

AIAA-2001-3528

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Aeropropulsion Applications

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**37th AIAA/ASME/SAE/ASEE Joint
Propulsion Conference and Exhibit**
8–11 July 2001
Salt Lake City, Utah

DEVELOPMENT OF TEMPERATURE-SENSITIVE PAINTS FOR HIGH-TEMPERATURE AEROPROPULSION APPLICATIONS

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Abstract

Fluorescence from a phosphor coating will indicate the temperature of the substrate to which it is attached, assuming thermal equilibrium is achieved. The goal of this investigation is to identify phosphors for making temperature measurements on aerospace surfaces with temperatures varying from ambient to 1000°C and to identify and test binders/adhesives that may be mixed with thermographic phosphors and sprayed onto surfaces of interest to provide a durable and uniform coating. The surfaces of interest include various high-strength metal alloys, such as stainless steel and nickel with and without thermal barrier coats, ceramics, carbon/carbon composites, and copper. Our initial efforts have concentrated on the most challenging substrates, the high-strength nickel alloy without the thermal barrier coating. Several candidate phosphors have been identified, and we are considering mixing two or more phosphors to cover the full temperature range. The phosphors being considered are Y₂O₃:Eu, YAG:Eu, YAG:Dy, YAG:Cr, and YPO₄:Eu,Dy. The initial results indicate that two binders—Sauereisen's Thinning Liquid #14 and a mix of ZYP, Inc.'s, LK and HPC will function well on high-strength nickel alloys to 800°C. Furthermore, the LK and HPC mix

performed well on high-strength stainless steel substrates coated with a thermal barrier coat to a temperature of 1000°C.

Introduction and Background

Phosphor coatings are the basis for a viable means of measuring temperature in a wide variety of situations. A phosphor is a fine powder that efficiently fluoresces when suitably excited by sources such as lasers, light-emitting diodes, ultraviolet lamps, or electron beams. A phosphor is thermographic when the fluorescence characteristics change with temperature. Fluorescence from a thermographic phosphor coating will indicate the temperature of the substrate to which it is attached, assuming thermal equilibrium is achieved. Noel et al. and Grattan and Zhang provide in-depth descriptions of the physical basis and many useful applications.¹⁻³

Goal

Described in this paper is a recently initiated effort aimed at an application for temperature measurement on aerospace surfaces wherein the temperature may vary over the entire range from ambient to 1000°C. There is a further constraint regarding the method by which a phosphor coating may be applied. Earlier work has indicated that sputtering or E-beam deposition of a pure phosphor onto a surface makes a very useful and

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durable coating. But this finding presumes the timely availability of such equipment and that samples to be coated are small enough to fit into a vacuum sample chamber. The present effort is therefore aimed at identifying and testing inorganic binders and adhesives that may be mixed with thermographic phosphors and sprayed onto any surface of interest and that will be durable and function up to the design temperature. Candidate surfaces include copper, various stainless steels, high-temperature alloys coated with thermal barrier coatings, and carbon/carbon composites. The high-temperature alloys will be the most challenging materials because of the large difference in the coefficient of expansion between the metal and the phosphor. Our early work has been centered around these high-temperature alloys in order to address the most difficult problems first.

Binders

The following paragraphs provide a description of the five candidate binder materials that are under investigation in this research. Each of these materials is designed for use in high-temperature applications and is available in the commercial market.

Sperex Flameproof SP-115

Sperex Flameproof SP-115 is manufactured by VHT in Scottsdale, Arizona. This clear silicone resin is designed for use as a fireproof coating for automobile exhaust systems, stoves, fireplaces, and other high-temperature applications. The maximum recommended use temperature for the clear formulation is 815°C. However, it may be used to above 1000°C with suitable filler materials. Sperex is solvent-based with a shelf life of 6 months. The following curing procedure should be used in order for the coated product to withstand the maximum possible temperature:

- Heat sample to 121°C for 15 minutes.
- Raise temperature to 316°C and hold for 30 minutes.
- Raise temperature to 427°C and hold for 60 minutes.
- Raise temperature to 538°C and hold for 30 minutes.

Sperex requires no primer and can be sprayed on an object to a nominal thickness of 38 to 51 µm.

