FINAL REPORT FOR DEVELOPMENT OF THIN TRANSPARENT PHOSPHORS

7 July 1965 to 31 October 1969

Contract NAS 5-9224

Prepared by

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for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Goddard Space Flight Center
Greenbelt, Maryland

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ABSTRACT

Silver-activated zinc sulfide phosphor films having high sensitivity have been produced by a three step process. A layer of zinc sulfide is first deposited by vacuum sublimation. Silver sulfide is deposited on the surface by immersion in a soluble silver salt. This is followed by firing in a non-oxidizing atmosphere containing sodium chloride. These films show good response to low energy protons, and when coupled to a suitable photomultiplier tube, provide a useful means of discriminating protons from other types of radiation.

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I. INTRODUCTION

This project is directed toward the development of instrumentation for detection of low energy protons, and to distinguish such radiation from other types of radiation such as electrons and gamma rays which are usually associated with the protons in outer space. Approximately four and one half years have been devoted to this work, resulting in the production of sensitive phosphor films, which, in combination with a suitable photomultiplier tube, are capable of detection of protons having energies as low as 10 Kev.

II. OBJECTIVE

The specific objective as outlined in the original contract was the development of thin transparent phosphor films having high proton sensitivity. The films were to be deposited on glass or other transparent substrates, suitable for coupling to the photomultiplier tube.

III. LINES OF ATTACK

Based on literature reports and our previous experience, it appeared that zinc sulfide would be the most promising candidate. A procedure described in the literature* for preparation of ZnS phosphor films was tried initially. This procedure, with suitable modifications yielded films having the required sensitivity, and major effort was directed toward optimization and evaluation of the response.

Twelve other phosphors originally proposed as alternate candidates were also investigated, with generally negative results.

IV. EXPERIMENTAL RESULTS

4.1. Zinc Sulfide

The zinc sulfide films were formed by vacuum deposition, followed by activation and aluminizing, in the following steps:

A. Preparation of substrates.
B. Vacuum deposition.
C. Activation.
D. Etching.
E. Aluminizing

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* A. Vecht and B. Ely, "The Migration of Activators in ZnS and ClS" Paper #41 - Toronto Meeting of Electrochemical Society, May 1964.

The material used for making the evaporated zinc sulfide films was commercial grade P11 zinc sulfide phosphor. A limited number of sources were tried in an attempt to obtain the best quality films. However, the material from which the zinc sulfide could be deposited, due to its sensitivity to contamination, was limited. Small quantities of some elements either cause an undesirable color shift or poison the luminescence completely.

4.1.1. Preparation of Substrates

Three types of substrates were used in determining which was best for this particular application. Corning 7059, Vycor and quartz substrates were used in the early stages of this project. Quartz was finally selected by the contracting agency as being the most desirable for this application because of its stability at the high activation temperature.

Substrates were cleaned in the usual manner for thin film depositions made in our thin film laboratory. This consisted of the following process.

1. Wash each substrate in detergent and water using an abrasive action of the hand.
2. Rinse under running water for 3 minutes.
3. Ultrasonically clean 2 times in trichloroethylene for 10 minutes each time.
4. Ultrasonically clean 2 times in acetone for 10 minutes each time.
5. Ultrasonically clean in boiling 50% nitric acid for 10 minutes. (Omit steps 5 and 6 for 7059 substrates).
6. Rinse 3 times in demineralized water for 1 minute each rinse while agitating the water and substrates.
7. Ultrasonically clean 3 times in demineralized water for 10 minutes each time.
8. Ultrasonically clean in methanol 2 times for 10 minutes each time.
9. Pour off last methanol cleaning solution and store dry.

Outgassing of the substrates was very important for good adherence and quality films. This was accomplished by heating the substrate in a pressure of less than 10^{-4} torr with lamps which utilized tungsten filaments and quartz envelopes. The temperature of the substrate during the outgassing period was approximately 400°C.

The time required for outgassing was dependent upon the condition of the substrate and its environment since the heating (outgassing) was continued until the pressure would approach

2×10^{-5} torr. In cases where this practice was not followed, there was a problem of film adherence to the substrate during the post deposition treatment.

4.1.2. Vacuum Deposition

Depositions were made in a conventional glass bell jar system, with oil diffusion pump and liquid nitrogen trap. The system was capable of reaching about 5×10^{-6} torr. The substrate was supported about 6" above the source.

