smaller, thus causing the quantum efficiency to drop. This is due to strictly quantum mechanical laws, and cannot be changed. The second reason for this drop in light emission is that the introduction of the matrix modifier, the cadmium or the beryllium, causes a partial deactivation of the phosphor. The reasons for this



radiation of any wavelength, but the only one which is  
ray excitation.

Since the emission and absorption spectra of the  
base materials at the very beginning, and the  
phenomena which are based on them. The first  
first, they were treated separately with the same  
second, they were comparatively easy to make a  
thirdly, they were independent of the  
the emission fulfilled the same conditions as the  
since the emission was found to be independent of the  
necessary to use emission in any case.

The ratio of the (that is, the ratio of the  
of fluorescence emission throughout the whole spectrum  
ultra-violet fluorescence line. The fluorescence  
more certain is added to the spectrum. In the  
and ultra-violet fluorescence is given, and the  
shifts toward the red as the ratio is added to the spectrum.

With either of the materials mentioned, the  
the production of fluorescence light depends on the  
tion toward the red end of the spectrum. For the  
quanta of the emitted light, a decrease in the  
efficiency to drop. This is one of the reasons  
cannot be changed. The second reason for the  
that the introduction of the material into the  
causes a partial deactivation of the spectrum. The



deactivation are not known at the present time. Thus, one of the main objectives of researchers in the field of luminescence in the past few years has been to find a phosphor that would produce a good red, with high efficiency.

For the reasons stated previously, silicate materials have many desirable properties. Therefore it occurred to Leverenz<sup>2</sup> in 1940 to try magnesium silicate as a base matrix for phosphors. He made two materials of the general composition  $\text{MgSiO}_4\text{-Mn}^b$ , and found that they would give a good red fluorescence under cathode ray excitation, but that they were completely inactive to ultra-violet excitation. Any further investigation was dropped because of the exceedingly high firing temperature ( $1600^\circ\text{C.}$ ) required by these materials. These experiments were repeated in 1944 by Applegate and Hopperton<sup>3</sup>, with the same results.

Early in 1945, H. C. Froelich<sup>4</sup> at the Lamp Development Laboratory of the General Electric Company began a series of investigations of the

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<sup>b</sup>  $\text{MgSiO}_4\text{-Mn}$ . The first part of this formula indicates that the base matrix is magnesium silicate in the stoichiometric ratio. The symbol after the dash indicates that the activator is manganese. Since no percentage is indicated, either this is not known, or is withheld. When a percentage is shown, it indicates the Mole per cent of the activator present.

<sup>2</sup> Leverenz, H. W., Notebook Reference, R.C.A. Laboratories, Princeton, New Jersey, (1940).

<sup>3</sup> Applegate, R., and Hopperton, J. D., Progress Report, R.C.A. Laboratories, Princeton, New Jersey, (1944).

<sup>4</sup> Froelich, H. C., Laboratory Report, Lamp Development Laboratory, General Electric Company, Nela Park, E. Cleveland, Ohio, (1945).







system calcium silicate-manganese. He found that this material would fluoresce under cathode rays, but was inert to ultra-violet. The color was a yellow-orange. After considerable experimentation, he found that the lack of ultra-violet activity in this material was caused by the lack of absorption of the impinging ultra-violet by the material. He thereupon added a small amount of lead to the matrix and obtained the desired ultra-violet activity. Because of the very high firing temperatures required for magnesium silicate phosphors, work was not attempted on this class of materials.



system calcium chloride. The system was  
flashed under vacuum and the system was  
was a yellow-orange. The system was  
the lack of ultra-violet activity in the system was  
lack of absorption in the ultra-violet region of the spectrum.  
The system was a weakly absorbing system and  
desired ultra-violet activity. The system was  
three regions for absorption in the ultra-violet region  
as this shows of absorption.



### STATEMENT OF THE PROBLEM

The purpose of the work herein described and discussed was to study the phosphor system built upon magnesium silicate as a base matrix material.

The particular phase of this study undertaken was a comprehensive survey of the activator materials, and an exhaustive study of one or two of these activator materials.



The purpose of this study is to study the physical properties of the matrix material.

The present study is a part of a series of studies on the physical properties of the matrix material. The results of the study are given in the following table.



## DISCUSSION

For a number of years there has been a definite need in the field of luminescence for a material that would produce a bright red emission under excitation from cathode rays, short and long ultraviolet, and other types of radiation. Magnesium silicate phosphors, according to the work of early investigators, showed some promise in this direction.

From Table 1, in the experimental section, it can be seen that the majority of magnesium silicate phosphors are not sensitive to ultraviolet excitation. Those that did show some sensitivity were either red or red-orange in color. All, except the cerium activated material, were of very low brightness, and therefore were not studied further.

In the preparation of a phosphor there are three main variables which must be kept under control in order to produce a satisfactory product. These variables are: composition, firing temperature, and firing time. Unless all three of these variables are investigated, and known, the best efficiency of the phosphor cannot be obtained. Therefore in the investigation of a new phosphor one must determine the optimum combination of these three factors.

Figures 1 through 3, together with Tables 2 through 9, show the results of these three variables on the brightness of magnesium silicate-cerium phosphor. Figure 2 is the typical brightness versus time curve obtained for a phosphor. The brightness is zero without firing, and then rises rapidly for the short time firings. After this rapid rise there is a slower rise to some limiting brightness.



## DISCUSSION

For a number of years there has been a general feeling of dissatisfaction for a material which would give a high emission under excitation from certain light sources. Various types of cathodes, violet, and other types of cathodes, have been investigated according to the work of early investigators, but no material has been discovered.

From Table I, in the experimental section, it can be seen that the majority of magnesium ribbons have been used in the violet excitation. Those that did not give satisfactory results were or red-orange in color. All, except one, were of high brightness, of very low brightness, and therefore were not used.

In the preparation of a phosphor, there are three main variables which must be kept under control in order to obtain a satisfactory product. These variables are: composition, time of burning, and time of drying. Unless all three of these variables are controlled, the best efficiency of the phosphor cannot be obtained. In the investigation of a new phosphor, the most important factor is the control of these three factors.

Figures 1 through 3, taken from Table I, show the results of these three variables on the efficiency of a certain phosphor. Figure 1 is the typical result of a phosphor obtained for a phosphor. The efficiency is low with a low rise, rises rapidly for the short time burning, and then falls to a slower rise to some initial brightness.



