NASA Technical Memorandum 81385

PRELIMINARY STUDY OF A SOLAR SELECTIVE COATING SYSTEM USING BLACK COBALT OXIDE FOR HIGH TEMPERATURE SOLAR COLLECTORS

(NASA-TM-81385) PRELIMINARY STUDY OF A SOLAR SELECTIVE COATING SYSTEM USING BLACK COBALT OXIDE FOR HIGH TEMPERATURE SOLAR COLLECTORS (NASA) 16 p HC A02/MF A01 CSCL 10A G3/26

N80-18156

Unclas 47351

G. McDonald
Lewis Research Center
Cleveland, Ohio

Prepared for the
International Conference on Metal Coatings
sponsored by the American Vacuum Society
San Diego, California, April 21-25, 1980

PRELIMINARY STUDY OF A SOLAR SELECTIVE COATING SYSTEM USING BLACK COBALT OXIDE FOR HIGH TEMPERATURE SOLAR COLLECTORS

by G. McDonald

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

E-293

ABSTRACT

Black cobalt oxide coatings (high solar absorptance layer) were deposited on thin layers of silver or gold (low emittance layer) which had been previously deposited on oxidized (diffusion barrier layer) stainless steel substrates. The reflectance properties of these coatings were measured at various thicknesses of cobalt oxide for integrated values of the solar and infrared spectrum. The values of absorptance, α, and emittance, ϵ, were calculated from the measured reflectance values before and after exposure in air at 650° C for approximately 1000 hours. Absorptance and emittance were interdependant functions of the weight of cobalt oxide. Also, these cobalt oxide/noble metal/oxide diffusion barrier coatings have absorptances greater than 0.90 and emittances of approximately 0.20 even after about 1000 hours at 650° C.

INTRODUCTION

In previous research at the NASA-Lewis Research Center (Refs. 1 to 3) it was determined that a black chrome layer plated on electroplated nickel is a very efficient solar selective coating in that it may be adjusted so that it absorbs strongly in the solar spectrum (absorptance, α, ≈ 0.95 at wave lengths of from 0.35 to 2.0 μm) and yet reradiates very weakly in the infrared (emittance $\epsilon \approx 0.1$ at wavelengths of 2.0 to 15 μm). Solar selective coatings of the general type of black chrome are made by covering a metal surface which has low emittance with a coating of highly absorbing material in a layer thin enough to be transparent to the infra-red but opaque to the visible. Black chrome has found very wide use in commercial flat plate solar collectors because it can be produced at relatively low cost since it is widely available and easy to apply, and because it has long term durability under solar radiation. For such applications black chrome is now applied to hundreds of thousands of square feet of solar collector surfaces each year.

In addition to the extensive use of flat plat solar collectors which reach a maximum temperature of approximately 200° C, concentrating collectors, (line focus and point focus) are in use which employ an intensified image of the sun that is focused on the absorber. These collectors are used in order to be able to reach higher absorber temperatures than is possible with a flat plate collector. Concentrating collectors which focus the sun's energy onto a line may have a concentration ratio of 10 or 20 to one and an operating temperature of approximately 300° C or higher with stagnation. Collectors such as a central receiver which focus on a single target have concentration ratios of 600-800 and a surface operating temperatures of approximately 650° C.

It is important to have high absorptance and low emittance for concentrating collectors due to the reduced areas receiving radiation. Black chrome is used as a selective coating on concentrating collectors of lower multiplication ratio. However, at temperatures above 300° C, in either air or vacuum, the black chrome irreversibly decreases in absorptance to $\alpha \approx 0.85$ or less, although there is no significant change in emmittance (Ref. 4).