Thinning Liquid #14

Sauereisen in Pittsburgh manufactures Thinning Liquid #14 (TL#14). This soluble sodium silicate solution is commonly used as a thinning liquid to adjust the viscosity of various cements. It is also used as a surface primer or binder for making heat-stable or chemical-resistant cements by mixing it with silica or other materials. The maximum recommended use temperature for the clear formulation is 1204°C. TL#14 is water-based with a shelf life of 12 months. The following curing procedure should be used to enable the coated product to withstand the maximum possible temperature:

- Heat sample at 66°C for 120 minutes
- Raise temperature to 93°C and hold for 60 minutes.
- Raise temperature to 121°C and hold for 60 minutes.
- Raise temperature to 177°C and hold for 60 minutes.
- Raise temperature to 232°C and hold for 60 minutes.
- Raise temperature to 288°C and hold for 60 minutes.
- Raise temperature to 343°C and hold for 60 minutes.
- Raise temperature to 399°C and hold for 60 minutes.
- Raise temperature to 454°C and hold for 60 minutes.
- Raise temperature to 510°C and hold for 60 minutes.

During application, TL#14 should be stirred continuously to achieve a more flowable consistency.

BNSL

ZYP Coatings in Oak Ridge, Tennessee, manufactures BNSL. When cured, the BNSL binder coating is composed of glassy carbon and magnesium aluminum silicate. The maximum recommended use temperature for this formulation is 1600°C. It is alcohol- and acetone-based with a shelf life of 12 months. The sprayed coating dries in 2 to 4 minutes after application. At temperatures from 500 to 700°C, BNSL will turn gray, a characteristic that may affect the optical properties of the coating. Once the temperature rises above 700°C, the organic materials will burn off and improve the optical properties of the

coating. In our study, the samples were cured by elevating the temperature to 700°C and then bringing them back to room temperature slowly. For best results, filler compounds (such as phosphors) can be added to BNSL in ratios of 10 to 50% by weight. This binder can be applied to almost any material. However, BNSL may pop off metal surfaces because of differences in the thermal expansion coefficient. One possible way to resolve this problem is by adding calcium carbonate to the filler.

HPC

ZYP Coatings in Oak Ridge also manufactures HPC. When cured, the HPC binder coating is not reactive and is composed of magnesium aluminum silicate. The maximum recommended use temperature for this formulation is 1500°C. It is water-based with a shelf life of 12 months. The sprayed coating dries at room temperature in 15 to 20 minutes after application. HPC is a softer coating than BNSL. To fully cure this binder, the temperature should be elevated to 700°C and then brought back to room temperature slowly.

LK

ZYP Coatings manufactures LK. When cured, the LK binder coating is not reactive and is composed of 75% SiO₂, 20% K₂O, and 5% Li₂O. The maximum recommended use temperature for this formulation is 1100°C. It is water-based with a shelf life of 12 months. The sprayed coating dries at room temperature in 15 to 20 minutes after application. LK is probably the hardest coating of all the tested high-temperature ZYP coatings. To fully cure this binder, its temperature should be elevated to 700°C and then brought back to room temperature slowly.

Phosphor Selection and Testing

An important goal of this effort is to identify and test phosphors to cover the entire temperature range from ambient to 1000°C. It is also an important procedure to mix the identified phosphors with the binders to elicit any possible deleterious chemical reactions and adverse effects on the fluorescence. Table 1 lists the five phosphors currently being tested, their temperature range, and pertinent comments.

Table 1. Phosphors under consideration

Phosphor	Expected temperature range (°C)	Comments
Y ₂ O ₃ :Eu	500–1000	Most widely tested. Short decay at 1000°C
YAG:Eu	~700–1200	Single exponential decay
YAG:Dy	~800–1600	Highest temperature material. Not-single exponential decay
YAG:Cr	Ambient–700	For lower portion of the temperature range
YPO ₄ :Eu,Dy	~700–1200 ?	Double-doped

Example data for the temperature dependence of YAG:Eu from 500 to 1000°C are presented in Figs. 1 and 2. Another factor to consider when choosing a phosphor for a high-temperature application is the effect of the blackbody background radiation on the temperature measurement system. As the temperature increases above 600°C, the blackbody radiation increases with temperature as well as wavelength. Figure 3 illustrates how, by choosing a phosphor such as YAG:Dy, one might chose an emission line further in the blue and minimize the effect of the blackbody radiation on the instrumentation system.

Bonding Study

The goal of the bonding study is to demonstrate that phosphors whose temperature dependence will cover a range from room temperature to 1000°C can be sprayed on candidate surfaces including copper, various stainless steels, high-

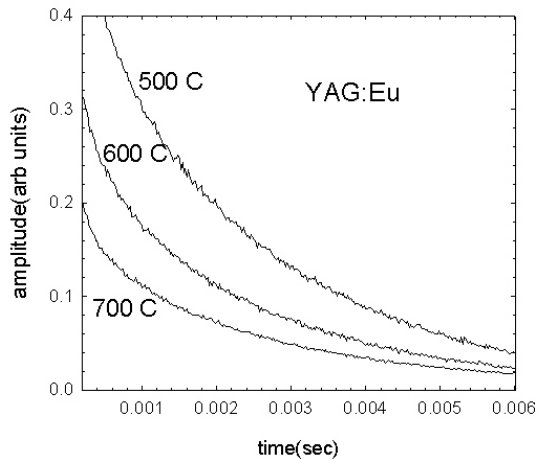


Fig. 1. YAG:Eu data at 500, 600, and 700°C.