The reason for this curve shape can be seen from an understanding of what happens in the firing process. There is no chemical reaction in the usual sense, because the composition of the product is unchanged from that of the starting material. Two main changes occur during the firing process: first, there is a diffusion of the various materials throughout each other to give a more complete and even mixing of the compounds present, and second, there is a crystallization of the base matrix into small, well formed, independent crystals. Unless this crystallization takes place there is no luminescence in the final product. This crystallization process is slow, and therefore the firing times must be long. Higher temperatures will speed up this crystallization process, but fusion must be avoided, since this destroys the crystalline nature of the solid.

Since there must be a crystallization of the material, and because brightness is dependent upon the completeness of this crystallization, the explanation of the shape of the observed curve can be seen readily. At first, there are no crystals present, and therefore no brightness. The curve then rises rapidly for the short time firings because the addition of a few crystals into the uncrystallized material makes a large percentage change in the total number of crystals present, and thus in the total brightness. But, as the firing times are increased and the crystallization becomes more complete, the percentage change in brightness, due to the addition of a few more crystals, is small, and therefore the curve bends and approaches a maximum value more slowly. When all the material has been crystallized, then further firing should produce no increase in







brightness. This is the case, if oxidation, reduction, or volatilization do not occur.

The curve of Figure 3 has the same general shape, and for the same reasons. The explanation of the greater ultimate brightness of the material represented by Figure 3 is the added silica which was put into this phosphor. Because of this added silica there is now enough silica present in the phosphor to allow for the complete crystallization of both magnesium silicate, and cerium silicate. In previous phosphors there was a deficiency of silica. When this is the case, the crystallization of the base matrix is disturbed, and the crystals formed under these conditions are not perfect, resulting in a loss of brightness.

When the amount of silica present is made even smaller, by the addition of excess magnesium oxide, the brightness is again lowered. This is shown in Tables 7 and 8. This loss is greatest at the short firing times, and is overcome by the use of longer firing times, which allows a more even distribution of the available silica.

The curves of Figure 1 show another effect that is observed in the preparation of phosphors, namely the effect of fusion. Curve A, the 1000°C. curve, shows the typical brightness versus time distribution. Since this curve is still rising at the end of the 24 hours, it indicates that crystallization is still taking place. Curve B, the 1100°C. curve, also shows the typical shape. Since it is almost at the maximum value by the end of the 24 hours of firing it indicates that crystallization is almost complete. But curve C, the 1200°C. curve, appears to be completely out of line. One would expect it to be above the other two curves, to reach a



brightness. This is the only case in which the brightness  
is not zero.

The curve of Figure 2 has the same shape as the curve of  
Figure 1. The explanation of the same phenomenon is the same.  
The material represented by Figure 2 is a mixture of the  
two phosphors. Because of the ratio of the two phosphors  
present in the phosphor mixture, the curve of Figure 2  
both negative all over, and positive all over. In fact,  
there was a deficiency of light. The curve of Figure 2  
action of the base matrix is different, and the curve of  
these conditions are not good, resulting in a curve of  
When the amount of light is small, the curve of Figure 2

action of the negative matrix, the curve of Figure 2  
is shown in Figure 3 and 4. The curve of Figure 3  
shape, and is overcome by the curve of Figure 4, which  
more even distribution of the curve of Figure 4.

The curve of Figure 4 is the same as the curve of Figure 3  
proportion of phosphor, which is the curve of Figure 4.  
curve, shows the typical shape of the curve of Figure 4.  
curve is still rising to the end of the curve of Figure 4.  
elliptical in the curve of Figure 4. The curve of Figure 4  
the typical shape. The curve of Figure 4 is the curve of Figure 4.  
the 25 hours of time of the curve of Figure 4. The curve of Figure 4  
plate. But curve 2, the curve of Figure 4, is the curve of Figure 4.  
line. One would expect it to be the curve of Figure 4.



steady state in a shorter time, and then to remain at that value.

The explanation of the different shape of this curve lies in the nature of luminescence in solids. It has been found that the actual production of the luminescent radiation takes place only on the surface of a crystal. There is no light produced from the body of the crystal. This can be best shown by fracturing a phosphor crystal under a microscope. When this crystal is then excited, it can be seen easily that the faces formed by the fracture are inactive and produce no brightness. This effect is also observed in another manner. When a fluorescent material is ball milled to produce a more uniform particle size, there always occurs a drop in brightness with this ball milling. This loss of brightness is caused by the fracturing of crystals, exposing dead or inactive surfaces, which absorb the incident radiation, but do not produce any fluorescent light from it. Fusion of a phosphor produces the same result. It destroys crystal surfaces and thereby reduces brightness.

This effect can be seen in curve C or Figure 1. At 1200°C. fusion can take place within the phosphor. The low brightness, even with the short time firing, indicates that fusion has taken place to a large extent. It can be presumed that, if the firing time were short enough, crystallization could take place without fusion, and a bright phosphor would be produced at this temperature. This is shown by the dotted portion of the curve. This firing time would in all probability be of the order of  $1/2$  to  $3/4$  of an hour. In the long time firings, fusion was complete and the brightness of the phosphor was almost zero.







Magnesium silicate is a very high melting material and should not undergo fusion at the low temperature used in these experiments. The explanation for this behavior of magnesium silicate is that the crystals in all probability are not pure magnesium silicate crystals. They more likely are a mixed crystal of magnesium and cerium silicate. This statement is based upon the fact that, as the amount of cerium in the phosphor was increased, the temperature at which fusion took place was lower.

In other phosphors where the activator was present in very small concentrations, and was not of the rare earth type, it was found that fusion would not take place until the temperature was raised several hundred degrees above the range used in the experiments of this paper.

Some discussion should be made of the other magnesium silicate phosphor studied in this work; i.e. magnesium silicate activated with vanadium. This material gave a bright yellow fluorescence when excited by long ultra-violet radiation, whenever perfect crystals were formed. The number of these crystals was very small at the low firing temperatures that had to be employed. While long time firings, of the order of three days were used, the temperature that could be obtained, 1200°C., was not high enough to give good crystallization. It is believed that this phosphor may have possibilities when it is more fully investigated.







## EXPERIMENTAL PROCEDURE

Reagents: All the phosphors synthesized during this work were made from highest quality reagents. The silica used was obtained from the Mallinckrodt Chemical Company and is known as "phosphor" grade fluffy silica. The magnesium oxide was obtained from the same source and was of the same degree of purity. The lead salts used were Merck Reagent grade, while the cerium nitrate came from the G. Friderick Smith Chemical Company and was of reagent purity. All the water used in the syntheses was obtained by a simple distillation of Albuquerque City water through a conventional Barnstead still. No analysis was made to determine the purity of the water.

