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# IMPROVEMENT OF BLACK NICKEL COATINGS

BY: R. E. PETERSON AND J. H. LIN

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Systems and Research Center  
Minneapolis, Minnesota 55413

for

George C. Marshall Space Flight Center  
National Aeronautics and Space Administration  
Marshall Space Flight Center, Alabama 35812

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16 Abstract  Selectively absorbing black nickel coatings are one of the most optically efficient low cost coatings for use on flat plate solar collectors. However, this Ni-Zn-S-O coating is quite susceptible to a humid environment, degrading badly in less than ten days at 38°C (100°F) at 95 percent relative humidity. In this program a new black nickel formula was developed which can withstand such exposures with no loss of optical efficiency, solar absorption of > 0.92 and an infrared emittance (at 100°C) of < 0.10 were still present after 14 days of humidity exposure. This compares to a solar absorptance of only 0.72 for the previous formula after a similar time period. The electroplating bath and conditions were changed to obtain the more stable coating configuration. The effect of bath composition, temperature, pH, and plating current density and time on the coating composition, spectral optical properties and durability were investigated systematically.			
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## FOREWORD

This is the final report describing the work performed by Honeywell, Inc., Systems and Research Center, for the NASA Marshall Space Flight Center, Huntsville, Alabama, under contract number NAS8-31545, "Black Nickel Coating Improvement Study".

The authors acknowledge the guidance provided by Mr. James R. Lowery, NASA Project Manager.

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The Auger composition analysis of the coatings was done at the University of Minnesota by P. Lindfors under the direction of Professor G. K. Wehner.

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# IMPROVEMENT OF BLACK NICKEL SOLAR ABSORBER COATINGS

By J. H. Lin and R. E. Peterson  
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## SUMMARY

This is the final report describing work performed by Honeywell, Inc. for the NASA Marshall Space Flight Center, Huntsville, Alabama, under contract No. NAS8-31545, "Black Nickel Coating Improvement Study."

Use of selective solar absorber coatings is a cost-effective technique for improving the performance of flat-plate solar collectors<sup>1</sup>. Among low-cost selective coatings (excluding only vacuum-deposited coatings) electroplated black nickel (a Ni-Zn-S-O complex) has the best optical characteristics, with a solar absorptance  $\alpha$  of  $\sim 0.96$  and a thermal emittance  $\epsilon$  of 0.07. However, black nickel has shown a tendency to degrade in accelerated humidity tests and possibly in the humidity environment of a solar collector over long periods. The purpose of this program was to improve black nickel humidity resistance without sacrificing the excellent optical properties.

The chemistry of the plating bath was studied and the effect of changes in plating parameters determined experimentally. Plating time, current density, bath temperature, pH, and the concentration of  $\text{SCN}^-$ ,  $\text{Zn}^{++}$ , and  $\text{Ni}^{++}$  were all found to have significant effects on coating properties. Essentially, these plating parameters control the proportions of metal sulfides, metal hydroxides, and free metals in the coating. The main effect of humidity is to convert metal sulfides to metal hydroxides near the coating surface. The significance of this change was found to be minimized by producing a coating rich in metal hydroxides to begin with. The hydroxide rich coating was achieved by increasing both pH and plating current density. The resulting coatings withstood 14 days at 95 percent relative humidity at  $38^\circ\text{C}$  ( $100^\circ\text{F}$ ) with little change in optical properties ( $\alpha = 0.92$  and  $\epsilon = 0.10$  after testing) compared to major degradation ( $\alpha = 0.72$  after test) for coatings produced with the previous formula.

## TECHNICAL DEVELOPMENT AND RESULTS

Significant technical factors and results discussed in this section are: state of the art; experimental and analytical techniques; chemistry of black nickel plating; the effect of several plating parameters including pH, temperature, current density,  $Zn^{++}/Ni^{++}$  ratio, and  $SCN^-$  and  $NH_4^+$  concentration on the coating composition, optical properties and humidity resistance. Results of the parameter study are then summarized, the rationale behind the selection of new coating formulas is discussed, and properties of coatings produced with the new formulas are given. Finally, another technique studied, organic overcoats, will be discussed.

### State of the Art

The black nickel coating is applied by a process that was described as early as 1921.<sup>2</sup> Serfass<sup>3</sup> proposed a theory explaining the plating process, and more recent recipes for fabricating wavelength selective black nickel coatings for solar energy applications have been given by Tabor<sup>4</sup> and NASA/MSFC.<sup>5</sup>

The coating is applied to an infrared reflective metal substrate. Most often, this reflective substrate is achieved by plating a cheaper metal with about  $3 \times 10^{-3}$  cm of nickel. The nickel layer remains reflective in the infrared over long periods and protects the base metal substrate from corrosion. The thin ( $0.1 \mu m$ ) black nickel layer is absorptive in the solar spectrum due to both a natural absorption in that region and an optical interference effect. In the infrared, the coating is transparent, resulting in a low emittance "show through" of the nickel-coated substrate. The spectral reflectance of such a coating is shown in Figure 1. Note that the reflectance remains low over the entire  $0.4-1.5 \mu m$  wavelength region before rising rapidly to  $>90$  percent reflectance above  $8 \mu m$ , which is nearly the ideal behavior for a low-temperature selective solar absorber coating.

When coated to the proper thickness, the common black nickel coating used in the electro-plating industry has a solar absorption ( $\alpha$ ) of 85 to 90 percent and infrared emittance ( $\epsilon$ ) at  $100^\circ C$  of 6 to 8 percent. The NASA/MSFC coating uses a similar process and achieves roughly the same optical properties.

Tabor<sup>4</sup> first pointed out that there are two stable black nickel coating compositions corresponding to different plating current densities. The two compositions have different optical constants that can be used advantageously in two-layer black nickel coating systems to achieve higher solar absorptances. Tabor was able to get  $\alpha = 92$  percent in this way. At Honeywell,

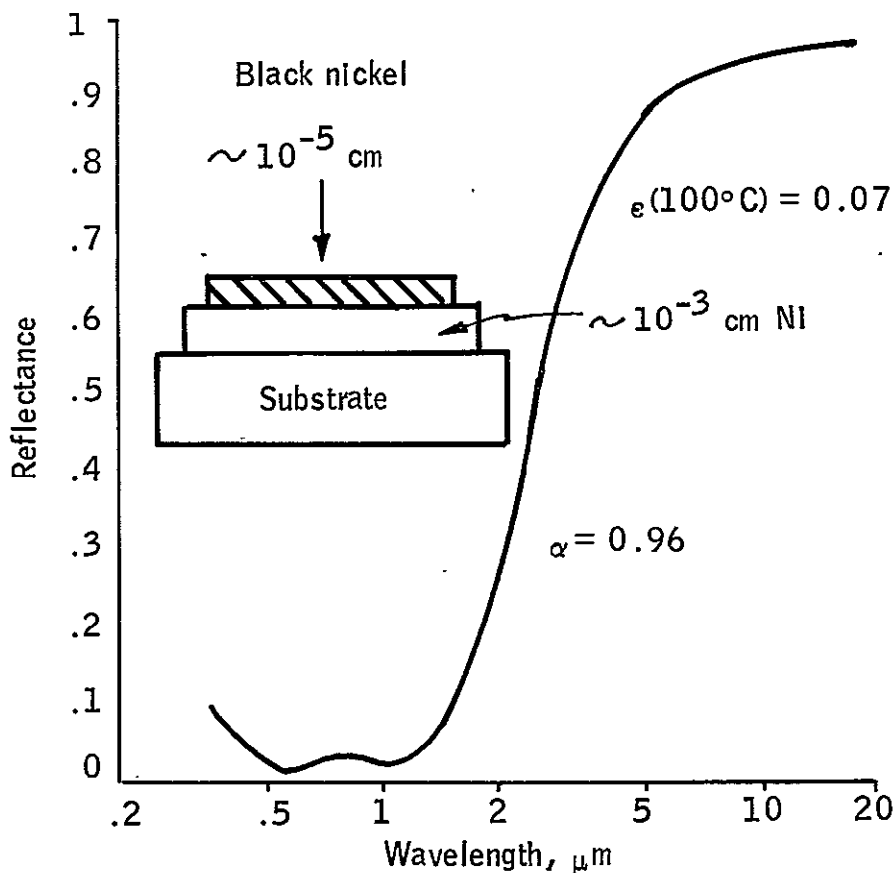


Figure 1.- Spectral reflectance of black nickel coating.

we previously used a formula and two-layer technique similar to Tabor's to achieve coatings with  $\alpha = 96$  percent and  $\epsilon = 7$  percent after considerable effort to optimize the procedure. Coatings with  $\alpha = 94$  percent were obtained consistently over several months with this formula. No effort was made to optimize the durability of this earlier coating.