4.1.2.1. Deposition from Resistance Heated Source

A majority of the depositions were made from tungsten boats. However, some depositions were made from tantalum boats since they are easier to handle without damage than tungsten boats. Tungsten boats produced the better quality phosphors when the post deposition treatment had been completed. Phosphors evaporated from tantalum boats did not have the luminescence intensity nor the strong blue color of the phosphors evaporated from tungsten boats.

Each boat was cleaned after each deposition by an airbrasive action of Al_2O_3 from a S.S. White unit. Due to the brittleness of tungsten, only a few depositions, perhaps half a dozen, were made from each boat before it was replaced.

Only carbon crucibles proved satisfactory in making depositions of zinc sulfide. Carbon crucibles proved desirable because of its lack of change due to temperature, its thermal conduction characteristics and its non-interference with deposition of the zinc sulfide. These crucibles were heated by resistance heated tantalum heaters. The best depositions were made from crucibles with a carbon top, which was friction fitted with an opening of approximately 1/16 of an inch in diameter near its center.

Between one and four quartz substrates were positioned on the deposition mask which resulted in a round deposition with 1/2 inch diameter in the middle of the 1 inch round substrate.* Then the vacuum system was closed and evacuated to a pressure of approximately 10^{-4} torr for outgassing, as described previously. Upon completion of the outgassing, the substrate temperature was reduced from the outgassing temperature to approximately 150°C. The best quality films were deposited after the outgassing process when the substrate temperature was between 125°C to 175°C. When the substrate

* The actual configuration of the deposited phosphor was determined by the contractor.

temperature was too high, the deposition buildup was extremely slow or non-existent, and when the substrate temperature was too low, the film peeled in post deposition treatment.

Phosphor grade zinc sulfide must be heated slowly to prevent expulsion from the boat or crucible. An observed phenomena was two distinct stages of outgassing. The first stage takes place at rather low temperature compared to the sublimation temperature and the other stage just below the sublimation temperature. When either of these stages were approached too fast, the charge was expelled from the boat or crucible. The charge can move with enough energy to move the friction fitted crucible top or jam the charge against the top, blocking the opening in the crucible top.

Outgassing phosphor grade zinc sulfide from an open boat may require 30 to 40 minutes, due to the energy imparted to the charge by the expansion and release of the trapped gasses. This produces bouncing by the charge and it is possible for the charge to bounce out of the boat if heated too fast. However, outgassing the charge in a crucible with a top could be achieved in 3 to 5 minutes but this charge is not as large, usually, as the one in the open boat. When the crucible was heated too fast, there was the possibility of blowing the charge or jamming the charge against the top, which results in a very slow and undesirable deposition.

Care had to be taken not to overheat the charge during the deposition, or small pieces of the charge would actually hit the substrate and adhere to it. These small pieces of the charge produced holes in the deposition after they had been removed if they happened to adhere to the substrate near the beginning of the deposition. Pieces of the charge that adhered to the deposited film would leave indentations in the film of varying depths, depending on when they adhered to the film.

The carbon crucibles and their friction fitted tops reduced the number of pieces hitting and adhering to the substrate and film. Also, this reduced the time required in making a given deposition compared to the time required for an open boat, since the charge was heated to a slightly higher temperature.

Zinc sulfide, phosphor grade, was deposited after it had been outgassed with a temperature in the range of 1300°C which agrees fairly well with Holland. *

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* L. Holland, "Vacuum Deposition of Thin Films", page 297, John Wiley and Son, Inc., New York, N. Y., 1960.

The temperature was measured with an Optical Pyrometer, (Leeds & Northrup Co.) through the bell jar of the vacuum system. Depositions made from an open boat required 2 or 3 hours under desirable conditions to produce a deposition of approximately one micron. This same deposition thickness normally could be produced from a carbon crucible and its top in approximately 12 to 15 minutes. For depositions of greater than 1 to 1.5 microns, two or more deposition runs were required from the boat, while deposition of approximately 2.5 microns were made from a single deposition run with the carbon crucible.