Apparatus: The equipment used in this project can be divided into two groups: that necessary for the compounding of the phosphor, and that necessary for the heat treating of the phosphor. All the vessels, stirring rods, etc. used in the compounding of the phosphors were of glass. All storage vessels were of glass, both for unfired and fired materials.

The furnace for the firing of these materials was of the Glo-Bar type. The materials of construction used were Babcock and Wilcox K-20 and K-26 bricks. The hearth was a Corundum slab. The volume of the firing chamber was approximately  $1\frac{1}{2}$  cubic feet, heated by four 55V-25A. Glo-Bar elements. These elements were arranged in such a manner as to have two of the elements operating all the time, and two elements operating on an intermittent basis. The element nearest the door was made out of the continuous elements, in order to minimize the effect of the colder wall of the door. The two intermittent elements were controlled by means of a Wheelco Capacitrol controller. The controller was actuated by a Platinum-Platinum,



1. Introduction

The purpose of this study is to investigate the effect of the concentration of the solution on the rate of reaction. The reaction studied is the reaction between potassium dichromate and oxalic acid in the presence of sulfuric acid. The reaction is as follows:

$$K_2Cr_2O_7 + H_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 2CO_2 + 2H_2O$$

The rate of reaction was determined by measuring the volume of carbon dioxide gas evolved over a period of time. The experiment was carried out at different concentrations of potassium dichromate and oxalic acid, and the effect of temperature was also studied.

The results of the experiment show that the rate of reaction increases with an increase in the concentration of potassium dichromate and oxalic acid. The rate of reaction also increases with an increase in temperature. The order of reaction with respect to potassium dichromate was found to be one, and with respect to oxalic acid it was also found to be one. The overall order of reaction was found to be two. The activation energy of the reaction was calculated to be 50 kJ/mol.

The following table shows the effect of the concentration of potassium dichromate on the rate of reaction:

Concentration of $K_2Cr_2O_7$ (M)	Rate of reaction (mol/l.s)
0.01	0.001
0.02	0.002
0.04	0.004
0.08	0.008

The following table shows the effect of the concentration of oxalic acid on the rate of reaction:

Concentration of $H_2C_2O_4$ (M)	Rate of reaction (mol/l.s)
0.01	0.001
0.02	0.002
0.04	0.004
0.08	0.008

The following table shows the effect of temperature on the rate of reaction:

Temperature (°C)	Rate of reaction (mol/l.s)
25	0.001
35	0.002
45	0.004
55	0.008



13% Rhodium thermocouple placed in the roof of the furnace. This couple was so placed as to register as accurately as possible the temperature of the samples in the furnace.

By means of the control apparatus mentioned above it was possible to control the temperature of the furnace to within 5 degrees Centigrade in the temperature range of 900 to 1300°C.

All firing of the phosphors was conducted in Corning Vycor Brand vessels. These vessels, being over 96% silica will give the least contamination of the phosphor during the firing. They also will withstand the temperatures of firing better than anything except fused quartz.

The final piece of apparatus used in this work was a simple photo-cell photometer. The cell used was a General Electric Type 88x565 photo-voltaic cell directly connected to a Weston 0 to 30 microampere microammeter. No shunts or series resistances were used in this circuit. This cell was then placed in such a position that it looked at a specific portion of the sample under test. The phosphor samples were excited by radiation of approximately  $3650 \text{ Å}$  from a General Electric H-4 mercury arc lamp. This lamp was covered with a Corning No. 5860 ultra-violet filter. This filter eliminated almost all the visible radiation from the source. The H-4 lamp was operated from the 110V. line through the recommended ballast transformer. The line was connected to this transformer through a variac so that the applied voltage could be controlled. This applied voltage was measured by means of a voltmeter, and adjustments were made of the variac to keep this applied voltage constant. The distance between the lamp and the sample, and between the sample and the cell were kept







constant for all measurements. In order to have all the measurements directly comparable, a standard sample was measured from time to time, and corrections made through the use of this sample.

Qualitative tests as to light output under excitation by 2537 Å radiation and cathode rays were made also. The 2537 Å source was a General Electric 8-watt Germicidal lamp, operated through its recommended ballast. For the testing with cathode rays, the phosphors were placed in an evacuated chamber, and the cathode rays generated by means of a Shelton coil.

All measurements were made after 9 P.M. in the evening to preclude any interference from stray daylight.

Procedure: In all the syntheses made for this project the wet process of phosphor synthesis was used. The main steps in this process are as follows.

1. The activator compound to be used was weighed on a suitable balance and dissolved in an appropriate volume of distilled water.
2. The magnesium oxide was weighed and added to the water solution of the activator with vigorous stirring. Before this addition care was taken to be sure all the activator was dissolved. The stirring was continued for at least fifteen minutes after the addition of the magnesium oxide.
3. The silica was weighed and also added to the solution of activator and suspension of magnesium oxide. This addition was made slowly. The vigorous stirring was continued for at least thirty minutes after the addition of the silica was complete.



constant for all measurements. A series of tests was made to determine the effect of the concentration of the solution on the rate of reaction and corrections were made to the rate of reaction.

Qualitative tests were made to determine the effect of the concentration of the solution on the rate of reaction. The results of these tests are given in Table I. The rate of reaction was found to be directly proportional to the concentration of the solution. The rate of reaction was also found to be directly proportional to the square of the concentration of the solution. The rate of reaction was also found to be directly proportional to the cube of the concentration of the solution.

All measurements were made at 25°C. in the presence of 0.1M sodium chloride. No interference from other ions was observed.

Procedure: In all the experiments made for this study, the same procedure was used. The reaction mixture was prepared by adding a known volume of a known concentration of the reactants to a known volume of a known concentration of the catalyst. The reaction was allowed to proceed for a known time and the reaction was then stopped by adding a known volume of a known concentration of a reagent.

1. The catalyst compound was dissolved in a known volume of water and the solution was diluted to a known volume. The catalyst was then added to the reaction mixture. The reaction was allowed to proceed for a known time and the reaction was then stopped by adding a known volume of a known concentration of a reagent. The reaction was then allowed to proceed for a known time and the reaction was then stopped by adding a known volume of a known concentration of a reagent.

2. The reaction mixture was then allowed to proceed for a known time and the reaction was then stopped by adding a known volume of a known concentration of a reagent. The reaction was then allowed to proceed for a known time and the reaction was then stopped by adding a known volume of a known concentration of a reagent. The reaction was then allowed to proceed for a known time and the reaction was then stopped by adding a known volume of a known concentration of a reagent.



4. The resulting suspension was allowed to stand in a warm place, such as on a sand bath, until all the water had evaporated.