These performance values for black nickel are compared to properties of other selective coatings on Table I. We have been examining the composition, durability and optical properties of many of these other coatings under contract with ERDA (Reference 1). From Table I it is clear that black nickel coatings have the best optical properties but far from the best durability, especially under environmental humidity tests. Due to apparent durability of the black chrome and black iron coatings, our ERDA program has emphasized improvement of their optical properties.

TABLE I.-PERFORMANCE VALUES FOR SOME SOLAR ABSORBER COATINGS

Coating	Substrate	$\alpha$	$\epsilon$	Breakdown temperature, (°C)	Humidity resistance
Black nickel	Nickel	.96	.07	300	Poor
Black copper	Copper	.90	.14	200	Poor
Black chrome	Nickel	.93	.12	450	Excellent
Black iron	Iron	.85	.08	---	Good
MnO <sub>x</sub>	Aluminum	.70	.10	---	---

An equally reasonable approach, however, is to improve the durability of black nickel coatings. How much is the better optical performance of the black nickel worth in terms of solar collection efficiency? Based on results of recent NASA/MSFC analysis,<sup>6</sup> Honeywell solar simulator tests and computer-generated yearly solar collection averages, an increase in absorption of 1 percent increases overall collector performance by ~3 percent, while a 1-percent decrease in emittance (from 8 percent to 7 percent for example) would increase collector performance by ~1.5 percent. These calculations are for an ~100°C collector operating temperature with two glass covers. Therefore, the better optical properties of black-nickel coating are fairly significant (equivalent to ~15 percent better overall collector performance relative to black chrome, for example). Thus, successful development to improve the durability of black nickel has an important impact on flat-plate collector systems.

Some physical tests that have been given to black nickel coatings at Honeywell are listed below.<sup>1</sup>

- Heating at 280°C for one week caused no optical change
- One-third sun year of UV caused no change
- 14,000 cycles from 28° to 104°C (equivalent to 40 years) caused no change
- MIL STD coating abrasion test (erasure rub) badly scratches the coating
- The MIL STD coating adherence test (Scotch tape pull) could not remove the coating.

The key problem with black nickel coatings is of course its lack of humidity resistance. It degrades very rapidly in accelerated humidity exposures. Improving this humidity resistance was the main goal of the present program.

### Experimental and Analytical Techniques

Coating Preparation. - About 200 black nickel samples were plated in this program in ~8 l (2 gallon) baths of plating solution. The samples were 8 cm x 10 cm, from which four 2.54 cm diameter samples were punched for the various optical and durability tests. One sample was used to find the spectral reflectance and other optical properties, one was sent for Auger composition analysis, one was given an environmental humidity test followed by composition analysis, and the fourth sample was given a humidity test followed by an optical characterization. Often this fourth sample was returned to the humidity chamber for prolonged testing, with periodic optical measurements to monitor any degradation.

The coatings were all applied to bright nickel-coated steel substrates. The bright nickel plating, to 0.0025 cm thickness, was done by a local electroplater. Due to the lapse of time between the bright nickel electroplate and the black nickel coating in our lab, the oxide layer that forms on Ni had to be removed before the black nickel coating could be applied. The cleaning and oxide removal (activation) procedure used in our lab was as follows:

- Cleaning with dish-soap and water. Rinse.
- One minute in a boiling 30 percent solution of NaOH. Rinse.
- One minute in 30 percent solution of HCl at room temperature. Rinse.

This procedure gave a consistently good surface for subsequent black nickel plating. In a production-line process, the bright nickel plating would most likely be performed just before the black nickel plating, and the activation process would then be unnecessary.

Optical Tests. - The solar absorptance (at air mass two) was measured right after the coating deposition with a Gier Dunkle Solar Reflectometer. This measurement was followed by measurement of spectral reflectance from 0.3 to 12  $\mu\text{m}$  in an integrating sphere reflectometer, and from 2.5 to 40  $\mu\text{m}$  in a Beckman IR 20A Spectrometer. The solar absorptance (at air mass two) and the infrared emittance (at 100°C) were calculated from the spectral reflectance curves using appropriate solar and black body spectra to weight the data in the integration.

This technique gives  $\alpha$  and  $\epsilon$  values accurate to  $\pm 0.02$ . The accuracy of this technique for the emittance values has been verified by direct measurement of total emittance at 100°C. The solar absorptance, as determined by the integrated spectral reflectance, disagreed with the Gier Dunkle value by at most two percent.

Physical Tests. - Programmable humidity test chambers were used for the two types of humidity tests given in this program, namely:

- A constant environment of 95 percent relative humidity at 38°C (100°F). Throughout this report, this environment will be referred to as the standard NASA humidity test since it was recommended for use as the basic test of the program in the RFP.
- The second test used is the much more severe MIL-STD-810B, Method 507, Procedure I. This test consists of a thermal and humidity cycle from room temperature to 71°C (150°F) at 95 percent relative humidity (RH) and from 71°C to room temperature at >85 percent RH over a 24-hour period. This is one of the most severe accelerated environmental tests. The test conditions impose a vapor pressure on the samples that causes moisture penetration and migration.

The suitability of this test to accurately gauge the effects of long term, 10 to 20 years, exposure in an actual solar collector is difficult to determine. Coatings that have failed the 810-B test in only one day have now withstood two years of use in flat plate collectors in the relatively severe environment of Minnesota with no coating degradation, except in limited areas where pinholes through the bright nickel coating led to spots of rust from the steel substrate. Although there is no long term data to back it up, we feel the 810B test is probably a more severe test than is necessary to simulate the long term humidity environment.

Composition Analysis. - The key technique used for coating composition analysis was the sputter-Auger composition depth profile. These measurements were performed for Honeywell at the University of Minnesota under the direction of G.K. Wehner. In Auger electron spectroscopy the sample surface is bombarded with electrons of several Kev energy, and one observes ejected electrons with well-defined energies that are characteristic of the atom species from which they originated. An Ar ion gun operating at a pressure of  $5 \times 10^{-5}$  torr is used to sputter-etch the sample while analyzing the electron emissions. The low sputtering rate of  $\sim 70$  Å/minute allows a composition depth profile to be made. The ion beam diameter is much larger (3mm) than the analyzing electron beam (50 $\mu$ m). With the region of analysis in the center of the relatively flat bottom of the ion-sputtered crater, good depth resolution results. The depth from which Auger signals originate extends about 15 Å below the surface.

The energy spectrum of the emitted electrons has peaks at energies corresponding to the atomic species that are present, and the magnitude of the peaks gives a measure of the relative amounts of that atom that are present. The technique is insensitive to the interatomic bonding. Since black nickel coatings have a very complex chemical structure, it was essentially impossible to calibrate the Auger peaks to give a direct measure of absolute percentage of any particular element in the coating. That is, although the oxygen signal may be greater than the sulfur signal on a particular figure in this report, there may actually be more sulfur in the coating. However, the technique can be used very effectively to identify changes between coatings and as a function of depth. The comparison between different coatings can also be aided somewhat by using the Auger signal from the underlying pure Ni substrate to normalize the data.

### The Chemistry of Black Nickel Coating

The following discussion of the chemistry of black Ni coating summarizes an earlier theoretical analysis by Serfass, et. al.<sup>3</sup> It serves as the foundation for our experimental investigation of plating parameters.

The bath and plating conditions used as the basis for the work of this program are as follows:

#### NASA Standard Bath

Nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )	75 g/l
Nickel ammonium sulfate ( $\text{NiSO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ )	45 g/l
Zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ )	37.5 g/l
Sodium thiocyanate ( $\text{NaSCN}$ )	15 g/l
Current density	4.3 ma/cm <sup>2</sup>
Temperature	21 - 26.7°C
pH	5.6-5.9
Plating time	30 s
(or until a coating of 1500Å is produced.)	