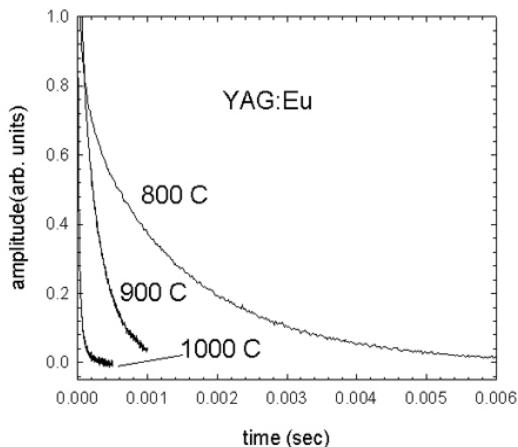


Fig. 2. YAG:Eu data at 800, 900, and 1000°C.

temperature alloys coated with thermal barrier coatings, and carbon/carbon composites and provide a durable, uniform coating. Our initial work is being done with the most challenging substrate, a high-strength nickel alloy, and the temperature cycles will be limited to 800°C. The high-strength metal alloy will be the most challenging because of the large differential in coefficient of expansion between the metal alloy and the thermographic phosphor.

After some initial work with each of the binders described in the binder section, and discussions with representatives from the various manufacturers, an initial test matrix and sample

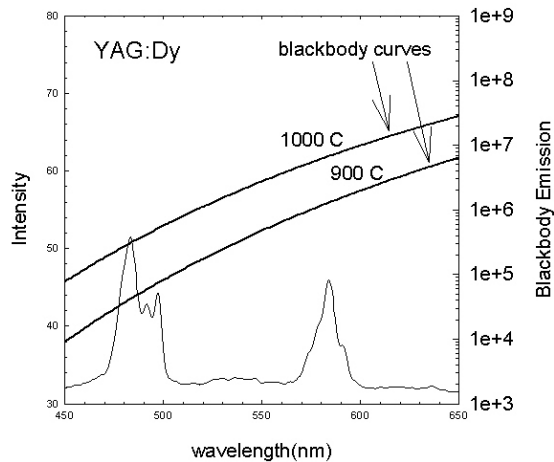


Fig. 3. Blackbody radiation curve superimposed on the YAG:DY spectra

preparation procedure were formulated to evaluate the binders at two loading conditions. The sample evaluation consists of a visual inspection and fluorescence emission spectra for each sample as coated, after curing, and after each temperature cycle. The samples were elevated to 800°C at a ramp rate of 25°C/minute, held for one hour and then slowly cooled to room temperature in the oven. The binders used in the initial study were two water-based binders, Sauereisen TL#14 and a mixture of half ZYP LK and half ZYP HPC binders, and two solvent-based binders, Sperex SP-115 and ZYP BNSL binder. The two loading conditions chosen were 20% and 10% phosphor to binder. The phosphor chosen was YAG:Eu. The substrates used were high-strength nickel-alloy rods supplied to Oak Ridge National Laboratory by the U.S. Air Force for previous phosphor development programs. The following sample preparation and coating procedure was used.

1. Roughen and remove oil, etc. on sample surface with 150 grit sand paper.
2. Clean and remove all grit with Lacquer Thinner or acetone.
3. Prepare binder phosphor mix with two loadings by volume.
4. Load 20% phosphor to binder, 1 part phosphor to 4 parts binder.
5. Load 10% phosphor to binder, 1 part phosphor to 9 parts binder.

6. Heat sample surface to 125°C, remove from oven, and apply phosphor-binder mix to the heated surface.
7. Ensure the phosphor and binder are mixed well and apply a thin layer of phosphor to the rods supplied by the Air Force.
8. Mark each sample.

To evaluate the samples, a visual inspection and emission spectra were performed on each sample as coated, as cured, after the first temperature cycle, and after the second temperature cycle. Emission spectra were taken using 260-nm light as the excitation source. The as-coated samples are shown in Fig. 4. The as-coated samples all appeared to provide a uniform, durable coating.