5. After this was completed, the resulting phosphor cake was broken up in a mortar, and then pulverized. It was then ready for firing.

6. The material was then fired under the desired conditions, cooled in air, and stored until suitable measurements could be made.

The above procedure was carried through on all the samples prepared for this report. At times, due to circumstances, slight modifications were necessary, but these deviations from the above procedure were of a minor nature and had no effect upon the results. In those cases where these minor changes were necessary, cross checks were made at a more convenient time, and no differences were found.



4. The resulting magnetite was allowed to stand in a warm place, such as on a sand bath, until all the water had evaporated.

5. After this was completed, the resulting phosphor cake was broken up in a mortar, and then pulverized. It was then ready for

analysis.

6. The material was then fired under the desired conditions, cooled in air, and stored until suitable measurements could be made.

The above procedure was carried through on all the samples prepared for this report. At times, due to circumstances, slight modifications were necessary, but those deviations from the above procedure were of a minor nature and had no effect upon the results. In those cases where these minor changes were necessary, cross checks were made at a later convenient time, and no differences were found.



## EXPERIMENTAL RESULTS

In the course of the work 19 different single activator, 3 different double activator, and 1 triple activator phosphors were synthesized. None of these phosphors showed any response to excitation of 2537  $\overset{\circ}{\text{A}}$  wavelength. The results of these preliminary investigations are shown in Table 1. Also in this table are shown the colors observed for these materials under the various excitation wavelengths.

From this list of possible phosphors, two were selected for further study. The two were the cerium and the vanadium activated materials. Of the two, the cerium phosphor appeared to be the most promising, and was therefore given the more intensive investigation.

The results obtained with the cerium activated phosphors are shown in Tables 2 through 9. The brightness values given in these tables are all reduced to a common base, and therefore are directly comparable to each other.

Three of the more representative Tables have been plotted. See Figures 1 through 3.

Several additional isolated experiments were made to determine whether the addition of either lead or manganese, or both would have any effect upon the long ultra-violet efficiency of the magnesium silicate phosphor. It also was thought that, as in the case of calcium silicate phosphor, the addition of lead might cause the excitation sensitivity band about 2537  $\overset{\circ}{\text{A}}$  to appear. The results from these experiments indicate that there is little or no effect from the addition of either lead or manganese, or both, to this series of phosphors. In all cases tried, there was either no



## EXPERIMENTAL RESULTS

In the course of the work it was found that the

element double absorption, which is a characteristic

of some of these elements, is not observed in

232V  $\gamma$  rays. The results of these experiments are

shown in Table I. Also in this table are given the

three materials under the action of which

from this list of possible absorbers, was found to be

that of the two, the action of the other is not observed.

Of the two, the action of the other is not observed.

Therefore given the above results

The results obtained with the action of the

in Table I. The results of these experiments are

all reduced to a common base, and it is seen that

other.

Thus of the more than 20 elements listed in Table I, the

Figures 1 through 3.

Several additional experiments were made to determine

whether the addition of other elements to the

effect upon the long absorption coefficient of the

phases. It also was found that, as in the case of

the addition of lead with some of the elements

232V  $\gamma$  rays appear. The results of these experiments are

is little or no effect upon the absorption of the

both, so this series of experiments is all negative.



change or a decrease in brightness upon addition of these compounds. For this reason, this path was not followed any further.

After the completion of the work on the cerium phosphor, work was begun on the vanadium activated phosphor. This work was hampered by the lack of a suitable furnace for the proper firing of this material. All indications, at the present time, are that this group of phosphors will require firing temperatures in excess of  $1500^{\circ}\text{C}$ . The proper firing temperatures are in all probability about  $1600$  to  $1650^{\circ}\text{C}$ .

Since the simple Glo-Bar furnace constructed would not be safe to operate at such temperatures, even if it would do so, the only work on these vanadium phosphors was of an exploratory nature. All firings were made at  $1200^{\circ}\text{C}$ ., the highest safe operating temperature for the laboratory furnace.

From these preliminary tests, it appears that the proper activator concentration for this phosphor is about 0.01% vanadium. Several phosphors were made with a range of activator concentrations, and from an examination of these materials, the above mentioned figure was obtained.







TABLE 1

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<u>Activator Element</u>	<u>Firing Time and Temperature</u>	<u>Color</u>	
		<u>3650 Å</u>	<u>Cathode Rays</u>
None	3 hours - 1200°C.	None	None
Manganese	5½ hours - 1200	None	Red
Lanthanum	3 hours - 1200	None	Red
Europium	5½ hours - 1200	None	White
Neodymium	4½ hours - 1200	None	Red-yellow
Cerium	3 hours - 1200	Red	Red
Chromium	6 hours - 1200	None	Red
Yttrium	4½ hours - 1200	None	White
Samarium	4½ hours - 1200	None	Orange
Vanadium	3 hours - 1200	Yellow	Yellow-green
Dysprosium	3 hours - 1200	None	Yellow
Scandium	3 hours - 1200	None	Blue
Gadolinium	3 hours - 1200	None	Blue
Nickel	2 hours - 1200	None	None
Cobalt	2 hours - 1200	None	None
Iron	2 hours - 1200	None	None
Titanium	6 hours - 1200	Pink	Blue
Tantalum	6 hours - 1200	None	None
Ruthenium	6 hours - 1200	None	Red
Lead	2 hours - 1100	None	None
Manganese and Lead	2 hours - 1200	Red	Red
Manganese and Lanthanum	3 hours - 1200	Red	Red
Cerium and Lead	11 hours - 1100	Red	Red
Manganese Cerium and Lead	15 hours - 1100	Red	Red