A very limited amount of testing was also done using a bath described by Tabor<sup>4</sup> but with current densities, times, and pH levels optimized earlier at Honeywell for maximum optical efficiency. This other solution is referred to as the "Honeywell black nickel" coating in the discussion below, where it will be described in more detail.

The NASA standard bath for black nickel plating contains the ions of  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{Na}^+$ ,  $\text{H}^+$  and  $\text{OH}^-$ . Using a bright nickel-plated substrate as the cathode and pure nickel as the anode, a diagram of the plating bath is given in Figure 2. Some important reactions at each electrode during the plating process are listed below:

Anode (Pure nickel)



Cathode (Bright nickel plated metal)

a. Reduction of thicyanate ion in acidic solution

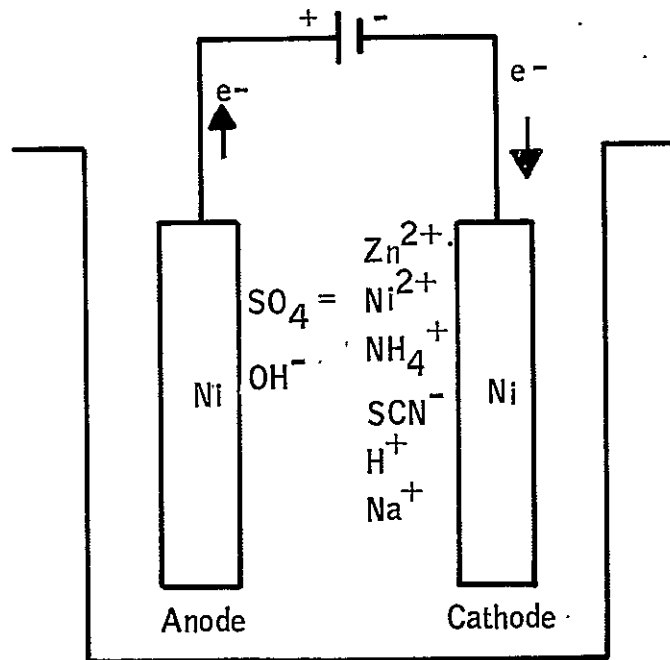
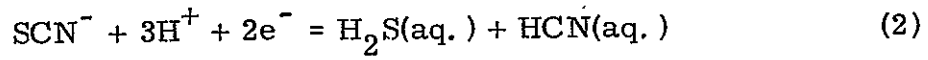
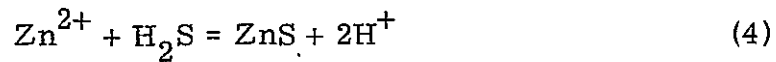
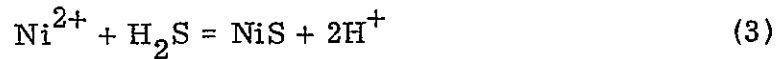


Figure 2. - Black nickel electroplating bath.



b. Formation of nickel and zinc sulfides



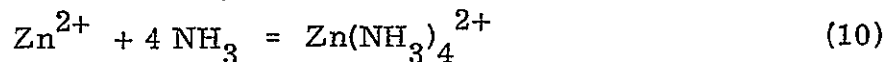
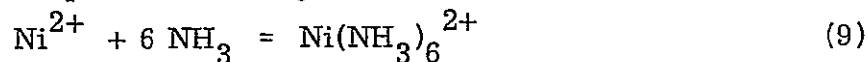
c. Evolution of hydrogen gas



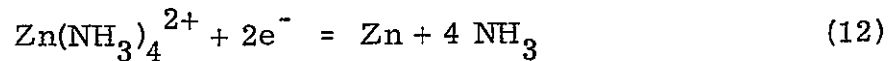
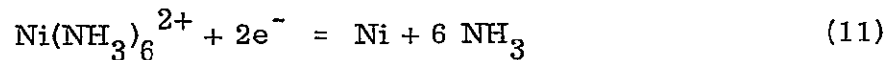
d. Deposition of nickel and zinc metals from their ions



e. Function of the ammonium ion



f. Deposition of metallic nickel and zinc from their ammonia complex ions

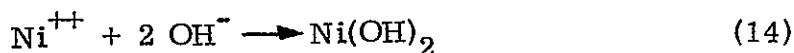
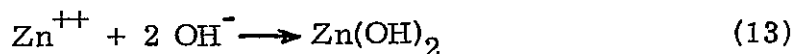


While nickel, zinc, thiocyanate and ammonium ions play an important role in plating, the sodium ion does not participate in the reaction due to its highly negative reduction potential, and the sulfate ion remains unchanged because of the predominant reaction of nickel at the anode.

Essentially, there are two basic reactions of primary importance, the deposition of the metal sulfides [Equations (3) and (4)] and the deposition of the elemental metals [Equations (6) (7) (11) and (12)]. The rates of these two depositions can be controlled by the plating conditions. In the actual coating there is a mixture of metal sulfides and free metals, both of which are necessary to obtain the desired solar absorption properties. As will be shown clearly below, coatings with too little free metal do not have sufficient absorption in the solar spectral region, causing the spectral reflectance curves to show an oscillating, optical-interference pattern. If there is too much free metal in the coating, there is a flat spectral reflectance curve due to absorption by the metal atoms, but often then the reflectance is too high (~ 15 percent) in the solar region (it looks metallic), and

the coating transmittance in the IR is too low (giving a high emittance). Thus, good optical properties depend on the proper mixture of metal sulfide and free metals.

Another basic reaction not discussed above is the possible deposition of metal hydroxides under high pH conditions.



This hydroxide precipitation can also occur when the solution is over driven, e. g., by too high current density. When the current density is too high, hydrogen evolution near the cathode causes the local pH to increase over that of the bulk solution. In electroplating, the conditions at the solution-metal interface are much more important than that of the bulk solution. Thus a locally high pH near the cathode can cause the precipitation of nickel and zinc hydroxides.

The repeated pattern observed in our study of plating parameters was the appearance of three regions where the deposition of either metal sulfides, free metals, or metal hydroxides predominates over the other two. The coating composition depends on the rates of these competing reactions. Since pH is a dominant parameter, the rates of various reactions will be discussed in the subsection below which covers the effect of the pH parameter. First, however, the mechanism of the humidity breakdown of the coating will be discussed.

#### Mechanism of Humidity Degradation of Black Nickel Coatings

The Auger spectra of a black nickel plated coating using the standard NASA bath and conditions is shown before and during a NASA standard humidity test in Figure 3. Note the decrease in S and increase in O content near the coating surface. The same basic change occurred, to varying degrees, for essentially all of the degraded samples in the program. Apparently the main reaction caused by the humidity is the replacement of metal sulfides by metal oxides or hydroxides in the coatings. Hydrogen atoms can not be detected by Auger analysis, so it is not possible to be sure if oxides or hydroxides are being formed. However, based on the analysis of bath chemistry, it is most likely that hydroxides are being formed. As shown below, the degradation process can be greatly retarded by changes in plating conditions. Also, the reaction often moves to a certain depth in the coating and then stops.