4.1.2.2. Deposition from Electron Beam Heated Source

Pellets were prepared from the phosphor grade zinc sulfide for electron beam evaporations. This did not prove successful since the pellets were only pressed to hold it together in an attempt to keep foreign material out of the zinc sulfide. When the electron beam hit the zinc sulfide, it would almost instantly evaporate that portion of the pellet without any of the normally observed characteristics other than one big outgassing surge. By the time the outgassing stage was over, the zinc sulfide that the electron beam hit, had evaporated without any visible signs of a zinc sulfide film on substrate.

4.1.2.3. Deposition by Radio Frequency Sputtering

The first attempts to produce zinc sulfide films by R. F. sputtering were not successful, since the films were not very thick (a few hundred angstroms), and did not respond like conventionally evaporated films. By further examinations it was determined that a better method of making a target was needed. This resulted in a target made by pressing the desired quantity of zinc sulfide into a cake or pellet, placed in a vacuum system, evacuated to a pressure of approximately 10^{-4} torr and heated to an elevated temperature of approximately 500°C for approximately 45 minutes. Mounting the target was achieved by conventional means and produced films that appear to be very good. Unfortunately, the phosphors produced by this process were made very near the end of the contract and have not been evaluated as to their efficiency for proton detection.

4.1.3. First Inspection

Zinc sulfide films were inspected immediately after being cooled and opening the vacuum system. Such things as pieces of the raw zinc sulfide on and/or in the deposited film as well as cracks or peeling were sufficient to reject a deposited film of zinc sulfide before the post deposition treatment began.

Films that were not rejected were measured for thickness on a Carl Zeiss Interferometer. When films were considered too thin for a phosphor, they were replaced in the vacuum system for another deposition. The more depositions that were made to produce a single phosphor, the greater the chance of having it rejected before post deposition treatment.

4.1.4. Activation

Films as deposited show little or no luminescence probably due to separation from the silver and halich activators by the sublimation process. The activation is accomplished by chemically depositing silver sulfide on the surface from a silver solution:

$$2Ag^{+} + ZnS \longrightarrow Ag_2S + Zn^{++}$$

The film was then heated in contact with zinc sulfide powder, containing sodium chloride. The chloride serves as co-activator as the Ag diffuses into the ZnS lattice, while the surrounding of pure ZnS phosphor protects the film from oxidation and introduction of impurities.

The silver was applied by immersing the substrate and film in a 7.5% solution of silver nitrate for 1-3/4 to 2 minutes. The formula for this silver nitrate solution was:

> Dissolve 0.8 grams of silver nitrate in 4 milliliters of ammonium hydroxide. Then add 8 milliliters of denatured or grain alcohol.

Upon being removed from the silver nitrate solution, the zinc sulfide film and substrate was rinsed thoroughly with denatured or grain alcohol. The substrate and film are then dried at room temperature for a minimum of 10 minutes.

After the substrate and film have dried for 10 minutes or more, they were heated for 15 to 20 minutes at approximately 900°C. Preparation for this firing included the following:

> Place 7.5×15^{-4} to 1×10^{-3} grams of sodium chloride in a silica crucible. To this, add approximately 9.4 grams of the same phosphor grade zinc sulfide used to make depositions. Place the substrate (only one) on top of the zinc sulfide approximately in the middle of the crucible with the deposited film side up. Add approximately 3.1 grams of the same zinc sulfide on top of the substrate. Jar the silica crucible slightly, to settle the powder zinc sulfide in the crucible, being careful to keep the substrate submerged in the zinc sulfide. Place a silica cover on the crucible and place in the pre-heated, 900°C oven.

When the firing time was up, the crucible was removed from the oven and allowed to cool with the silica cover in place.

The object of the firing was to activate the zinc sulfide film and disperse silver and chloride ions in the zinc sulfide crystal. Phosphors produced in this manner have a deeper or darker hue, with greater luminescence than the zinc sulfide films activated by the same temperature without the silver and chloride.

After the substrate and phosphor had cooled enough to be safe to touch, it was removed from its bed of zinc sulfide. Forced air was used to remove any zinc sulfide that might be on the substrate and silver-activated zinc sulfide phosphor.