Isotopic elements

Isotope	Atomic weight	Abundance	Half-life
Hydrogen	1.0078	99.985%	
Deuterium	2.0141	0.015%	
Helium	4.0026	100%	
Lithium	6.941	92.5%	
Beryllium	9.0122	100%	
Boron	10.811	80.1%	
Carbon	12.011	98.9%	
Nitrogen	14.0064	99.6%	
Oxygen	15.9994	99.96%	
Fluorine	18.9984	100%	
Neon	20.1797	90.5%	
Sodium	22.9897	100%	
Magnesium	24.304	78.9%	
Aluminum	26.9815	100%	
Silicon	28.0855	92.2%	
Phosphorus	30.9737	100%	
Sulfur	32.06	95.0%	
Chlorine	35.453	75.8%	
Argon	39.948	99.6%	
Potassium	39.0983	93.3%	
Calcium	40.078	96.9%	
Scandium	44.9559	100%	
Titanium	47.88	92.5%	
Vanadium	50.9415	99.8%	
Chromium	51.9961	73.8%	
Manganese	54.9380	100%	
Iron	55.845	91.7%	
Cobalt	58.9332	100%	
Nickel	58.6934	68.1%	
Copper	63.546	100%	
Zinc	65.38	100%	
Gallium	69.723	100%	
Germanium	72.630	70.0%	
Arsenic	74.9216	100%	
Selenium	78.96	62.9%	
Bromine	79.904	50.7%	
Krypton	83.80	56.0%	
Rubidium	85.4678	27.8%	
Strontium	87.62	91.0%	
Yttrium	88.9058	100%	
Zirconium	91.224	51.5%	
Niobium	92.9063	62.6%	
Molybdenum	95.94	15.9%	
Technetium	98.9062	0.012%	
Ruthenium	101.07	1.87%	
Rhodium	102.9055	100%	
Palladium	106.9051	100%	
Silver	107.8682	100%	
Cadmium	112.411	24.1%	
Indium	114.818	96.9%	
Thallium	118.710	100%	
Lead	127.403	22.1%	
Bismuth	125.754	100%	
Polonium	209	100%	
Astatine	210	0.0000001%	
Radium	226	0.0000001%	
Actinium	227	0.0000001%	
Thorium	232	100%	
Protactinium	231	0.0000001%	
Uranium	238	99.274%	
Neptunium	237	0.0000001%	
Plutonium	244	0.0000001%	
Americium	243	0.0000001%	
Cerium	140.12	100%	
Lanthanum	138.905	100%	
Praseodymium	140.9076	100%	
Neodymium	144.242	100%	
Europium	151.964	100%	
Gadolinium	157.25	100%	
Terbium	158.9253	100%	
Dysprosium	162.5001	100%	
Ytterbium	173.045	100%	
Lutetium	174.967	100%	
Hafnium	178.49	100%	
Tantalum	180.9479	100%	
Tungsten	183.84	100%	
Rhenium	186.207	100%	
Osmium	190.23	100%	
Iridium	192.222	100%	
Platinum	195.083	100%	
Gold	196.966569	100%	
Mercury	200.59	100%	
Thallium	204.377	100%	
Lead	207.2	100%	
Bismuth	208.9804	100%	
Polonium	209	0.0000001%	
Astatine	210	0.0000001%	
Radium	226	0.0000001%	
Actinium	227	0.0000001%	
Thorium	232	100%	
Protactinium	231	0.0000001%	
Uranium	238	99.274%	
Neptunium	237	0.0000001%	
Plutonium	244	0.0000001%	
Americium	243	0.0000001%	
Cerium	140.12	100%	
Lanthanum	138.905	100%	
Praseodymium	140.9076	100%	
Neodymium	144.242	100%	
Europium	151.964	100%	
Gadolinium	157.25	100%	
Terbium	158.9253	100%	
Dysprosium	162.5001	100%	
Ytterbium	173.045	100%	
Lutetium	174.967	100%	
Hafnium	178.49	100%	
Tantalum	180.9479	100%	
Tungsten	183.84	100%	
Rhenium	186.207	100%	
Osmium	190.23	100%	
Iridium	192.222	100%	
Platinum	195.083	100%	
Gold	196.966569	100%	
Mercury	200.59	100%	
Thallium	204.377	100%	
Lead	207.2	100%	
Bismuth	208.9804	100%	
Polonium	209	0.0000001%	
Astatine	210	0.0000001%	
Radium	226	0.0000001%	
Actinium	227	0.0000001%	
Thorium	232	100%	
Protactinium	231	0.0000001%	
Uranium	238	99.274%	
Neptunium	237	0.0000001%	
Plutonium	244	0.0000001%	
Americium	243	0.0000001%	



TABLE 2"A" Series

Magnesium Silicate - 1% Cerium raw material used (see note No. 1)

<u>Sample Number</u>	<u>Firing Temperature</u>	<u>Firing Time</u>	<u>Brightness</u>
1	1000 deg. C.	1 hour	5
2	1000	2	10
3	1000	3	40
4	1000	5	50
5	1000	10	50
6	1000	24	70
7	1100 deg. C.	1 hour	80
8	1100	2	80
9	1100	3	85
10	1100	5	85
11	1100	9	90
12	1100	24	100
13	1200 deg. C.	1	23
14	1200	2	20
15	1200	3	20
16	1200	5	15
17	1200	15 $\frac{1}{2}$	5
18	1200	24	5

Note No. 1. In referring to the concentration of the activator in a base matrix it is common practice to list the Mole per cent of the activator directly after the base matrix formula. Thus the 1% Cerium above indicates that 1 mole per cent of cerium as metal exists in the base matrix of magnesium silicate. When other compounds are also added to the matrix, such that it no longer exists as a true stoichiometrical compound, these are also mentioned as Mole per cent given directly after the activator concentration. (For example, see Table 5)

TABLE 3"B" Series

Magnesium Silicate - 0.1% cerium

These Phosphors did not develop any brightness, due to the low activator concentration.







TABLE 4

"C" Series  
Magnesium Silicate - 10% cerium

<u>Sample Number</u>	<u>Firing Temperature</u>	<u>Firing Time</u>	<u>Brightness</u>
4	1100 deg. C.	2 hours	90
3	1100	3	95
5	1100	9	95
2	1100	11	100
1	1100	25	100

TABLE 5

"D" Series  
Magnesium Silicate - 10% cerium - 100% added Silica

<u>Sample Number</u>	<u>Firing Time</u>	<u>Firing Temperature</u>	<u>Brightness</u>
1 Fusion occurred	3 hours	1200 deg. C.	5
2	2 hours	1100 deg. C.	100
5	5 $\frac{1}{2}$	1100	130
4	11 $\frac{1}{2}$	1100	130
3	24	1100	130

TABLE 6

"E" Series  
Magnesium Silicate - 25% cerium

<u>Sample Number</u>	<u>Firing Time</u>	<u>Firing Temperature</u>	<u>Brightness</u>
5	2 hours	1100 deg. C.	100
3	4 $\frac{1}{2}$	1100	120
4	6 $\frac{1}{2}$	1100	120
2	13	1100	120
1	23	1100	100



19th Series  
Hagnum Series - 100 Series

Sample Number	Time (min)	Time (min)	Time (min)
1	1100	1100	1100
2	1100	1100	1100
3	1100	1100	1100
4	1100	1100	1100

20th Series  
Hagnum Series - 100 Series

Sample Number	Time (min)	Time (min)	Time (min)
1	1100	1100	1100
2	1100	1100	1100
3	1100	1100	1100
4	1100	1100	1100