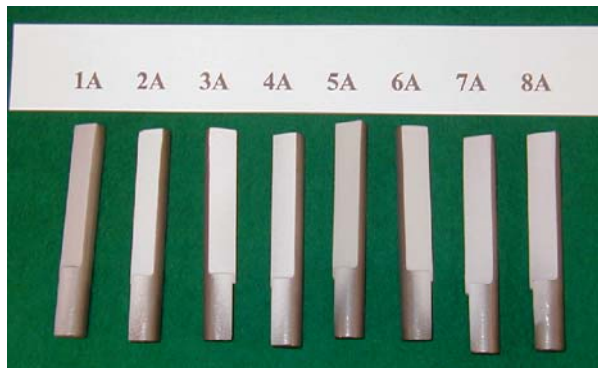


Fig. 4. As-coated samples

The results of the initial study are summarized in Table 2. Figure 5 shows the sample set after two heating cycles to 800°C. As indicated in Table 2 and shown in Fig. 5, the Sauereisen TL#14 (samples 1A and 2A) and the ZYP, Inc. LK/HPC (samples 3A and 4A) binders performed well at both phosphor loading levels. The Sperex SP-115 with a 10% phosphor loading (sample 5A) flaked off and failed during the curing cycle. The second SP-115 sample with a 20% phosphor loading (6A) flaked off and failed after the second heating cycle to 800°C. The ZYP BNSL binder at both loading levels (sample 7A and 8A) became very chalky after curing and failed to provide suitable durability or uniformity upon visual inspection.

The final part of the matrix study evaluation was the performance of emission spectra on the samples after each stage. Emission spectra for the YAG:Eu samples were taken using 260-nm light as the excitation source. Typical YAG:Eu



R2 bond 2 800.jpg

Fig. 5. YAG:Eu coated samples after two cycles to 800 °C.

spectra taken as cured, after a single heating cycle to 800 °C, and after a second cycle to 800°C, are shown in Fig. 6.

YAG:Eu #4A HPC and LK binder 20% Loading
Emissions Spectrum
Excitation Wavelength: 260.47 nm
Ex slit: 15 nm Em slit: 5nm

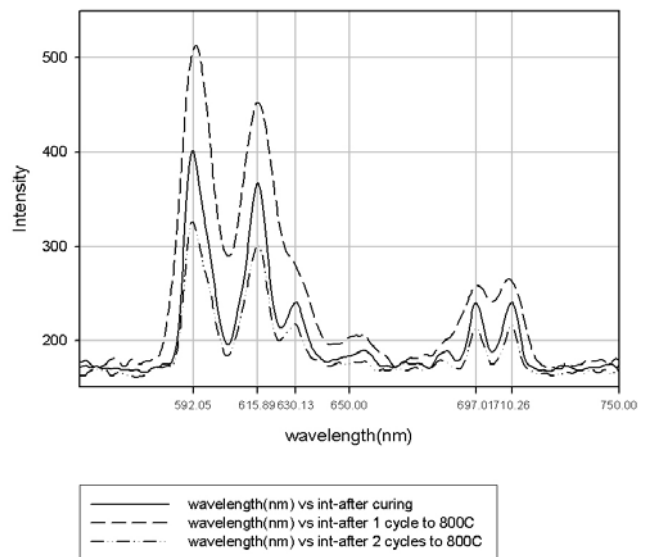
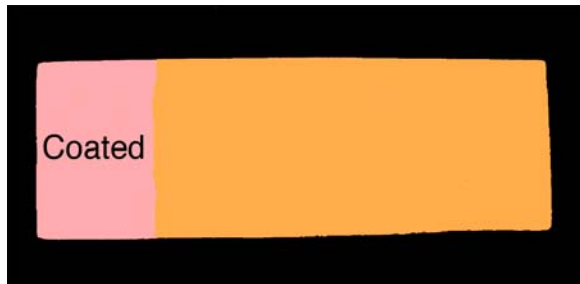


Fig. 6. YAG:Eu spectra taken as cured, after a single heating cycle to 800 °C, and after a second cycle to 800 °C.