4.1.5. Second Inspection

The phosphor was then placed in a small chamber which was partially evacuated by a small mechanical pump for Tesla coil excitation. Generally, this would give a good indication of the uniformity of the luminescence and brightness of color. Also, spots which were contaminated would show up under this type of excitation. Other methods of excitation included cathode rays and a mercury lamp with a filter to produce a wavelength of 2537 angstroms. Upon removal from the Tesla coil chamber the phosphor was inspected for small holes, cracks, peeling or any physical broken areas in the phosphor. Only phosphors that were physically sound with no observed discontinuities in the phosphors were processed beyond this step, since they would not be suitable for flight operation.

4.1.6. Etching

Phosphors that were good after being activated were etched in a dilute solution of acetic acid to remove an inert or dead layer of the silver-activated zinc sulfide phosphor. The formula for this etch was as follows:

By volume: 3 parts demineralized water
1 part acetic acid

Etching time was only 15 to 30 seconds to prevent etching away the active phosphor. The phosphor was rinsed by the following fluids.

1. Demineralized water.
2. Ammonium Hydroxide.
3. Denatured or grain alcohol.

Following the rinses, the phosphor was allowed to dry in air.

4.1.7. Third Inspection

A final test under Tesla coil excitation was performed to insure that the etching process had not produced or turned up contamination that had not been visible in the first Tesla coil test. Some of the phosphors were mounted in a demountab le cathode ray tube for further tests but they proved similar to the Tesla coil results. The objective was to use the cathode rays in an attempt to get some idea of the possible response of the phosphors to low energy protons, but this was not accomplished.

4.1.8. Aluminizing

The application of the phosphor films for proton detection required that they be coated with a thin film of aluminum having high specular reflection to increase the light reaching the photo tube. At the same time, the film must be thin enough to permit passage of the low energy protons.

If the aluminum is evaporated on the film surface, a specular film is not obtained due to the roughness of the phosphor layer. Specular films were produced, however, when a thin plastic film was applied to the phosphor prior to the evaporation of aluminum,- a process similar to that used in the manufacture of cathode ray tubes.

The phosphors were first coated with a thin collodion film. Cleaned phosphors were submerged in demineralized water, phosphor up, on a wire frame. Once the substrate and phosphor was in position, 5 drops of a collodion, amyl acetate and ethyl cellulose solution were dropped from an eye dropper into the water. A cover was placed over the container for 20 to 25 minutes. A film of collodion formed on top of the water as it dried. The wire frame was lifted straight up, bringing the phosphor and substrate in contact with the collodion film, removed from the water and placed at an angle so that the water could drain off and the remainder evaporate.

Once the film dried, it was inspected for a thin and continuous film across the phosphor. Films that were not continuous or were too thick, were dissolved in acetone and the process was started again.

The formula for the collodion, amyl acetate and ethyl cellulose solution was:

> To 5 milliliters of 3% collodion and 97% amyl acetate, by volume, add one drop of 10% ethyl cellulose and 90% amyl acetate.

After the phosphor had a continuous collodion film, it was aluminized by evaporating 250 to 300 angstroms of aluminum on the collodion. These aluminum films were checked for a continuously reflective surface across the phosphor and its thickness was measured on the Carl Zeiss Interferometer. Films that were not continuously reflective across its surface were assumed not to be continuously reflective next to the collodion. The reflective film was desired on both sides, first to keep outside light from the phosphor and to reflect the light emitted by the phosphor back through the phosphor. Aluminum films that did not appear to be continuously reflective were removed by placing the substrate in a beaker containing acetone and placing the beaker in an ultrasonic cleaner.

Attempts were made to remove the collodion film and leave the reflective aluminum film, but they were not successful. First, an aluminum film was deposited on a plain glass substrate floated off in water and attached on the phosphor. However, the wrinkles were always present, making a nonuniform layer of aluminum.

Second, a very thin cellulose nitrate film was floated on the surface of the phosphor and the reflective aluminum was deposited on this. The phosphor was then baked to remove the cellulose nitrate layer. This was not successful because of the carbonization of the cellulose nitrate and the raising of the aluminum film, even with a very thin layer of cellulose nitrate.

Third, an aluminum film was deposited on a plain substrate covered with a thin cellulose nitrate layer and floated off. The aluminum film was turned over with the cellulose nitrate layer facing up and floated on the phosphor. Again the cellulose nitrate film was baked out leaving the reflective aluminum film. However, the aluminum film and the cellulose nitrate film always curled and wrinkled when floated off the original substrate, producing a nonuniform aluminum layer.