21st Series  
Hagnum Series - 100 Series

Sample Number	Time (min)	Time (min)	Time (min)
1	1100	1100	1100
2	1100	1100	1100
3	1100	1100	1100
4	1100	1100	1100



TABLE 7"F" Series

Magnesium Silicate - 5% cerium

<u>Sample Number</u>	<u>Firing Time</u>	<u>Firing Temperature</u>	<u>Brightness</u>
2	2 hours	1100 deg. C.	110
4	4	1100	110
5	6	1100	110
1	13 $\frac{1}{2}$	1100	100
3	26	1100	110
6	13 hours	1000 deg. C.	110

TABLE 8"G" Series

Magnesium Silicate - 5% cerium - 50% added Magnesium Oxide

<u>Sample Number</u>	<u>Firing Time</u>	<u>Firing Temperature</u>	<u>Brightness</u>
1	2 $\frac{1}{2}$ hours	1100 deg. C.	85
2	4	1100	95
3	6	1100	100
5	16	1100	110
4	27 $\frac{1}{2}$	1100	110

TABLE 9"H" Series

Magnesium Silicate - 5% cerium - 50% added Silica

<u>Sample Number</u>	<u>Firing Time</u>	<u>Firing Temperature</u>	<u>Brightness</u>
2	2 hours	1100 deg. C.	100
3	4 $\frac{1}{2}$	1100	105
4	8	1100	110
1	12 $\frac{1}{2}$	1100	90
5	26	1100	110



# TABLE 1

Wet Series  
Wet Series - 100 series

Sample Number	Wet Series	Wet Series	Wet Series
1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100
5	100	100	100
6	100	100	100

# TABLE 2

Wet Series  
Wet Series - 100 series

Sample Number	Wet Series	Wet Series	Wet Series
1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100
5	100	100	100
6	100	100	100

# TABLE 3

Wet Series  
Wet Series - 100 series

Sample Number	Wet Series	Wet Series	Wet Series
1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100
5	100	100	100
6	100	100	100



SUMMARY

1. Magnesium silicate will serve as a base matrix for phosphors that are sensitive to long ultra-violet and cathode ray excitation.
2. Magnesium silicate-cerium is a satisfactory phosphor for the production of red emission under long ultra-violet excitation.
3. Many of the other rare earths can also serve as activators for the magnesium silicate base, but due to the great expense, and limited amounts of these materials available, their use will be limited.
4. Magnesium silicate-vanadium phosphor appears to have promise as a yellow fluorescing material.



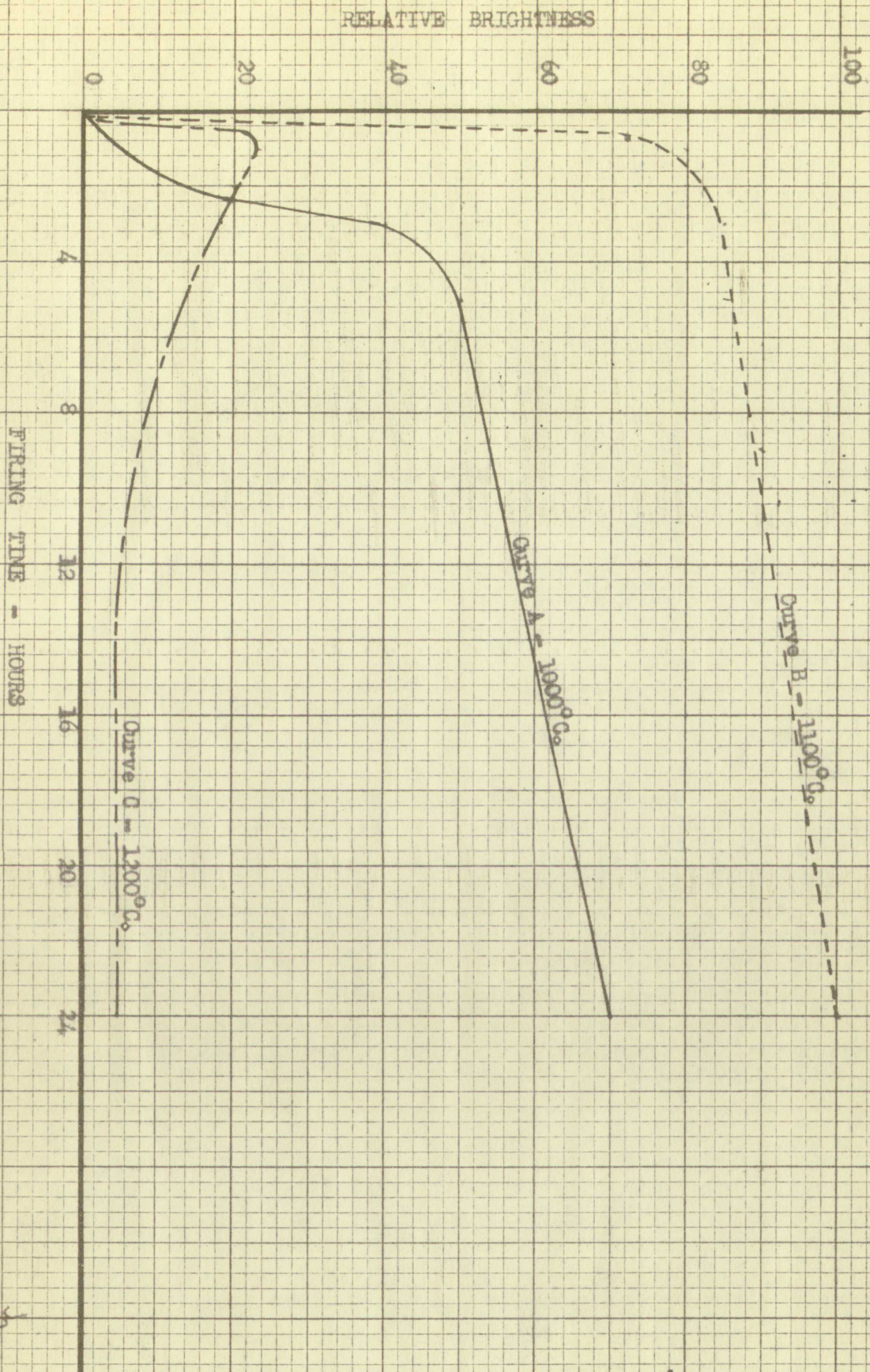
# Summary

1. Magnesium silicate will serve as a bone matrix for phosphorus that are sensitive to long ultra-violet and infrared ray irradiation.
2. Magnesium silicate-sulfate is a satisfactory preparation for the production of red injection under long ultra-violet irradiation.
3. Many of the other rare earths can also serve as substitutes for the magnesium silicate base, but due to the great expense, and limited amounts of these materials available, their use will be limited.
4. Magnesium silicate-yttrium phosphate appears to have promise as a yellow fluorescent material.