Because black chrome has an unacceptable loss of absorptance above 300° C, for higher temperature applications a solar selective coating is needed which has high absorptance and yet retains low emittance after long term exposure to air from 300° to 650° C. If such a coating is to endure exposure to air at temperatures up to 650° C, the coating must be both thermally stable in physical structure to retain high absorptance and resistant to oxidation since oxidation of the substrate increases the emittance. (Above approx. 2 μm, such an oxidation layer will determine the emittance). In addition, either the coating must be impervious to oxygen or the low emittance substrate must resist oxidation for long exposures at the temperature of use. Since the absorbing layer must be of necessity be very thin (1 to 2 μm) to minimize its contribution to emittance, it is difficult to use this layer to protect the substrate from oxidation. Figure 1 shows the effect of 650° C oxidation on the emittance of electrolytic nickel, 304 stainless steel, and Incoloy 800 (the latter is used in one central receiver design). While the oxidation resistant alloys 304 and Incoloy 800 increase in emittance more slowly than electrolytic nickel, these alloys have a higher initial emittance than nickel.

Thus, in order to avoid the increase in emittance of a solar selective coating system exposed to air at high temperature, a low emittance, nonoxidizing noble metal emitter layer was required between the absorber and substrate. Finally, since this nonoxidizing noble metal would eventually diffuse into the base metal substrate if placed on it directly, it was felt that the noble metal layer must be separated from the base metal by adiffusion barrier. In this coating concept an oxide, formed in situ, was used.

Metals such as silver, gold, and platinum have low infrared emittance. In addition, these metals do not oxidize when exposed to air at elevated temperatures up to 650° C or more, and therefore do not irreversably increase in emittance on exposure.

This report describes the pursuit of the above approach to develop a solar selective coating which has the desirable desirable optical properties of high absorptance and low emittance at temperatures up to 650° C and maintains these properties in an oxidizing environment. As a result of this approach, a duplex coating consisting of a cobalt oxide/noble metal combination was identified. This paper describes the method of producing this solar selective coating and the experimental results and measurements of the absorptance and emittance of this coating after long term exposure to air at 650° C.

EXPERIMENTAL

Selection of Absorber

In addition to the requirement that the surface oxide absorbing layer have high absorptance, that is, be black, it must be stable against oxidation and reduction at the temperature of operation (up to 650° C) and must also not melt or vaporize in this temperature range. Thus, the structure of the oxide deposit is critical, since, in order to have maximum absorptance with the minimum layer thickness it is essential that this layer have a porous, open structure for light trapping. Unless the oxide is refractory, sintering reactions would destroy the porous, fluffy structure of an such absorbing oxide layer and decrease its absorptance. In preliminary experiments, cobalt and manganese oxides and some mixed oxides of elements 23 thru 29 were identified as having satisfactory combinations of absorptance and refractory properties so as to be able to form an absorbing layer which would be stable at 650° C (Ref. 5).

Selection of Emitter Layer

The emitter layer must be stable against oxidation and chemically stable against reaction with the substrate oxide diffusion barrier layer and the metal oxide absorber layer. In addition the emitter layer must be thermally stable against melting, evaporation or coalescing. Again, in preliminary tests, gold, silver or platinum were identified as being satisfactory for use as the emitter layer.

Diffusion Barrier Layer Selection

Any chemically inert refractory oxide may be used as a barrier against diffusion of the noble metal emitter layer into the base metal substrate. However, it is most convenient to form the oxide barrier layer in situ by oxidation of the base metal. Based on initial furnace oxidation experiments with stainless steel or nickel base alloys, thin oxide layers could be formed that were both adherent and continuous.

Coating System Sample Preparation

Base metal samples of 304 stainless steel and Incoloy 800 were oxidized at 650° to 950° C for 15 minutes or longer in air to form barrier layers against noble metal diffusion. Next the noble metal reflector layers were deposited on these oxidized surfaces by either vacuum evaporation or by thermal decomposition at 650° C in air of an organo-metallic of the noble metal which had been applied on the oxidized base metal by spraying or dipping.