Another supporting film was used in an attempt to float the reflective aluminum film on the phosphor, collodion. A collodion film was suspended across a wire frame and aluminum was evaporated on it. The collodion and aluminum were then floated on the phosphor with the collodion film side up. Heat was applied to bake out the collodion film and the results were the same as with the other attempts.

One of the first attempts to aluminize the phosphors involved polishing the surface of the phosphor by metallographic methods. This did not produce the smooth surface desired and tended to produce holes, probably due to the grain structure which resulted in a scaly film. When these phosphors were aluminized, they were similar to the unpolished phosphors which produced a very nearly nonreflective and uneven aluminum surface film.

4.1.9. Results

Listed below are the silver-activated zinc sulfide phosphors delivered to the contracting agency for proton tests. The response to low energy protons is listed relative to the best of these phosphors that have been tested. Films rated good or very good are considered to be of flight quality.

Phosphor No. P11	Phosphor Thickness in Å	Reflective Aluminum Thickness in Å	Response To Low Energy Protons	Comments
1A	< 2,000	None	Extremely Poor	
3A	∿ 5,000	"	"	
4A	∿ 7,000	"	"	
5A	∿ 5,800	"	"	
13A	∿ 13,500	"	Very Poor	
20A	∿ 6,600	"	"	
22A	∿ 5,000	"	"	
26A	∿ 10,000	"	"	
27B	∿ 10,000	"	"	
29A	∿ 12,000	"	"	
29B	∿ 12,000	"	"	
30A	∿ 9,000	"	"	
30B	∿ 7,000	"	Fair	
50A			Very Poor	
63A	∿ 4,000		Fair	
65A	∿ 13,000		"	
67A	∿ 7,000		"	
89A	∿ 32,000	Thin		
89B	∿ 32,000	Thick		
91A	∿ 10,000			
92A	∿ 18,900			
93A	∿ 16,000			
96B	∿ 10,000	∿ 400		
100A	∿ 10,000	∿ 400		
100B	∿ 38,000	∿ 400		5 depositions produce total thickness.

Phosphor No. P11	Phosphor Thickness in Å	Reflective Aluminum Thickness in Å	Response To Low Energy Protons	Comments
101A	∿ 40,000		Fair	2 deposition layers
101C	∿ 17,000	∿ 400		
104A	∿ 40,000			Multiple deposition layers
108B	∿ 33,000	∿ 400		Multiple deposition layers
125A			Very Poor Good	Aluminized Unaluminized
126A			Very Poor Good	Aluminized Unaluminized
129A			Very Poor Good	Aluminized Unaluminized
140B			Poor Good	Aluminized Unaluminized
142A	∿ 12,000	No	Good	GSFC to aluminized
142C	∿ 12,000	No	Good	" " "
143A	∿ 15,000	No	Very Good	" " "
144A	∿ 15,000	No	Good	" " "
146A	∿ 18,000	∿ 500	Very Poor Good	Aluminized Unaluminized
148B	∿ 16,000	∿ 400	Fair Good	Aluminized Unaluminized
149B	∿ 14,000	∿ 400		
150A	∿ 15,000	∿ 650		
151B	∿ 13,000	∿ 500		
155	∿ 19,000	∿ 350	Poor	
158	∿ 13,000	∿ 600	Good	
160	∿ 13,000	∿ 850	Good	
165	∿ 17,000			
170	∿ 15,000	∿ 800	Very Poor	
171B	∿ 15,000	∿ 400	Good	Original
171B		∿ 200	Fair	Realuminized
171B		∿ 400	Poor	" Second Time
173	∿ 18,000	∿ 500	Very Poor	
174B	∿ 16,000	∿ 300		