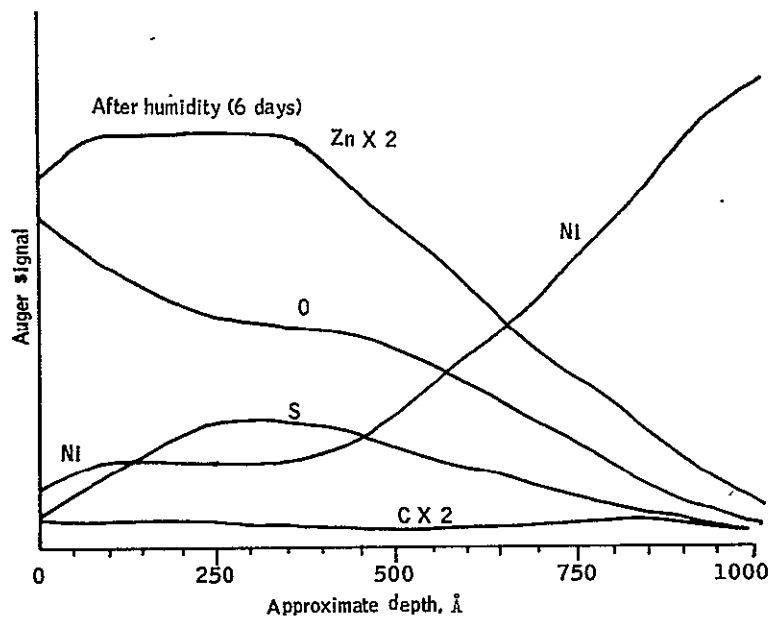
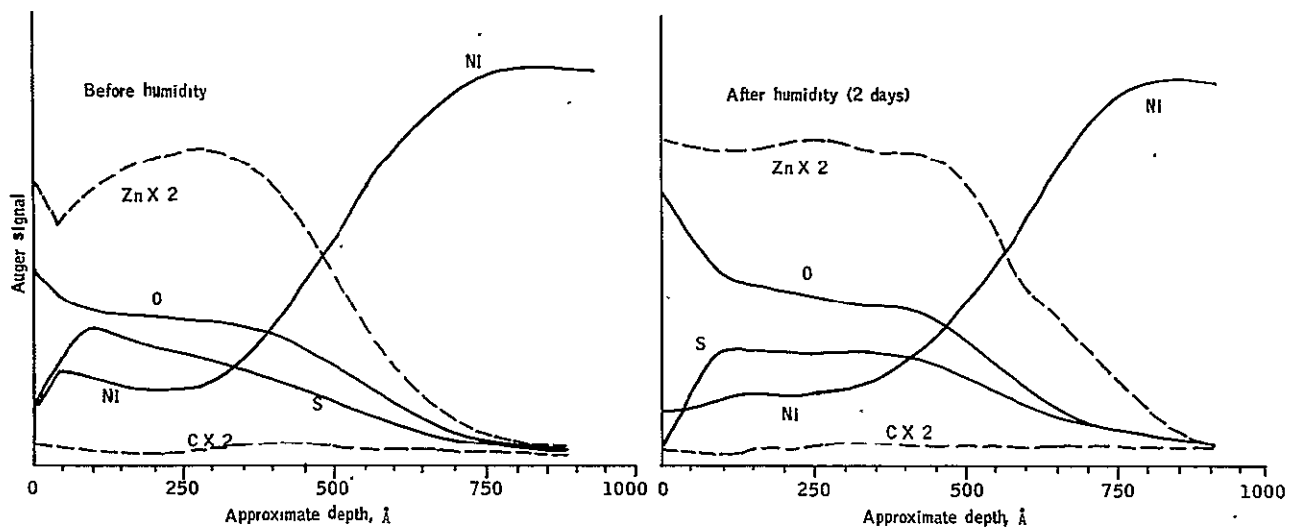


Figure 3. - Auger spectra of a NASA standard formula black nickel coating before and after NASA humidity test.

Table II shows the absorption and emittance of several coating samples all plated with the NASA standard formula after two different humidity degradation tests. These results are intended to show the variable properties that can be obtained with nominally identical black nickel coatings. Black nickel plating is inherently a complex and sensitive process with which many investigators have had trouble obtaining consistent results. The ~7 percent scatter of the results in Table II should be remembered when comparing results in the parameter study to be given below. In the study, inconsistencies were minimized by using identical plating techniques and only varying one parameter at a time. However, some variations in coating properties, especially between different batches of the "standard bath," were difficult to eliminate.

TABLE II. - HUMIDITY RESISTANCE OF FOUR SAMPLES PLATED USING THE NASA STANDARD FORMULA AND CONDITIONS AT VARIOUS TIMES DURING THE PROGRAM

Before humidity		After one day 810-B	After four days NASA test
$\alpha_s$	$\epsilon$	$\alpha_s$	$\alpha_s$
.86	.08	.826	.885
.93	.12	.857	.90
.91	.10	.896	.90
.90	.09	.805	.88
Average properties			
.90	.097	.846	.891

Note the average properties obtained on the Standard coating at the bottom of Table II. Also note that one day in the 810-B humidity test causes more degradation than four days of the NASA humidity test.

#### Effect of pH on Coating Properties

The pH of the plating solution is of key importance. The reduction of the thiocyanate ion offers a sulfide ion for black nickel sulfide formation, but the thiocyanate reduction potential is greatly affected by the pH of the plating solution. The relationship between reduction potential of thiocyanate and pH has been derived by Serfass<sup>3</sup> as:

$$E = +0.068 + 0.0295 \log (\text{SCN}^-) - 0.0885 \text{ pH} \quad (15)$$

A plot of this equation is included in Figure 4 for various thiocyanate concentrations. The more positive the potential E in Figure 4 (closer to the bottom of the graph) and Equation (15), the easier the reaction will proceed. The potential required for several other reactions to proceed at various pH values is also plotted in Figure 4.

It can be concluded from Figure 4 that:

- At lower pH, thiocyanate is easier to reduce, and thus nickel and zinc sulfides are easier to form.
- At lower pH, the hydrogen ion is also more easily reduced and causes the evolution of hydrogen gas.
- At higher pH, the reductions of hydrogen ion into hydrogen gas and the nickel ion into metallic nickel predominate over the reduction of thiocyanate (and hence NiS formation). This results in a grey metallic coating.
- The choice of pH is also restricted by the precipitation of nickel sulfide and nickel hydroxide. The nickel sulfide precipitates (or deposits) very slowly at pH less than 3, but at pH over 6 a precipitation of nickel hydroxide may occur.

Many of these predictions based on the computed reaction potentials were observed for the coatings deposited in this program at various pH values.

Effect of pH on Auger Spectra. - The Auger spectra of samples plated using the NASA formula but with eight different pH values were measured. The pH of the standard NASA formula is 5.6. The Auger spectra for four of these different pH's before and after the humidity tests that illustrate the effects are shown in Figures 5 and 6.

Before the humidity test, there are some composition differences among samples plated at different pH's. At pH higher than 6.0, the coating compositions are quite different from that of pH lower than 6.0. At pH = 6.5, the Zn and O concentrations are higher, while the Ni and S are lower near the coating surface. The higher O and lower S content can be explained by the precipitation and deposition of metallic hydroxides as was predicted by the computed reaction potentials for pH greater than 6.