FIGURE 1

MgSiO<sub>3</sub> - 1% Ce<sub>2</sub>

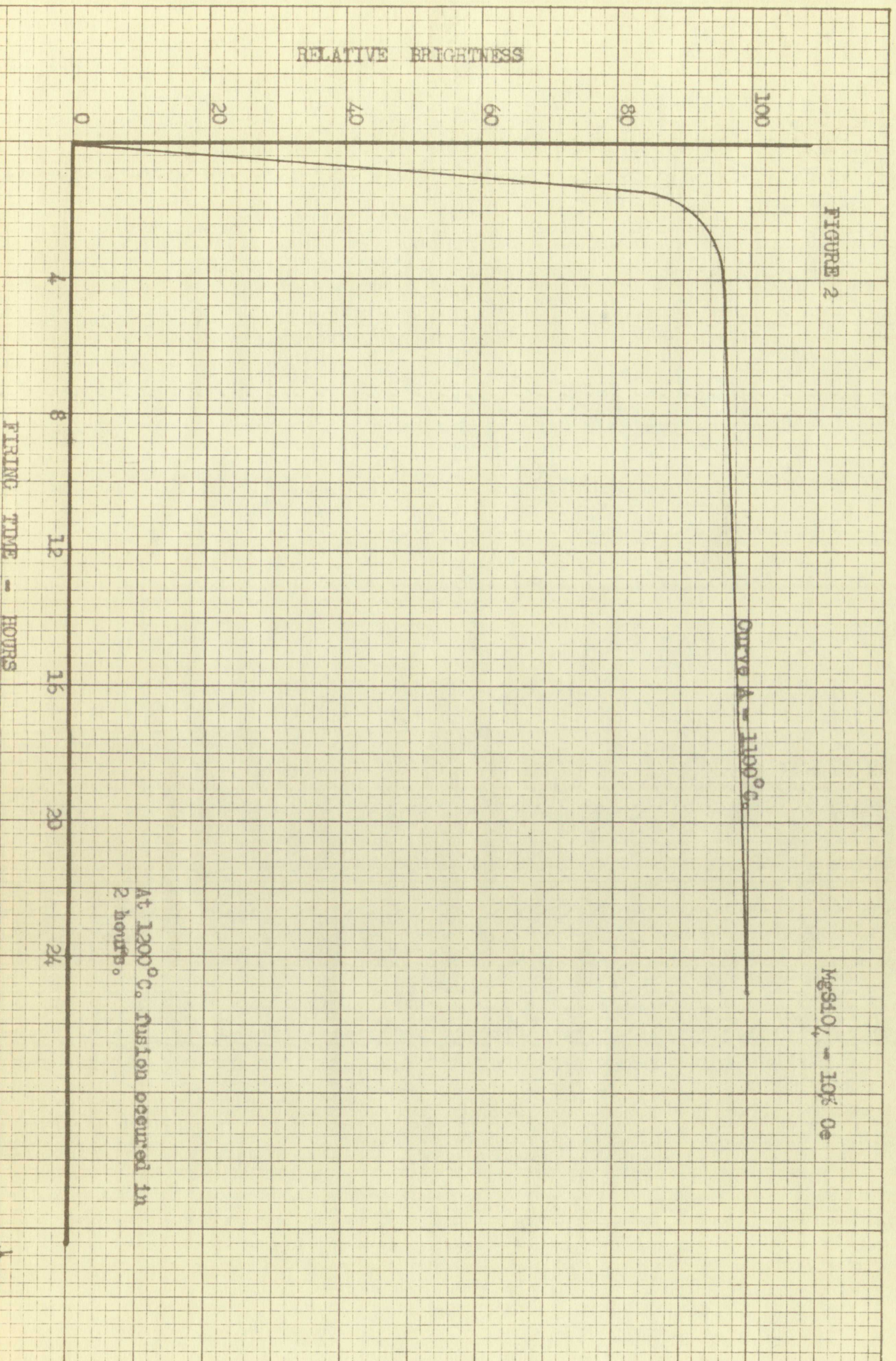


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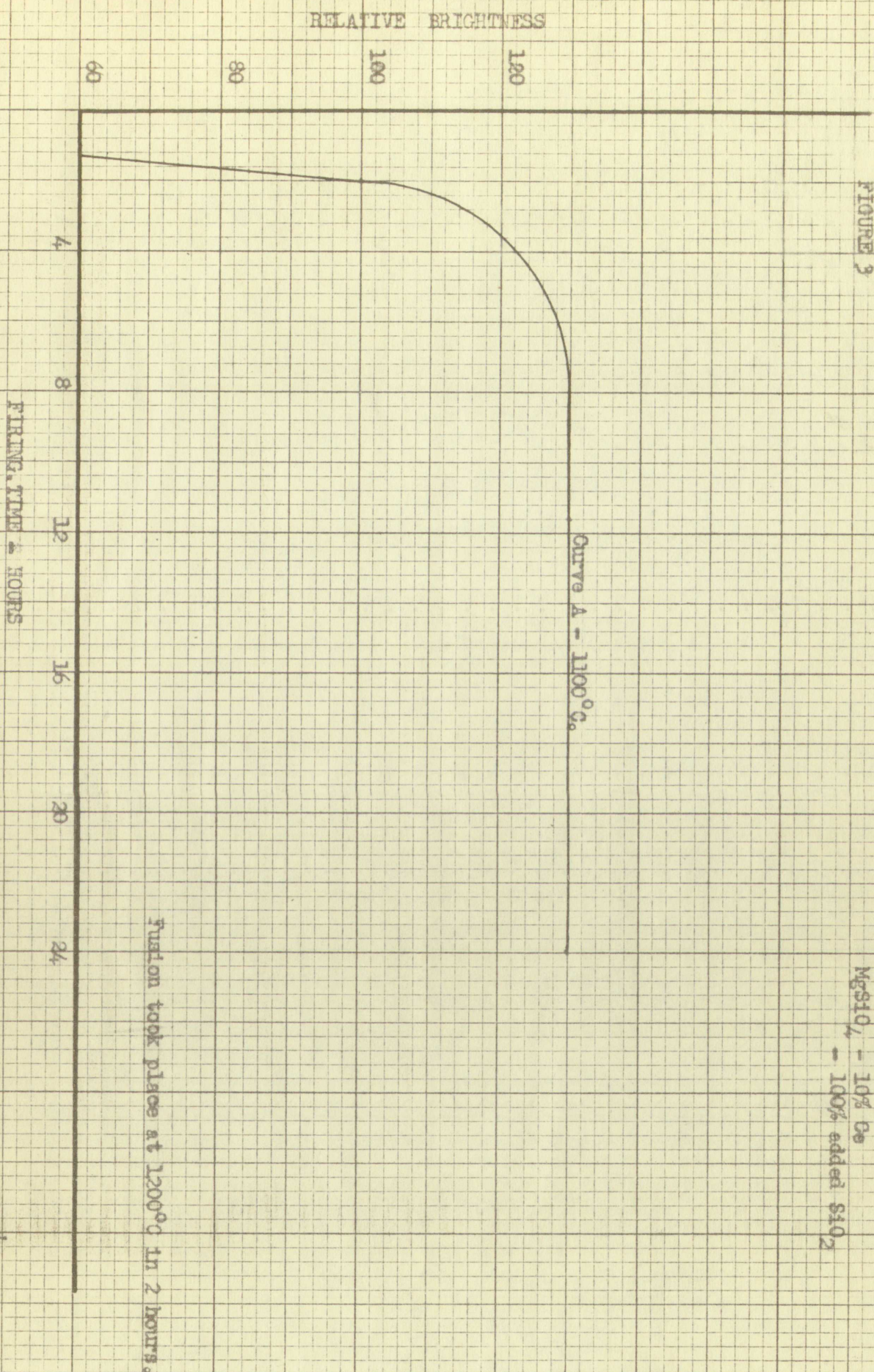