Phosphor No. P11	Phosphor Thickness in Å	Reflective Aluminum Thickness in Å	Response To Low Energy Protons	Comments
175A	∿ 20,000	∿ 400	Fair	
175B	∿ 18,000	∿ 375	Poor	
176A	∿ 18,000	∿ 450	Very Poor	
178A	∿ 16,000	∿ 400	Very Poor	
180B	∿ 19,000	∿ 190	Fair	
182B	∿ 14,000	∿ 425	Very Poor	
183A	∿ 14,000	∿ 500	Very Poor	
184B	∿ 12,000	∿ 425	Poor	
185A	∿ 14,000	∿ 375	Very Poor	
186A	∿ 14,000	∿ 400	Very Poor	
190A	∿ 20,000	∿ 275	Good	
191	∿ 14,000	∿ 375	?	
192	∿ 13,000	∿ 300	Poor	
193A			Very Poor	
193B			Very Poor	
194C			Very Poor	
195	∿ 8,000	∿ 265	Very Poor	
196B	∿ 8,000	∿ 190	Very Poor	
197A	∿ 9,000	∿ 190	Fair	
200B	∿ 12,000	None		
201B	∿ 8,000	None		
202B	∿ 17,000	None		
203	∿ 20,000			
204A	∿ 10,000	∿ 275	Poor	
204B	∿ 10,000	∿ 225	Poor	
204C	∿ 10,000	∿ 250	Poor	
205A	∿ 13,000	∿ 225	Good	
205B	∿ 14,000	∿ 175	Poor	
205D	∿ 14,000	∿ 250	Good	
206A	∿ 17,000	∿ 175	Good	
206C	∿ 18,000	∿ 150	?	

Phosphor No. P11	Phosphor Thickness in Å	Reflective Aluminum Thickness in Å	Response To Low Energy Protons	Comments
207*	∿ 10,000			
208*	∿ 4,600			
209*	∿ 6,200			

4.2 Other Phosphors

4.2.1. Calcium Tungstate (P-5)**

Calcium tungstate was deposited from tungsten boats and filaments. These depositions were made on Corning 7059 glass and fired at 650°C for two hours. A bright light blue luminescence was produced upon excitation by a Tesla coil. Tests by the contracting agency indicated that these phosphors were very inefficient and there was very little, if any, work after this report on this particular phosphor.

4.2.2. Cerium-Activated Calcium Magnesium Silicate (P-16)

Considerably more work was done on the cerium-activated calcium magnesium silicate than the calcium tungstate phosphor. Depositions were made from tungsten boats on Vycor and quartz substrates. A post deposition heat treatment consisted of heating the deposition for four hours at 400°C and then five minutes at 1100°C. When exposed to 2537 Angstroms or a Tesla coil discharge, these phosphors produced a pale blue luminescence.

An alternative procedure was tried in which the metal (Ca, Mg and Ce) fluorides were deposited on quartz and fired to form the silicate. After firing, these depositions were frosty and, except for the thinnest films, had a red luminescence. The luminescence color of these particular phosphors was probably due to contamination.

Later, another alternate method was used for this phosphor that involved the metal (Ca, Mg and Si) oxides activated by cerium which were deposited on Vycor or quartz substrates. After post deposition heat treatment these phosphors normally produced a bright purplish-blue luminescence.

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* R. F. sputtered at the very end of the project and have not been tested for proton detection.

**The designations P-5, P-16, etc. refer to the JEDEC standard phosphors for cathode ray tubes.

More than 70 deposition runs were made in attempts to produce evaporated cerium-activated calcium magnesium silicate phosphors using one or more substrates per run for low energy proton detection.

Proton tests showed this to be a weak phosphor when tested under the same conditions as the P11 silver-activated zinc sulfide.

4.2.3. Titanium-Activated Calcium Magnesium Silicate (P-18)

First attempts to evaporate the commercially available titanium-activated calcium magnesium silicate did not produce phosphors as anticipated, no luminescence was observed when heat treated deposited phosphor was exposed to Tesla coil discharge or 2537 Angstroms. However, phosphors were produced with calcium fluoride, magnesium fluoride and titanium ammonium fluoride (P18m) deposited on quartz after firing at 500°C for two hours at approximately 1100°C for five minutes.

Additional titanium in the form of titanium oxide in the P18 charge produced phosphors when processed similar to that stated above. Normally, when these phosphors were more than 3000 to 4000 Angstroms thick, they were made in layers with each layer being treated as if it were the final deposition. The luminescence of the phosphor ranged from a light blue to a slightly reddish color. The red color was a sign of contamination in the deposited phosphor.

Approximately 30 deposition runs were made with P16 phosphor material.