Finally, the absorber layer was deposited by either thermal decomposition of a metal compound (Ref. 6) or by electrodeposition. The principal oxide prepared by thermal decomposition in this research was cobalt oxide and the majority of these cobalt oxide coated samples were prepared by decomposition from an aqueous or organic (such as ethyl alcohol) solution of cobalt nitrate. The decomposition of nitrates, instead of electroplating, is especially advantageous for it was shown to allow the formation of absorber layers of mixed oxides as well as of simple oxides. While metal oxide layers may be formed on the low emittance layer by spraying (or dipping) and then drying, followed by thermal decomposition, it was found that a refractory oxide which has the desired open structure results if the solution of the metal compound is sprayed onto the low emittance layer at a somewhat elevated substrate temperature and at a rate of spraying such that simultaneous drying and decomposition occur. The strong evolution of vapor during decomposition produced a morphology which gave a maximum absorption/thickness ratio.

Alternately, cobalt oxide was also conveniently formed directly on the noble metal layer by electro deposition from a strongly oxidizing solution. Typically, the cobalt oxide was plated by a sequence such as:

(1) Cleaned by hand with alkaline pumice or by electrolytic alkaline chelating cleaner at 80° C and 600 amps/m^2

(2) Water rinsed

(3) Plated from $CoSO_4$ at 100 g/l with the addition of 10 ml/L of 30 percent H_2O_2 and at 800 amps/m^2 or plated from a solution of:

Cobalt sulfate	270 g/l
Cobalt chloride	37 g/l
Boric acid	30 g/l
pH	1.5-4.5
Temperature	45°-60°C
Current	400 amps/m^2
H_2O_2, 30 percent	100 ml/L

(4) Water rinsed

(5) Dried at 200° C

(4) and (5) may be replaced by (6-8):

(6) Heat for approximately one minute in a solution of 100 g/l of ammonium persulfate $(NH_4)_2S_2O_8$ and 50 g/l of sodium hydroxide

(7) Water rinse

(8) Air dry

The treatment in amonium persulfate solution, or the air drying, both complete the conversion of the cobalt deposit to Co_3O_4. The ammonium persulfate process, however, produced a more adherent oxide coating.

Optical Measurements

Optical measurements were made of coated specimen reflectance in the visible and the infrared wavelengths. Absorptance and emittance were calculated from the reflectance measurements by the standard techniques described below.

Measurements of reflectance in the visible range were made with a commercially available reflectometer. Magnesium carbonate was used as a high reflectance standard and a black cone was used as a low reflectance standard. Absorptance were calculated from these reflectance measurements with the relationship: Absorptance = 1 - Reflectance.

Reflectances in the infrared were measured with a infrared reflectometer. Gold was used as a standard for low emittance. Emittances were calculated from these reflectance measurements with the relationship: Emittance = 1 - Reflectance.

The accuracy of the measurements of the visible reflectance and the infrafred reflectances were estimated to be ±0.02 units.

Exposure at Temperature

The coated samples were also tested for resistance to degradation of optical properties by exposure to air at 650° F in an electrically heated muffle type furnace. Temperature was controlled at 650° C by balancing the power supplied and the heat lost. Temperature during life tests ranged between 625° and 650° C. Samples were placed in the furnace so that they had free circulation of air over the coated surface. At intervals the samples were removed from the furnace and the optical properties were measured at room temperature. The samples were then returned to the furnace for further exposure.

RESULTS AND DISCUSSION

Diffusion Barrier Layer

Type 304 stainless steel specimens oxidized at temperatures from 650° to 950° C produced oxide layers which served to prevent diffusion of the noble metal reflector layer into the base metal. Oxidation at the lower temperatures required a longer time to build sufficient thickness in the oxide layer to prevent diffusion. Oxidation of the 304 stainless steel for 15 minutes at 950° C yielded a sufficiently thick layer of oxide to serve as a diffusion barrier layer. Oxidation for 30 minutes produced a thicker oxide layer which had the advantage of having a rougher and more convoluted surface. Since the reflector layer and the absorber layer follow the contours of the oxide layer, the surface morphology of the thicker oxide was slightly better for trapping incident solar radiation. However, the thicker layers of oxide had the disadvantage that they contained larger voids and could be more susceptible to spalling. Thus, the results reported here represent specimens oxidized for 15 minutes at 950° C.