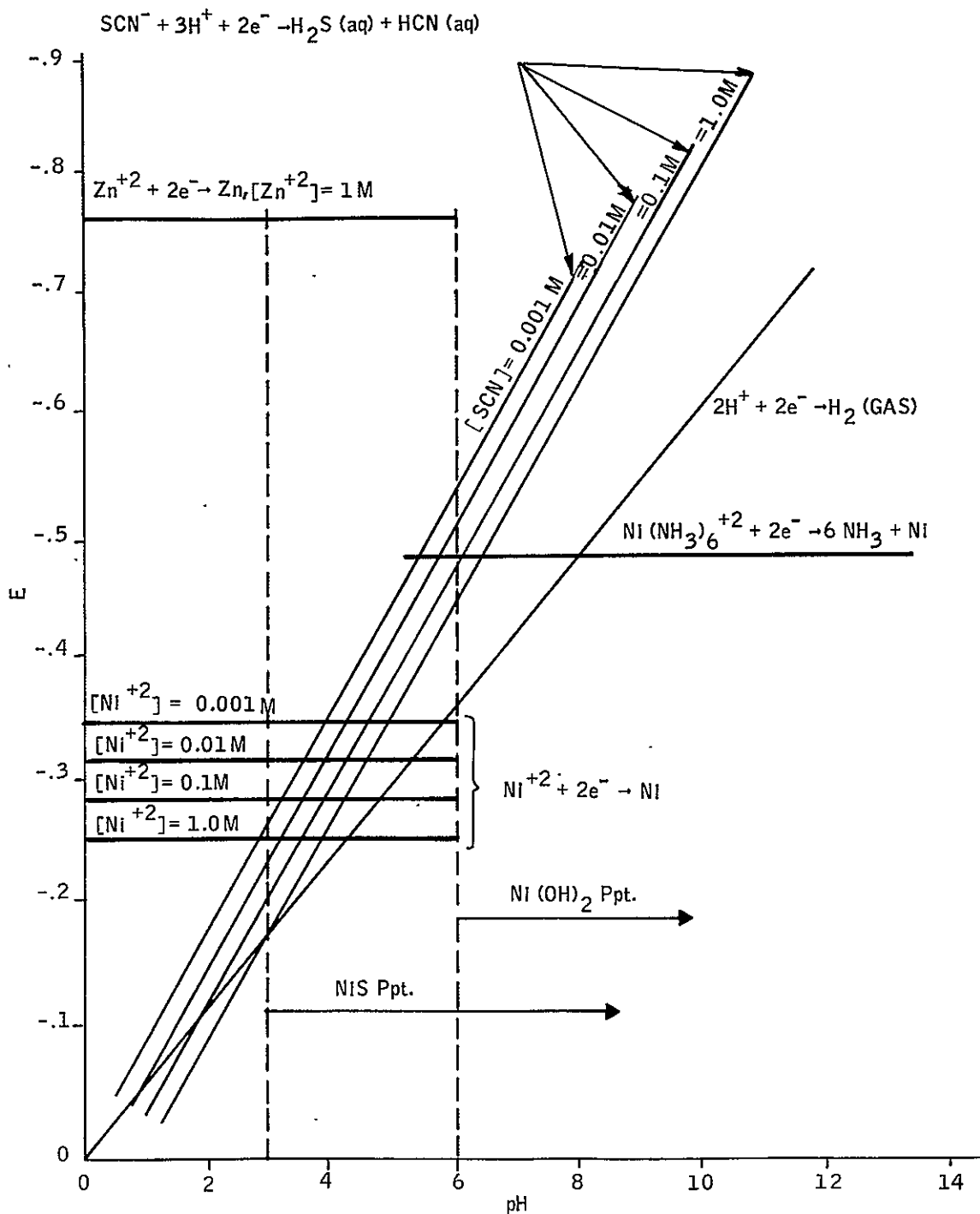


Figure 4. - Effect of pH on reduction potentials in black nickel plating electrolytes.

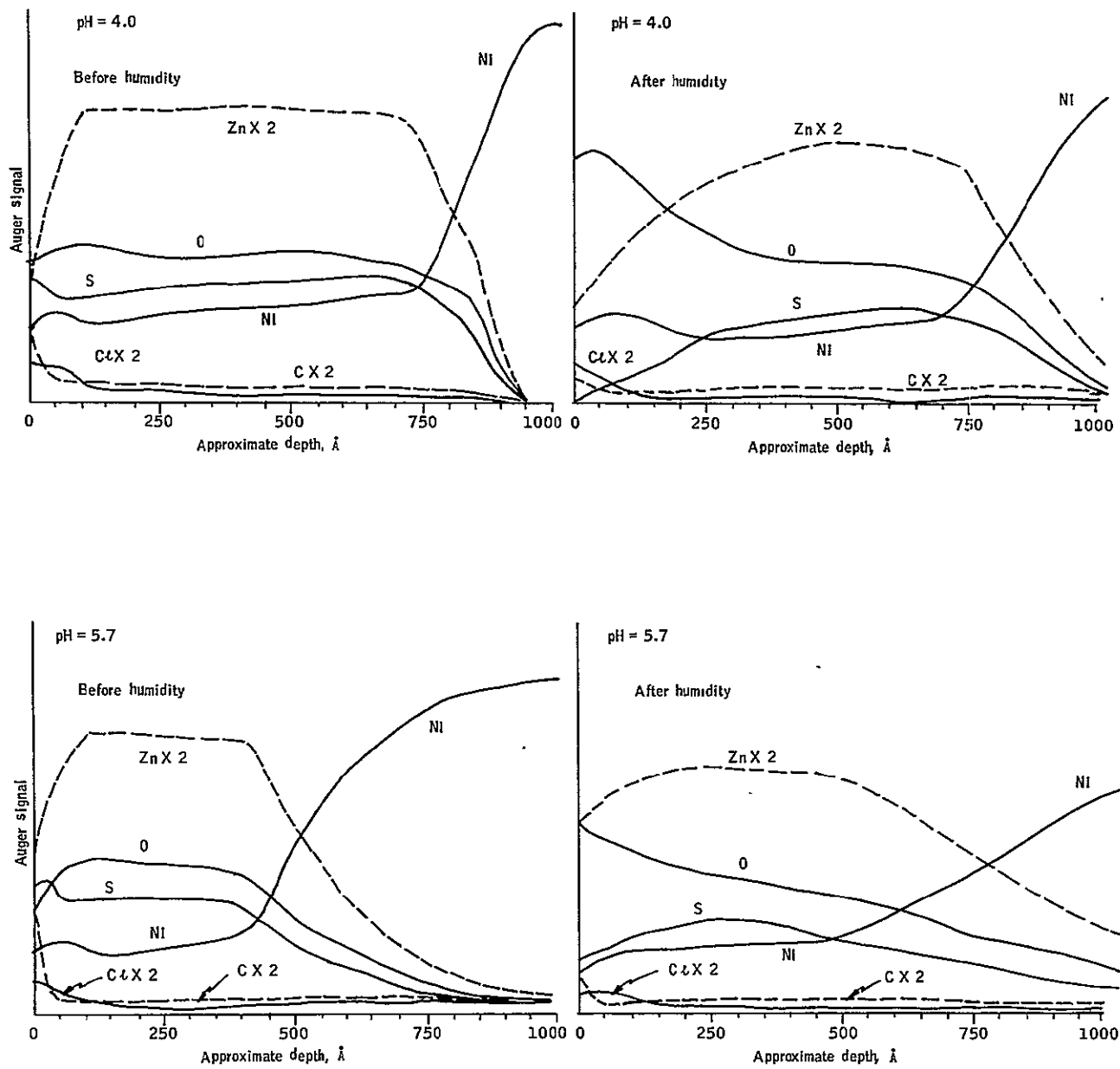


Figure 5. - Effect of pH on Auger spectra,  
pH: 4 and 5.7.