4.2.4. Titanium-Activated Zinc Silicate

Titanium-activated zinc silicate phosphor was synthesized in the conventional manner by firing a mixture of the oxides at approximately 1200°C. Depositions were made in the conventional manner on quartz and Vycor substrates. Post deposition treatment of these phosphors included firing them at approximately 1100°C for 15 to 20 minutes. Tesla coil discharge excitation produced a deep blue luminescence. Only five deposition runs were made with the titanium activated zinc silicate phosphor.

4.2.5. Silver-Activated Zinc Cadmium Sulfide (P-20)

First attempts to deposit this phosphor in the normal manner resulted in fractionation with the more volatile cadmium sulfide being the major constituent of the deposition as indicated by the orange colored luminescence of the excited phosphor. Increasing the quantity of zinc in the charge by adding P11 zinc sulfide phosphor did not produce the desired luminescence.

When deposited phosphors of this material were successfully produced, they exhibited a yellow-green luminescence. The procedure for depositing these phosphors was very similar to that used for P11 zinc sulfide. Samples of these deposited phosphors, that exhibited a luminescence which was very similar in color and brightness to that of the bulk phosphor powder when excited, were tested by the contractor. These tests indicated that these phosphors were approximately as good as the best P11 silver-activated zinc sulfide phosphors being made at that time in spite of the mismatch in the color of the luminescence and the spectral response of the phototube.

4.2.6. Zirconium Pyrophosphate

This phosphor is reported to have an emission band around 2900 Angstroms with a very fast time decay. It was formed by precipitation from a solution of zirconium nitrate in a 10 percent sulfuric acid solution by ammonium phosphate followed by firing the dried precipitate at approximately 1100°C.

Zirconium pyrophosphate was coated on a quartz substrate by standard screen settling procedures, using potassium silicate binder and barium acetate cushion. However, there was no detectable ultraviolet in a Tesla coil discharge using a Gaertner monochromator with an anthracene-coated glass screen in a dark room as anticipated.

No attempts were made to deposit this phosphor.

4.2.7. Zirconium Arsenate

Zirconium arsenate was formed by precipitation from a solution of zirconium nitrate in a 10 percent sulfuric acid solution by ammonium arsenate followed by firing the dried precipitate at approximately 900°C.

This phosphor was coated on a quartz substrate by standard settling procedures, again using potassium silicate binder and barium acetate cushion. When exposed to Tesla coil discharge and 2537 Angstroms, there was no visible emission, nor was there a detectable

ultra-violet in a Tesla coil discharge using a Gaertner monochromator with an anthracene coated glass screen in a dark room as anticipated.

No attempts were made to deposit this phosphor.

4.2.8. Europium-Activated Yttrium Oxide

Euopium-activated yttrium oxide was formed by the following process:

> Yttrium oxide, 0.02 moles, and europium oxide, 0.001 moles were dissolved in concentrated nitric acid. The liquid of the solution was evaporated to near dryness and 100 milliliters of distilled water was added. This solution was heated to 80°C and 10 milliliters of 30 percent hydrogen peroxide was added. The solution was held at 80°C for 15 minutes and removed from the heat source. To this solution, 50 milliliters of 10 percent oxalic acid was added and stirred for 5 minutes. The precipitate was allowed to settle and approximately half of the liquid poured out. The remaining solution was either evaporated or the precipitate was filtered out of the solution with a medium ceramic trap filter. The precipitate was then placed in an oven to dry overnight at approximately 110°C. Finally, the dry material was then placed in a silica crucible and fired without a cover at approximately 1000°C.

After the europium-activated yttrium oxide was prepared, conventional screen settled samples were prepared to determine visual response. Tesla coil excitation produced a reddish-orange luminescence.

No deposited films by the conventional boat evaporation method produced visual responses to Tesla coil discharge or 2537 Angstroms regardless of the type or duration of post deposition heat treatment used.

A R. F. sputtering target was prepared in the same manner as the first P11 zinc sulfide R. F. sputtering target. Three deposition runs were made producing films at 400, 1800 and 4800 Angstroms thick. These deposited films were heated at 700°C for one hour and produced a reddish-orange luminescence when excited by a Tesla coil discharge or 2537 Angstroms, which is in the range of the literature report of 6113 Angstroms.

Successful attempts to make deposited europium-activated yttrium oxide phosphors were made using an electron beam as the heat source. These deposited phosphors responded in the desired manner to Tesla coil and 2537 Angstroms after a post deposition heat treatment of approximately 1100°C for one hour.