Low Emittance Layer

If gold (m.p. 1063° C) or silver (m.p. 960° C) is used as the low emitter layer, the melting point of either of these is close enough to the design use-temperature, 650° C, of the selective coating for surface tension effects to cause break-up of the layer to become important. At a constant temperature, layer thickness controls the tendency coating to agglomerate. Figure 2(a) shows the appearance of gold as deposited on oxidized stainless steel by evaporation (to a thickness of 400 Å). The streamed appearance is caused by the surface structure of the stainless steel. Figure 2(b) shows the agglomeration of the gold after exposure for 18 hours at 650° C in air.

Figure 3 shows the increase in emittance over a long period for a 100 Å gold layer on stainless steel in which the gold has formed spherical agglomerates. The increase in emittance is due to both the smaller area of the gold seen by the infrared emissometer as the gold agglomerates and also by the increased emittance of the stainless as it continues to oxidize. In an attempt to decrease agglomeration thicker coatings were deposited. Figure 4 shows in cross section an approximate 20 000 Å silver low emittance film formed by thermal decomposition of a silver-metallo organic on oxidized stainless steel. Figure 5 shows in cross-section a a much thinner (5000 Å) gold low emittance film formed on oxidized stainless by decomposition of a gold organo-metallic. Both Figs. 4 and 5 are for the films after exposure at 650° C in air for 1680 hours. Figure 6 shows the emittance of these gold and silver low emittance films after exposure for 650° C in air for up to 1680 hours. In both cases these reflector films are thick enough to resist agglomerating forces.

The results shown in Fig. 6 indicate that noble metal layers in the 10 000 to 30 000 Å range can be prepared by organo-metallic decomposition and that these have low emittances and are stable for long times (~1680 hr) at 650° C in air.

Absorber Layer

Cobalt oxide was electroplated on selected low emittance layers from a cobalt Watts solution (as previously described. The variation of absorptance and emittance on 10^4 Å gold films is shown in Fig. 7. Similar to other duplex coatings (Ref. 7) the absorptance at first increases rapidly with only a smallchange in emittance until an absorptance of greater than 90 percent is reached, after which the emittance increases rapidly with only slight change in absorptance. Figure 8 shows the absorptance of cobalt oxide formed on $3\text{x}10^4$ Å silver films by thermal decomposition of cobalt nitrate. The same rapid increase in absorptance with only a slight increase in emittance occurred with the cobalt oxide formed by thermal decomposition of cobalt nitrate as was observed with cobalt oxide formed by electrodeposition. This behavior has also been observed with absorber films of copper oxide, black chrome, black nickel and black zinc in previous studies (Ref. 7). This is to be expected since the principle of forming a selective coating, that is, forming a thin coating of a highly absorbing material on a metal of low emittance, is identical for all of these materials.

The change of absorptance and emittance of cobalt oxide formed by thermal decomposition of cobalt nitrate is shown at various weights of cobalt oxide in Fig. 9. Similar to the results shown for the thickness of black chrome in Ref. 8, there is a minimum thickness or weight of cobalt oxide. Below the minimum absorptance is inadequate. Generally, there is also a maximum thickness above which emittance is excessive. From Fig. 9 it is evident that while, the emittance increased with the heavier deposits it had not reached an exponential or break-away increase at 0.14 mg/cm^2.

Figure 10(a) shows a scanning electron photomicrograph (SEM) at ×3000 of cobalt oxide on silver prepared by thermal decomposition of cobalt nitrate. Figure 10(b) shows a SEM photomicrograph at ×3000 of the same material after exposure in air for 984 hours at 650° C. The emittance and absorptance measured at intervals over the 984 hours are shown in Fig. 1. Some physical changes are evident in Fig. 10(b), but the surface is still rough and convoluted. No changes in optical properties were detected over this time interval for the cobalt oxide low emitter combination.