Our final evaluation consisted of taking a high-strength stainless steel substrate with a thermal barrier coat (yttria-stabilized zirconia) and applying YAG:Eu phosphor using the ZYP LK/HPC mix. The cycling test consisted of elevating the coated

Table 2. Results of bonding study						
YAG:Eu 1% binder type	Loading level	Sample no.	1. Emission spectra after curing	2. Emission spectra after single cycle to 800°C for 1 h	3. Emission spectra after 2 cycles to 800°C for 1 h	Observations and comments (uniformity, adherence, etc.)
Sauerisen Thinning Liquid # 14	10% loading	1A	Peaks: 596, 618, 701, 712 nm	Peaks: 594, 616, 698, 709 nm	Peaks: 592, 616, 628, 696, 710 nm	1. Bubbly, but adherence still good; good durability and uniformity 2. Bubbles eliminated; good adherence and uniformity 3. Good—no change
	20% loading	2A	Peaks: 596, 618, 699, 711 nm	Peaks: 593, 616, 654, 698, 709 nm	Peaks: 592, 616, 629, 697, 710 nm	1. Good adherence and uniformity 2. Good—slight yellowing; no change in adherence or uniformity 3. Good—no change
	10% loading	3A	Peaks: 592, 615, 630, 697, 709 nm	Peaks: 594, 616, 699, 710 nm	Peaks: 592, 616, 630, 698, 711 nm	1. A few cracks, but good adherence and uniformity 2. Good—light yellowing; no change in adherence or uniformity 3. Good—no change
ZYP, Inc., 0.5 LK and 0.5 HPC	20% loading	4A	Peaks: 592, 615, 630, 697, 710 nm	Peaks: 593, 616, 698, 709 nm	Peaks: 592, 616, 630, 697, 710 nm	1. Good adherence and uniformity 2. Good—slight yellowing; no change in adherence or uniformity 3. Good—no change
	10% loading	5A	Peaks: N/A	Peaks: N/A	Peaks: N/A	1. Whole coating flaked off 2. ----- 3. -----
Sprex SP-115	20% loading	6A	Peaks: 592, 615, 629, 697, 709 nm	Peaks: 592, 616, 630, 697, 710 nm	Peaks: 592, 616, 630, 697, 710 nm	1. Somewhat powdery, but adherence and uniformity still good 2. Still powdery; adherence fair to poor 3. Almost all of coating flaked off
	10% loading	7A	Peaks: 593, 616, 697, 709 nm	Peaks: 594, 617, 699, 711 nm	Peaks: 592, 616, 630, 697, 710 nm	1. Very chalky—unacceptable 2. Very chalky—unacceptable 3. Very chalky—unacceptable
ZYP, Inc., 0.5 BNSL and 0.5 Lacquer Thinner	20% loading	8A	Peaks: 504, 595, 617, 632, 698, 711 nm	Peaks: 592, 615, 630, 697, 710 nm	Peaks: 592, 616, 630, 680, 710 nm	1. Very chalky—unacceptable 2. Very chalky—unacceptable 3. Very chalky—unacceptable

sample to 1000°C for one hour twice. The phosphor coating performed well, providing a durable and very uniform coating. The emission spectra indicated no change from the as-coated state through the second 1000°C cycle. Figure 7 provides photos of the samples as coated and after two 1000°C temperature cycles.



YAG:Eu coating using ZYP LK/HPC binder

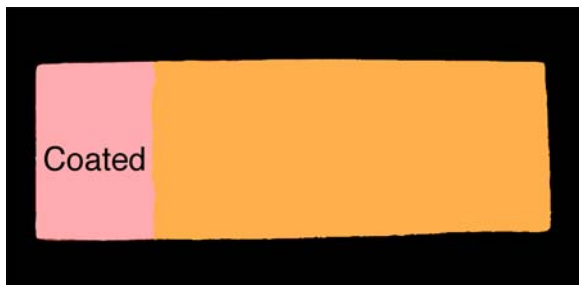


Fig. 7. Comparison of samples as coated (top) and after two heating cycles to 1000°C (bottom) and a yttria-stabilized zirconia thermal barrier coating.

Conclusions

Work will continue to finalize the choice of phosphors to be used for various applications. The YAG:Cr phosphor can be used to cover the temperature range from ambient to approximately 700°C. The other phosphors being studied, YAG:Eu, YAG:Dy, Y₂O₃:Eu, and YAG:Eu, Dy can all be mixed with the YAG:Cr to extend the temperature range to 1000°C. The high temperature phosphors will be chosen according to the requirements of the specific experiment.

The binder study will continue, and additional substrates will be evaluated. The studies to date indicate the ZYP LH/HPC binder and the Sauereisen TL#14 will perform well on the high-temperature metal alloys to at least 800°C. The samples that survived to 800 °C will be cycled to 900 °C and then 1000 °C, but this work was not complete at the time this paper was due. The ZYP LK/HPC binder performed well on thermal-barrier-coated stainless steel surviving a series of temperature cycling tests to 1000 °C.

In summary, the work on this program is going well, and ORNL expects to be able to meet all the project requirements.

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