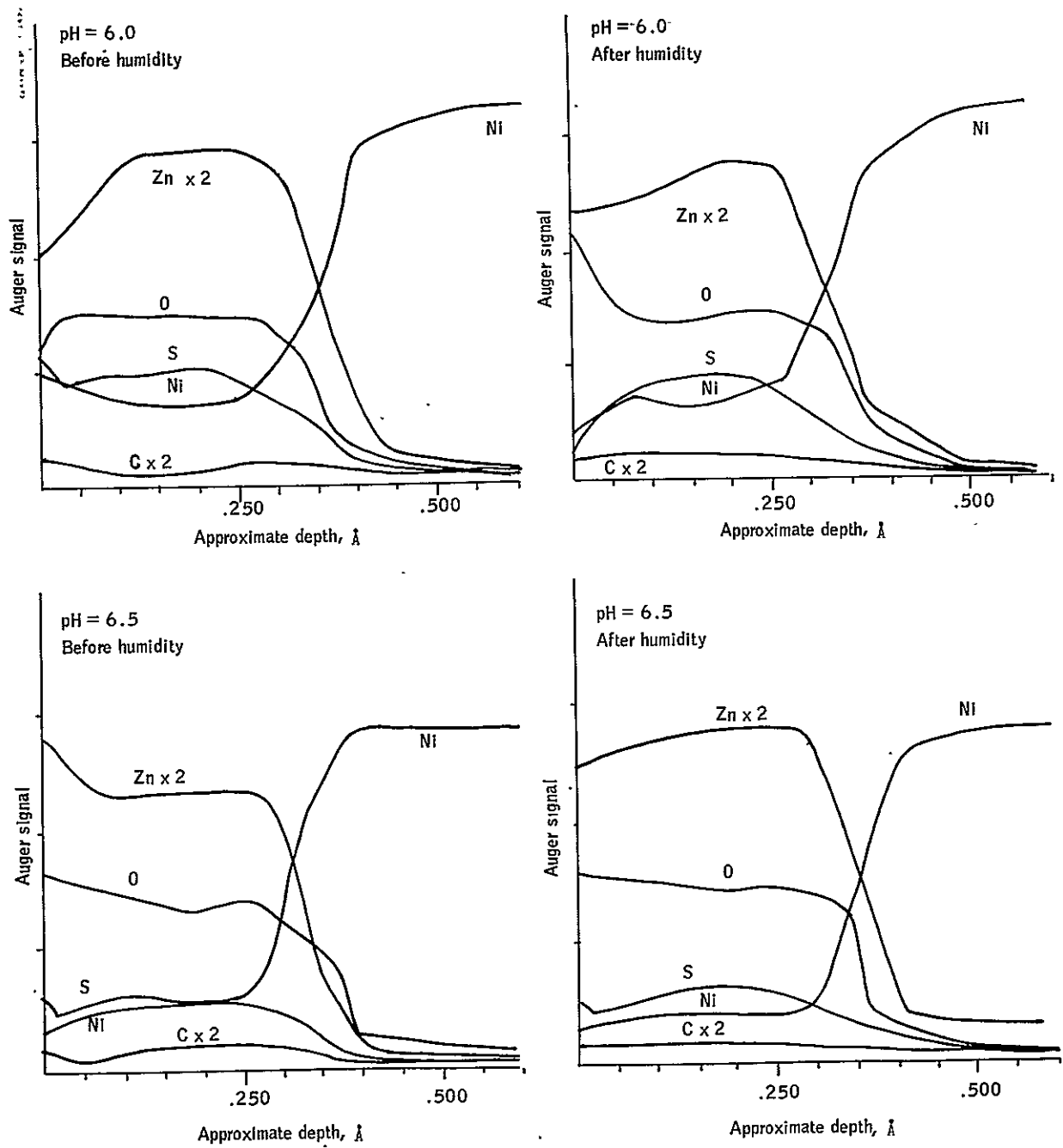


Figure 6. - Effect of pH on Auger spectra, pH: 6.0 and 6.5.



One consistent change due to the humidity test (seen on Figures 5 and 6) is the decrease in sulfur concentration near the coating surface and a corresponding increase in oxygen. This change occurred on all the Auger spectra received, but it is least distinct for the high pH samples of Figures 5 and 6. The pH = 6.5 sample seems most stable in humidity as far as the coating composition is concerned, and as we shall see below, the pH = 6.0 samples have the most stable optical properties. Probably the relatively high oxygen content in the high pH samples prevents further oxidation (or the formation of hydroxide) during the humidity test.

Effect of pH on Optical Properties. - The spectral reflectance of samples in the pH range 4.5 to 6.5 are shown in Figure 7. As the figure indicates, all samples have reflectance curves that are flat in the .35 to 1.5  $\mu\text{m}$  region. Their solar absorptance are all in the range of 91 percent to 94 percent. Except for two thick coatings plated at pH 6, and 6.5 for 92 seconds, all the samples have an infrared emittance between 9 percent and 12 percent.

The reflectance of the same samples after 48 hours in the humidity chamber at 100°F and 95 percent relative humidity are shown in Figure 8. The humidity has no significant effect on the optical properties, but it does flatten the reflectance curves in the .35  $\mu\text{m}$  to 1.5  $\mu\text{m}$  region somewhat and causes the reflectance to rise slightly faster at wavelengths beyond 2  $\mu\text{m}$ . The latter effect results in a slightly lower infrared emittance. A reduced emittance of black nickel samples is typically observed after humidity tests. The two-day humidity test improves both the  $\alpha$  and  $\epsilon$  values; longer tests, however, cause the coatings to degrade.

Table III shows the results of longer humidity tests for samples plated at pH values from 3.5 to 6.5. The samples plated at a pH of 6.0 have the best humidity resistance. Note the thick coating that was plated at pH 6.0 for 92 seconds showed almost no degradation at all after a 13-day humidity test. However, an undesirable property for this thick coating is its high emittance (23.2 percent before the humidity test). The sample with the best combination of optical properties and humidity resistance was the one plated at a pH of 6.0 for 40 seconds.

Summary of the Effects of pH. - Before the humidity test, samples plated at a pH higher than 6.0 differ significantly from those below 6.0. At a pH greater than 6.0, the Zn and O concentrations are higher than the Ni and S concentrations near the coating surface. This is due to the faster precipitation and deposition of Zn and Ni hydroxide compared to the deposition of metallic sulfides.

After the humidity test, all samples show a decrease in sulfur concentration near the coating surface and a corresponding increase in oxygen. This change is minimized for the high pH samples that have a high oxygen content to start with.

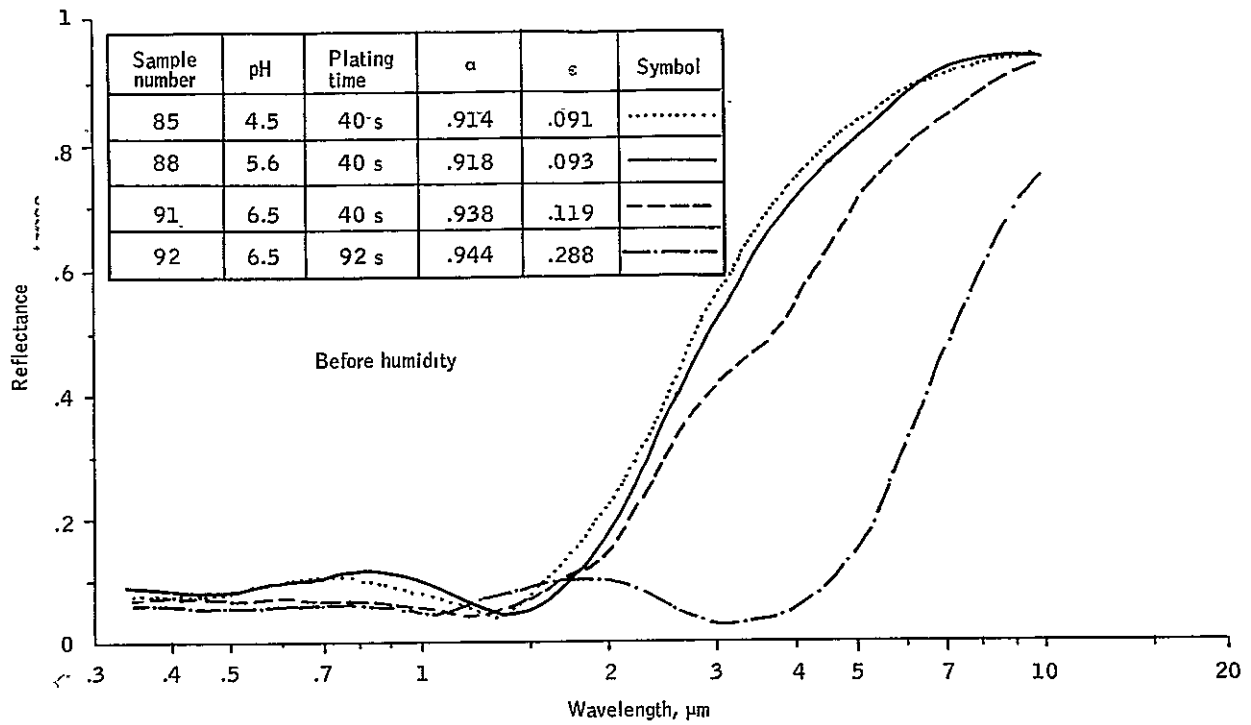


Figure 7. - Effect of pH on spectral reflectance - before humidity.