CONCLUDING REMARKS

In this exploratory study, a solar selective coating was identified that had low emittance and high absorptance with stability in air for long times at 650° C. A stable low emittance was achieved through the use of a noble metal layer deposited on an oxide diffusion barrier. The diffusion barrier was formed in situ by oxidation of the substrate alloy. The high absorptance was achieved by use of a cobalt oxide layer. These high absorptance cobalt oxide layers can be formed by either thermal decomposition or directly by electroplating from a cobalt solution containing oxidizing agents. This stable cobalt oxide is refractory, and retains high absorptance at 650° C.

In the as-deposited condition, the cobalt oxide absorber/noble metal low emittance/oxide diffusion barrier coating system on stainless steel, as shown in Figs. 8 and 9, had absorptance of about 0.90 and an emittance of approximately 0.20 as compared to black chrome which at equivalent absorptance has an emittance of less than 0.10. The exact value of the ratio of absorptance to emittance is controlled by both the electronic structure and the morphology of the absorbing material. For two materials of essentially equal blackness in the bulk state such as black chrome and cobalt oxide (i.e., generally similar types of electronic structure) the physical structure or morphology of the deposit determines the maximum absorptance/minimum emittance combination which can be obtained. A 'fluffy' structure which has low bulk density similar to the structure of normal electroplated black chrome has the tendency to improve the absorptance/minimum emittance combination. This is a result of the fact that the plating of black chrome is an electrochemically relatively inefficient process in that significant evolution of gas occurs. The inefficiency and the evolution of gas largely determine the fluffy, low density character of the black chrome deposit which acts as an efficient light trap and reabsorbs, on subsequent incidence, the light from any previous reflection. The addition of an oxidizing agent to the cobalt (or manganese) electroplating solution as developed in this work not only assures direct deposition of an oxide (or in some cases of a metal oxide or hydrated metal oxide intermediate which is readily converted to the desired final form of oxide) but it also produces a very gassy electroplating process, which in turn gives an open, porous, light trapping, structure to the deposited oxide.

However, the more highly divided structure with a larger surface area has a higher activity and will more easily undergo sintering when exposed to elevated temperature and will lose absorptance as it sinters. Any material used for solar coating, whose selective properties depend upon being deposited as a thin film on a surface of low emittance, may actually have an absorptance less than that of the bulk oxide if the film is heated to a sufficient temperature to cause sintering. The sintered film will have lost the light trapping effect but will be so thin as to be partially transparent to the visible. The loss of absorptance of normal black chrome at temperatures of approximately 350° C is apparently due to this coalesence since the loss of absorptance occurs when the black chrome is exposed to temperature in either air or vacuum. The cobalt oxide films which are reported here are structured so that the combination of absorptance/emittance is approximately 0.90/0.20. These properties were determined to be stable for exposures up to at least 1000 hours at 650° C. Other coatings presently used in high temperature solar collectors have emittances of 0.90.

CONCLUSIONS

A solar selective coating has been developed which is stable at high temperatures. The coating system is composed of a cobalt metal oxide absorber on a low emittance noble metal layer. The reflector layer is separated from the substrate by an oxide diffusion barrier layer. Electrodeposited cobalt oxide on either a gold or silver low emittance layer has been prepared which had absorptances greater than 0.90 with emittances less than 0.2. It was demonstrated that stable cobalt oxide layers can be formed by either electroplating from an oxidizing solution or by decomposition of a nitrate. The results showed that the cobalt oxide on the noble metal reflector combination had absorptance and emittance which was stable up to at least about 1000 hours at 650° C.

REFERENCES

1. G. E. McDonald, "Spectral Reflectance Properties of Black Chrome for Use as a Solar Selective Coating," NASA TM X-71596, 1974.

2. G. E. McDonald, Sol. Energy 17, 119-122 (1975).

3. G. E. McDonald, Selective Coating for Solar Panels," U.S. Pat. 4,055,707, Oct. 25, 1977.

4. R. R. Sowell and R. B. Pettit, Plating and Surface Finishing 65, 42-43 (1978).

5. L. S. Darken and R. W. Gurry, Physical Chemistry of Metals (McGraw-Hill Book Co., New York, 1953), pp. 349.

6. Hottel, H. C. and Unger, T. A., Sol. Energy 3,3, 10-15 (1959).

7. G. McDonald and H. B. Curtis, "Optimized Selective Coatings for Solar Collectors," NASA TM X-73498, 1976.

8. G. McDonald, B. Buzek, and H. Curtis, "Fundamental Studies of Black Chrome for Solar Collector Use," NASA TM X-73461, 1976.