Three screen settled samples of this phosphor were sent to the contractor for proton testing. Results of these tests from the same system used for testing P11 silver-activated zinc sulfide were extremely weak in relation to the best P11 phosphors that had been made and tested.

4.2.9. Gadolinium-Activated Yttrium Oxide

Gadolinium-activated yttrium oxide was made in a very similar manner as the europium-activated yttrium oxide stated above. However, the concentration of the gadolinium was increased to 25 percent by weight before the electron beam evaporated and post deposition heat treated phosphors responded to Tesla coil or 2537 Angstroms. This particular combination produced a luminescence very similar to the bulk phosphor powder which was cream-white color.

Screen settled samples responded to proton tests by the contractor about the same as the europium-activated yttrium oxide phosphors, very weak.

4.2.10. Indium-Activated Cadmium Sulfide

Indium-activated cadmium sulfide phosphor material is a commercially available product. Samples of this phosphor were screen settled for proton tests by the contractor. The luminescence produced by this phosphor under Tesla coil excitation was a very light green which is near the 5200 Angstrom response reported for the phosphor. Proton test results indicated this to be a weak phosphor when tested under the same conditions as the other phosphors.

No attempts were made to deposit this particular phosphor.

4.2.11. Gallium-Activated Zinc Oxide

Gallium-activated zinc oxide is another commercially available phosphor with its peak emission around 3900 Angstroms. No attempts were made to deposit this type of phosphor. Again three screen settled samples were prepared for proton tests by the contractor. The proton tests indicated this to be a weak phosphor when tested under the same conditions as the other phosphors.

4.2.12. Cesium Iodide

Cesium iodide was deposited from a quartz crucible and heated by a tantalum heater in the conventional manner. Cesium iodide excited by a Tesla coil and cathode rays produced a very faint purplish-blue luminescence. Heating the deposited cesium iodide in air to approximately 375°C changes the luminescence to a darker blue but it is still weak compared to the best zinc sulfide which has been silver activated.

Two cesium iodide phosphors as evaporated were sent to the contractor for proton detection tests. When tested under the same conditions as the P11 silver-activated zinc sulfide, they were very weak.

Two more cesium iodide phosphors have been deposited and heated in air to approximately 375°C. One of the phosphors will be aluminized and both delivered to the contractor if time permits.

Thallium activated cesium iodide has been reported to have an emission peak at 5800 Angstroms* which is in the yellow region of visible light. Also, activating the cesium iodide phosphors with thallium iodide is a little harder than normal deposits since the thallium iodide is more volatile than the cesium iodide and tends to evaporate first leaving almost pure cesium iodide as the last part of the deposition. Time permitting, two thallium activated cesium iodide phosphors will be delivered to the contractor, one plain and one aluminized.

V. NEW TECHNOLOGY

New technology Reports covering the preparation of Cerium Activated Calcium Magnesium Silicate Thin Films, and Silver-Activated Zinc Sulfide Thin Films were submitted. The latter appeared as NASA Technical Brief No. 68-10271. Copies of these documents appear in the appendix.

VI. CONCLUSIONS AND RECOMMENDATIONS

1. Silver activated zinc sulfide phosphor films are shown to have a strong response to low energy protons. When coupled with a suitable photomultiplier tube, they can detect protons with energies as low as 10 Kev.

2. A process was developed by which these phosphor films can be consistantly produced, with uniform fluorescence and other physical properties.

3. Careful control of the purity of all materials is required.

4. Based on a limited number of experiments zinc sulfide films formed by radio frequency sputtering are more uniform and less con-

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* Birks, J.B., "The Theory and Practive of Scintillation Counting", Page 83, The MacMillan Company, New York, New York, 1964.

taminated than those formed by vacuum sublimation in the conventional manner. Future work should emphasize this approach.

5. Replacement of a part of the zinc with cadmium causes a color shift with no loss in efficiency. To exploit this phosphor, improved phototubes with higher response in the yellow and green spectral regions are required.

6. Future work should also include further study of cesium iodide films. The few results obtained with unoptimized films are not considered representative in view of the known high sensitivity of the bulk form of this phosphor to heavy particle excitation.

7. Phosphors of the "oxide" type examined offer little promise as proton detectors.

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