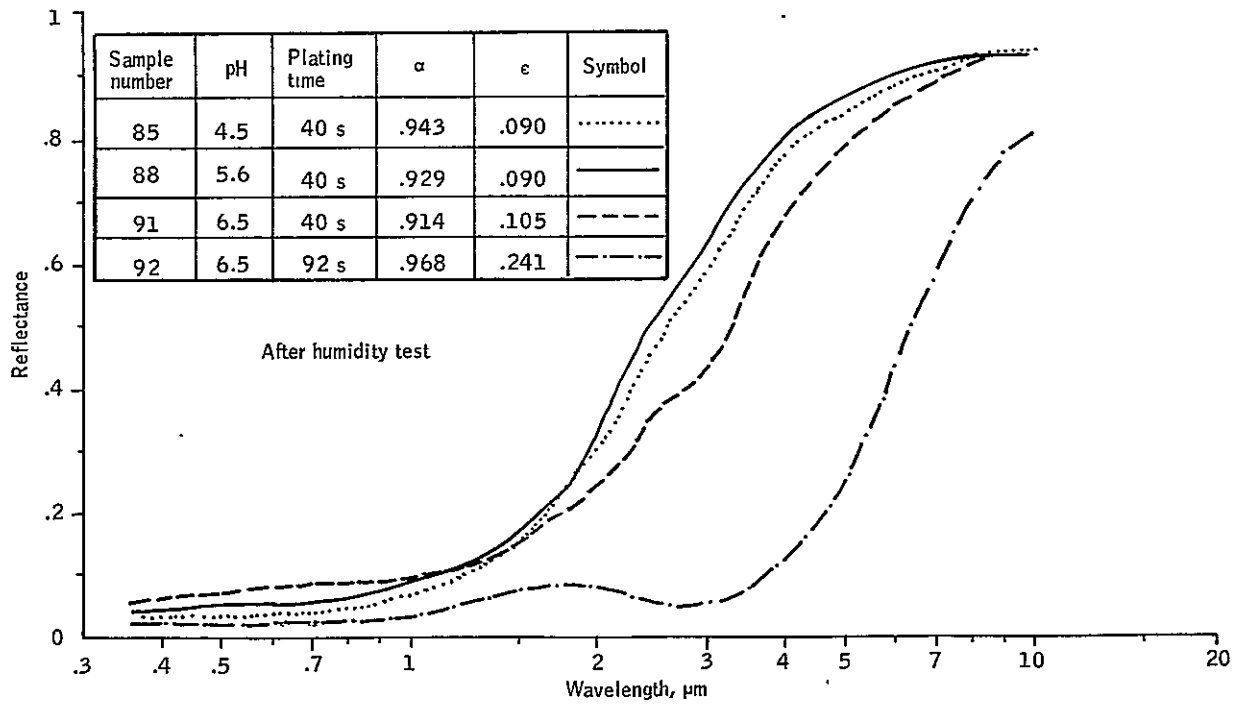


Figure 8. - Effect of pH on spectral reflectance - after 48-hour humidity test.

TABLE III.- HUMIDITY RESISTANCE OF BLACK NICKEL SAMPLES PLATED AT DIFFERENT pH

pH	Plating time (s)	Days at 38°C and 95% relative humidity									Days in MIL-STD 810B
		0		2		4	6	8	10		3
		$\alpha$	$\epsilon$	$\alpha$	$\epsilon$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$
3.5	40	.85	.09	-	-	.80	.80	.79	.82	.08	.77
4.0	40	.87	.07	-	-	.83	.84	.83	.80	.08	.81
4.5	40	.90	.09	.93	.09	.90	.89	.89	.87	.08	.79
5.0	40	.91	.11	-	-	.85	.84	.80	.83	-	.70
5.6	40	.90	.09	.92	.09	.88	.86	.84	.78	.07	.72
(Standard)											
6.0	40	.92	.12	-	-	.92	.92	.92	.87	.11	.87
6.0	92	.93	.23	-	-	.94	.94	.94	.94	.21	.92
6.5	40	.93	.12	.91	.10	.88	.87	.84	.84	.08	.74

The spectral reflectance curves of samples plated from pH = 4, 5-6.5 are all quite similar. After humidity testing, the curves are somewhat flattened in the 3.5  $\mu\text{m}$  to 1.5  $\mu\text{m}$  region, causing them to have a slightly lower infrared emittance. The sample plated at a pH of 6.0 for 40 seconds had the best combination of optical properties and humidity resistance.

#### Effect of Current Density on Coating Properties

The effect of current density on coating composition can be predicted somewhat from the computed potentials for various reactions as shown on Figure 4. At a given pH, it is expected that, if the current density is too low, the reduction of hydrogen and nickel may predominate over the reduction of thiocyanate; if the current density is too high, a multitude of reactions occur, including the evolution of hydrogen and the precipitation of nickel hydroxide. Faster hydrogen evolution was observed at higher current density in the present experiments.

Effect of Current Density on Auger Spectra. - The Auger spectra of five samples plated using the NASA formula but at different current densities before and after a humidity test are shown in Figures 9 and 10. The humidity test consisted of 48 hours at 38°C (100°F) and 95 percent relative humidity. The usual current density used in the NASA formula is 4.3 ma/cm<sup>2</sup>.

Before the humidity test, as can be seen in Figures 9 and 10, samples plated at different current densities have very similar compositions. This means that, for the NASA standard formula, the current density has very little effect on the coating composition. There is a less well defined interface between the black nickel coating and the underlying Ni layer when the higher current densities are used, but the compositions of the basic coating are not very different.

This is quite different from the Honeywell black nickel formula that gave two coatings of totally different compositions when they were plated at two different current densities as is shown in Figure 11. The sulfur and nickel content is much greater relative to the oxygen and zinc content for the lower current density (1 ma/cm<sup>2</sup>). Also, a large amount of carbon is present in the low current density coating. The Honeywell formulation is identical to a bath previously studied by Tabor (Reference 4), who also noticed the two distinct compositions. This change in compositions was exploited in the Honeywell two-layer coating to produce coatings with  $\alpha = .96$  and  $\epsilon = .07$ .

After the humidity test, most of the NASA formula samples show a similar increase in oxygen and a decrease in sulfur content near the coating surface (Figures 9 and 10). The change in oxygen and sulfur is less severe for the samples plated at the current densities of 2.0 ma/cm<sup>2</sup> and 5.0 ma/cm<sup>2</sup>, but basically there is little reason to choose one current density over another based on these Auger spectra for the NASA formula samples.

Effect of Current Density on Optical Properties. - Current densities covering the range of .5 to 5 ma/cm<sup>2</sup> were used in this study. To keep the thickness of plated coatings roughly equal, the plating time was reduced for the higher current densities, keeping the product of current density (CD) and plating time constant. The spectral reflectance of different current density samples are shown in Figure 12. The coatings plated from the baths with current densities less than 3.5 ma/cm<sup>2</sup> show an undamped oscillation in their spectral reflectance curves and have lower solar absorptions. Their reflectance cut-off points also change drastically. The samples prepared from current densities higher than and equal to 3.5 ma/cm<sup>2</sup> have reflectance curves damped by absorption and higher overall solar absorptance.

The spectral reflectance of the same samples after humidity tests is shown in Figure 13. The spectral reflectances of samples plated with CD  $\geq$  3.5 ma/cm<sup>2</sup> were more stable than those of the lower current density samples.