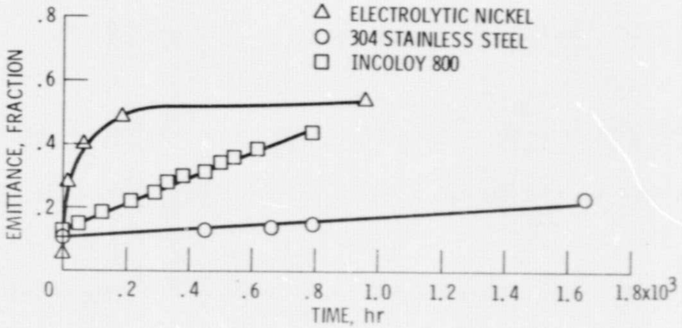
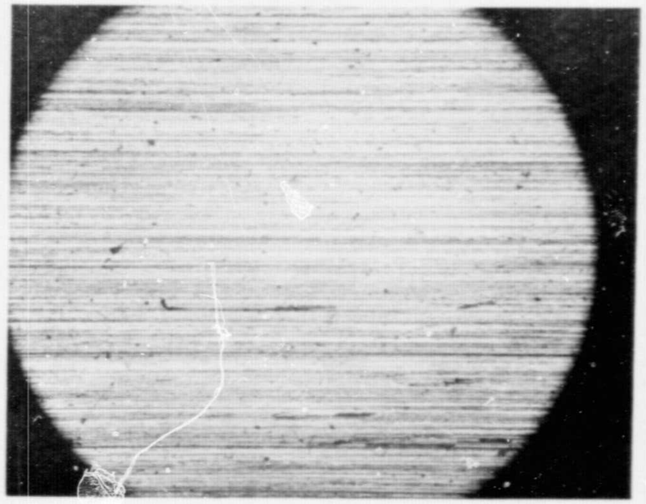
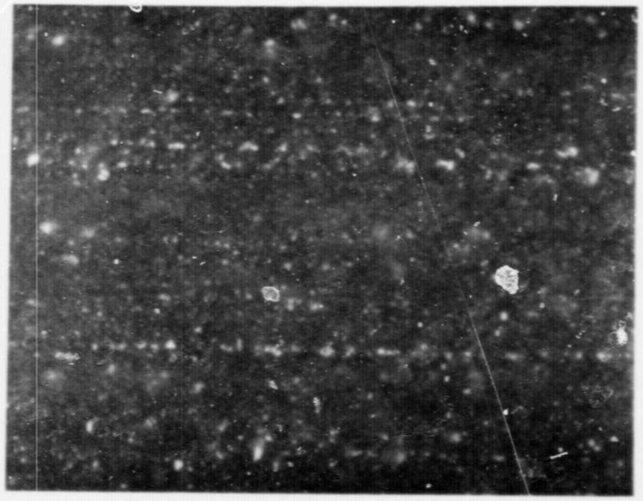


Figure 1. - Change of emittance with time at 650° C in air.



(a) EVAPORATED 400 A THICK GOLD REFLECTOR LAYER ON OXIDE DIFFUSION BARRIER ON STAINLESS STEEL, AS DEPOSITED.



(b) AGGLOMERATION OF EVAPORATED GOLD ON STAINLESS STEEL AFTER 18 hours AT 650° C, 1000X.

Figure 2. - Evaporated gold on stainless steel.