FIGURE 3

MgSiO<sub>4</sub> - 10% Ce  
- 100% added SiO<sub>2</sub>



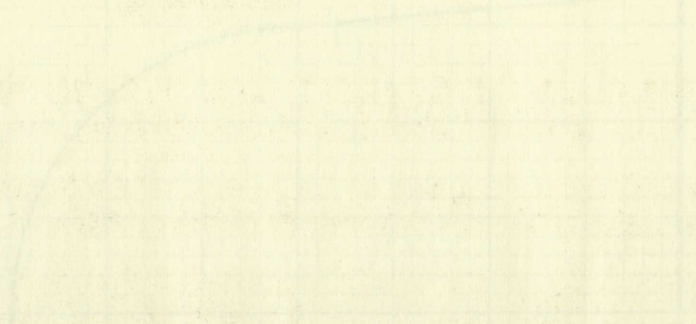
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SECTION 10

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SECTION 10





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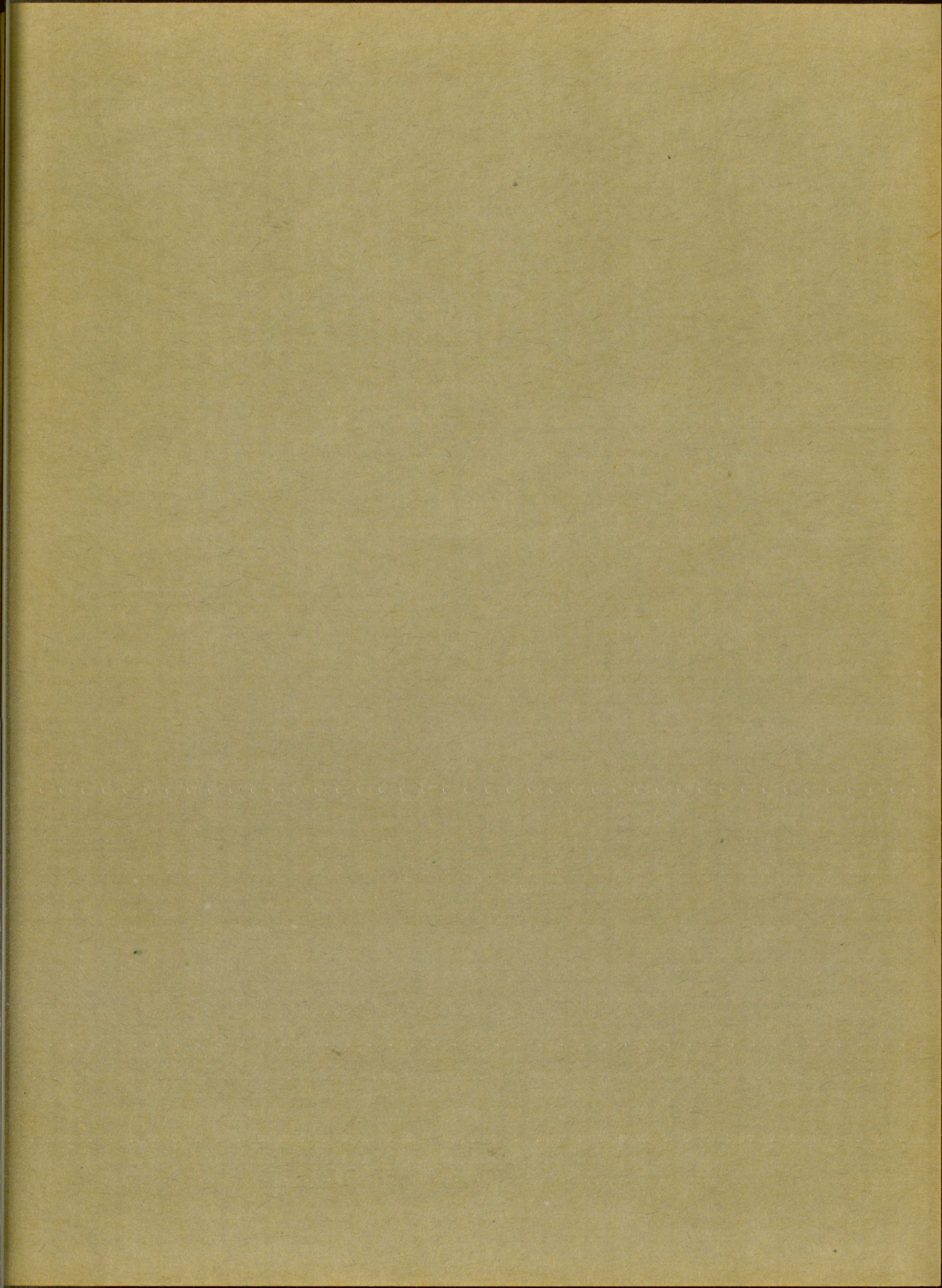














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