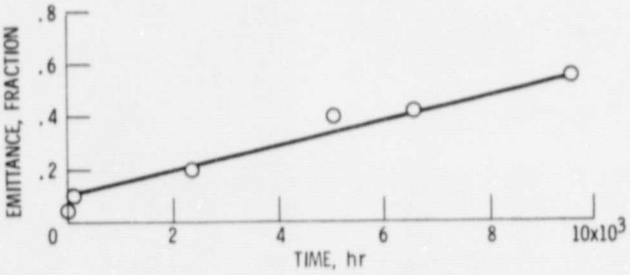


Figure 3. - Increase emittance of 400 Å evaporated gold on oxidized stainless versus time on exposure at 650^0 C in air.

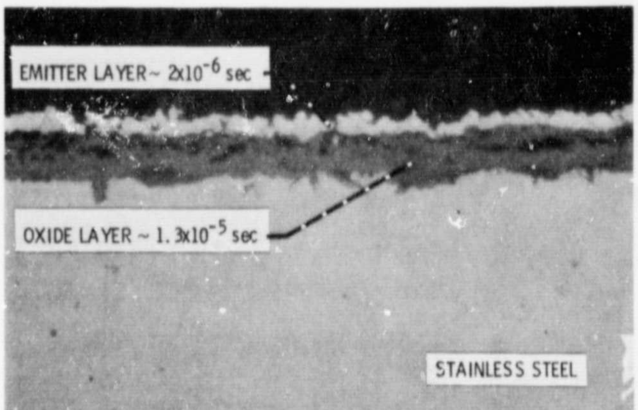


Figure 4. - Silver low emittance layer formed from organometallic decomposition on oxide diffusion barrier on stainless steel after exposure at 650^0 C for 1680 hours in air, 750X.

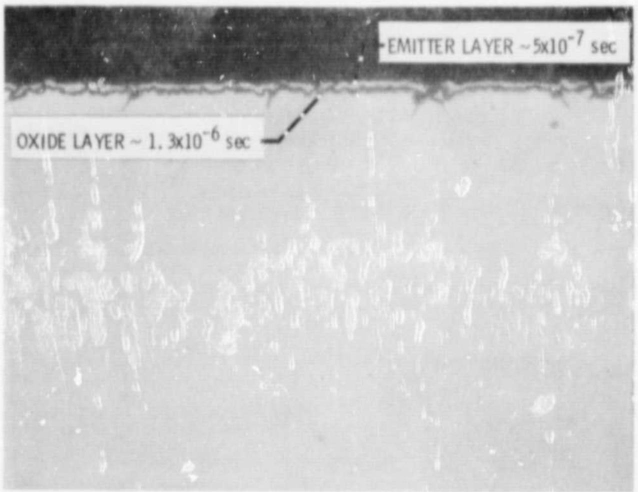


Figure 5. - Gold low emittance layer formed from organometallic decomposition on oxide diffusion barrier on stainless steel after exposure at 650° C for 1680 hours in air, 750X.

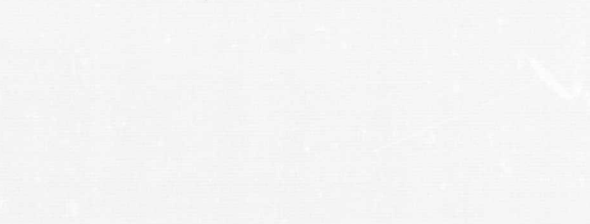


Figure 6. - Emittance stability of gold and silver films formed from organometallic decomposition on oxidized stainless steel versus exposure at 650° C in air.

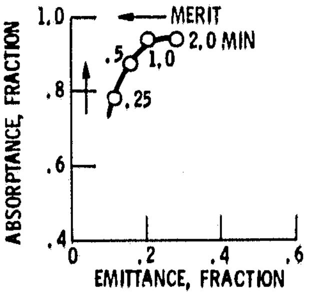


Figure 7. - Absorptance/emittance of cobalt oxide formed by electroplating from cobalt solution on 10^4 Å gold reflector films.

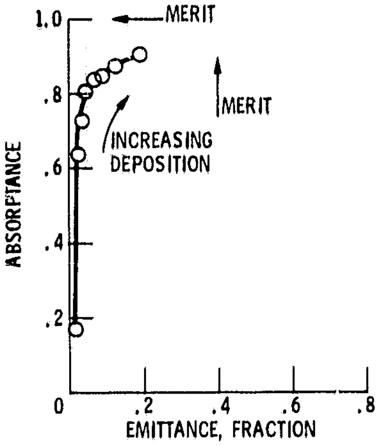


Figure 8. - Absorptance/emittance of cobalt oxide formed by thermal decomposition of cobalt nitrate on ~3×10^4 Å silver films.

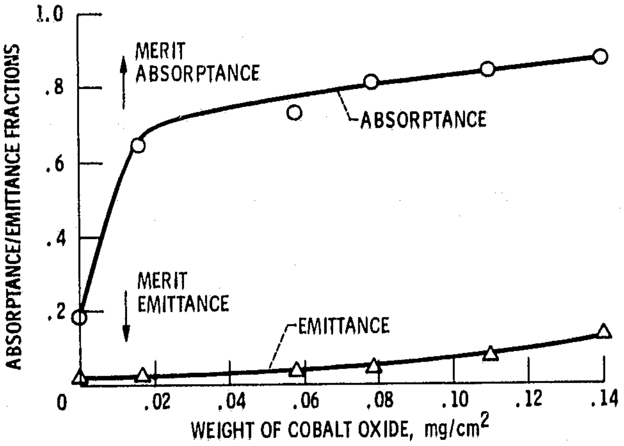


Figure 9. - Increase in absorptance/emittance with increasing weight of cobalt oxide formed on ~3×10^4 Å silver films by thermal decomposition of cobalt nitrate.

(a) AS DEPOSITED.

(b) AFTER 984 hours AT 650^0 C, 3000X, 30^0 TILT.

Figure 10. - Scanning electron micrograph of cobalt oxide prepared by thermal decomposition of cobalt nitrate on silver, 3000X, 30^0 tilt.

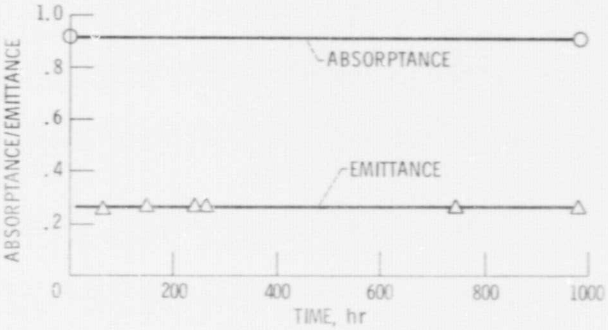


Figure 11. - Absorptance/emittance of cobalt oxide on silver on oxidized-stainless at 650^0 C.

1. Report No. NASA TM-81385	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle **PRELIMINARY STUDY OF A SOLAR SELECTIVE COATING SYSTEM USING BLACK COBALT OXIDE FOR HIGH TEMPERATURE SOLAR COLLECTORS**

5. Report Date

6. Performing Organization Code

7. Author(s)
G. McDonald

8. Performing Organization Report No.
E-293

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Technical Memorandum

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Black cobalt oxide coatings (high solar absorptance layer) were deposited on thin layers of silver or gold (low emittance layer) which had been previously deposited on oxidized (diffusion barrier layer) stainless steel substrates. The reflectance properties of these coatings were measured at various thicknesses of cobalt oxide for integrated values of the solar and infrared spectrum. The values of absorptance, α, and emittance, ϵ, were calculated from the measured reflectance values, before and after exposure in air at 650° C for approximately 1000 hours. Absorptance and emittance were interdependant functions of the weight of cobalt oxide. Also, these cobalt oxide/noble metal/oxide diffusion barrier coatings have absorptances greater than 0.90 and emittances of approximately 0.20 even after about 1000 hours at 650° C.

17. Key Words (Suggested by Author(s))
Solar
Energy
Coatings

18. Distribution Statement
Unclassified - unlimited
STAR Category 26

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161