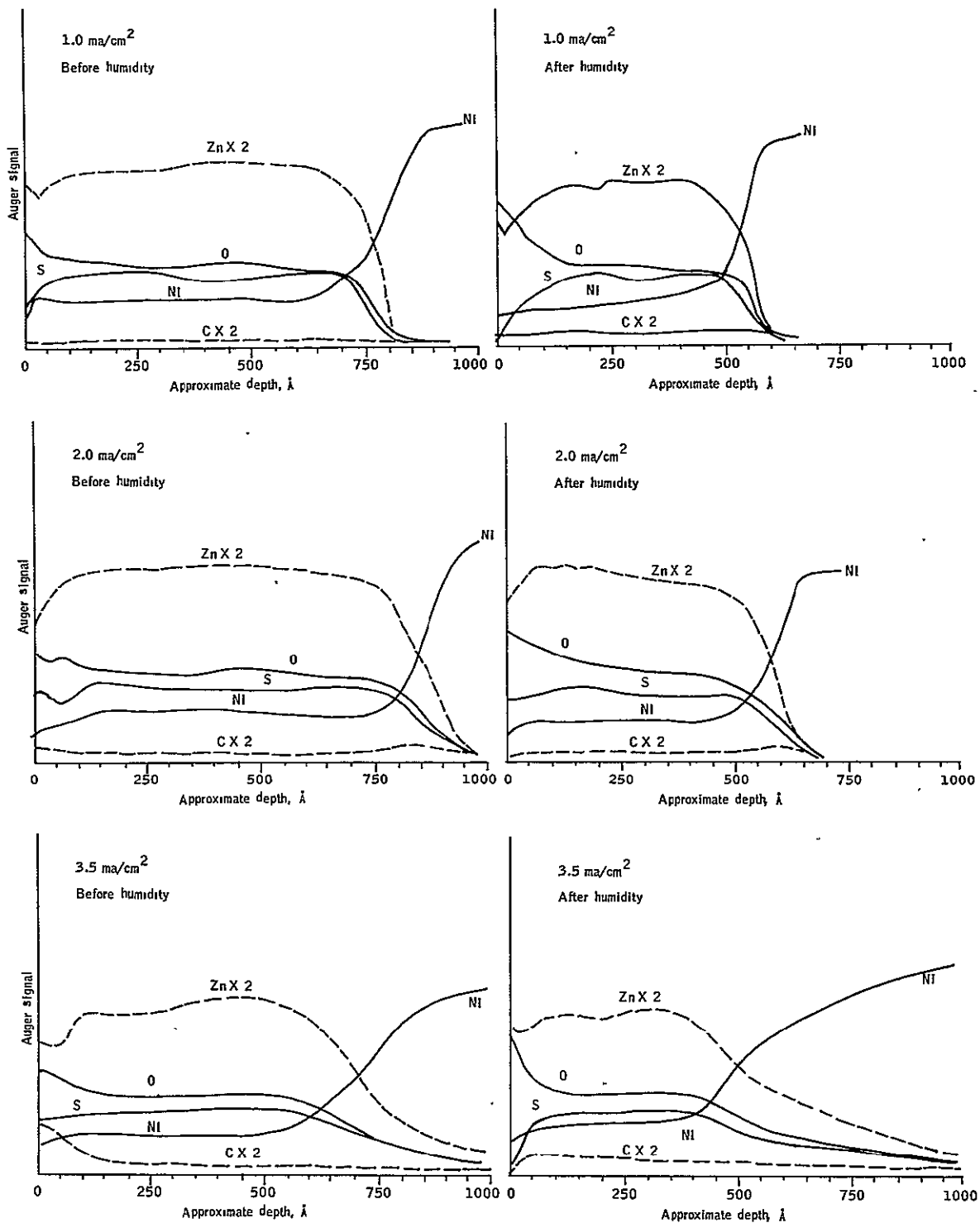


Figure 9.- Effect of current density on Auger spectra, 1 to 3.5 ma/cm<sup>2</sup>.

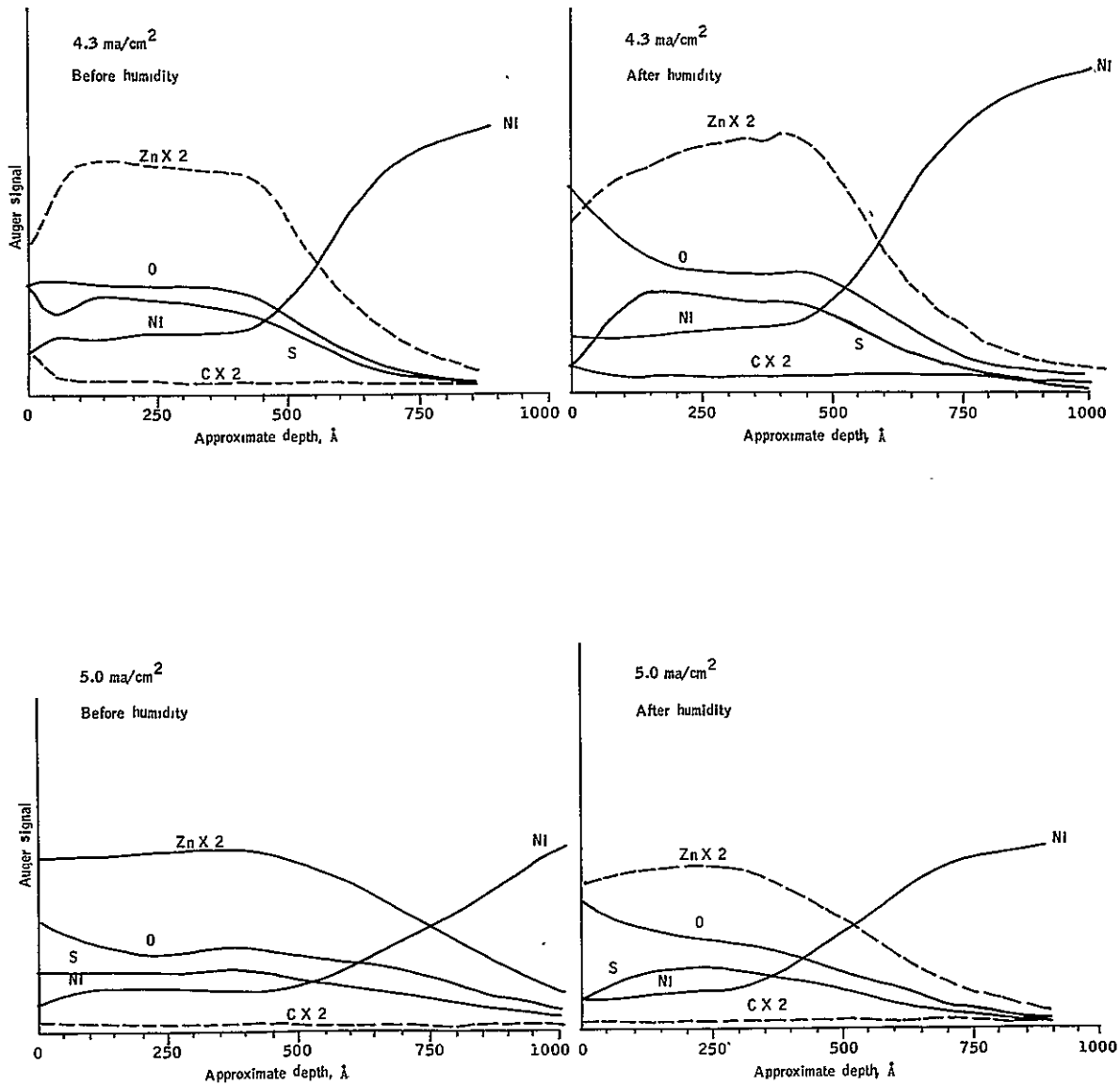


Figure 10. - Effect of current density on Auger spectra, 4.3-5.0 ma/cm<sup>2</sup>.

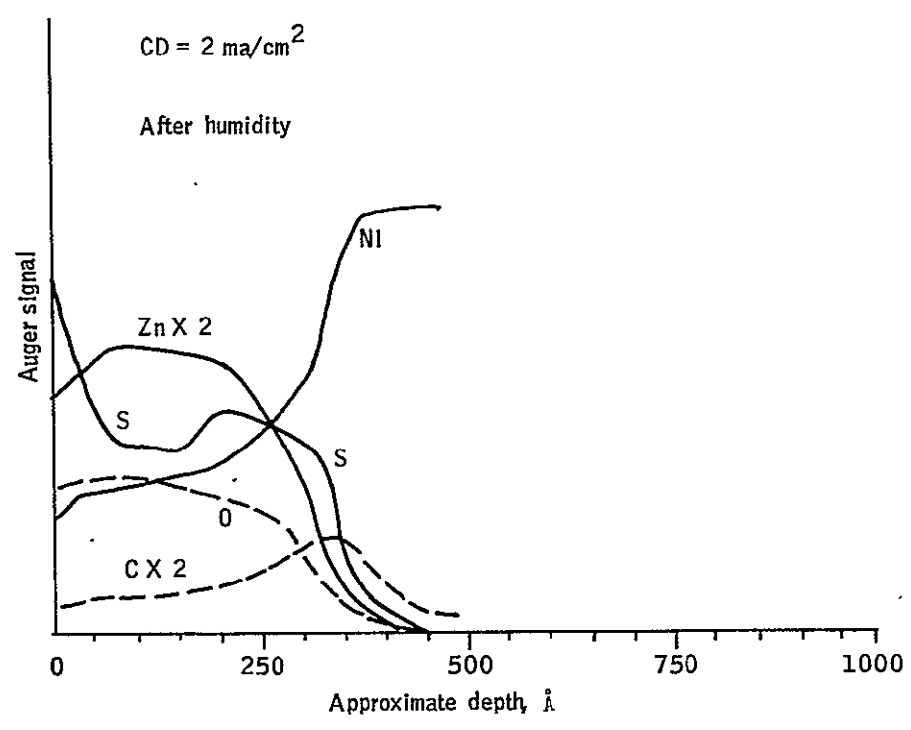
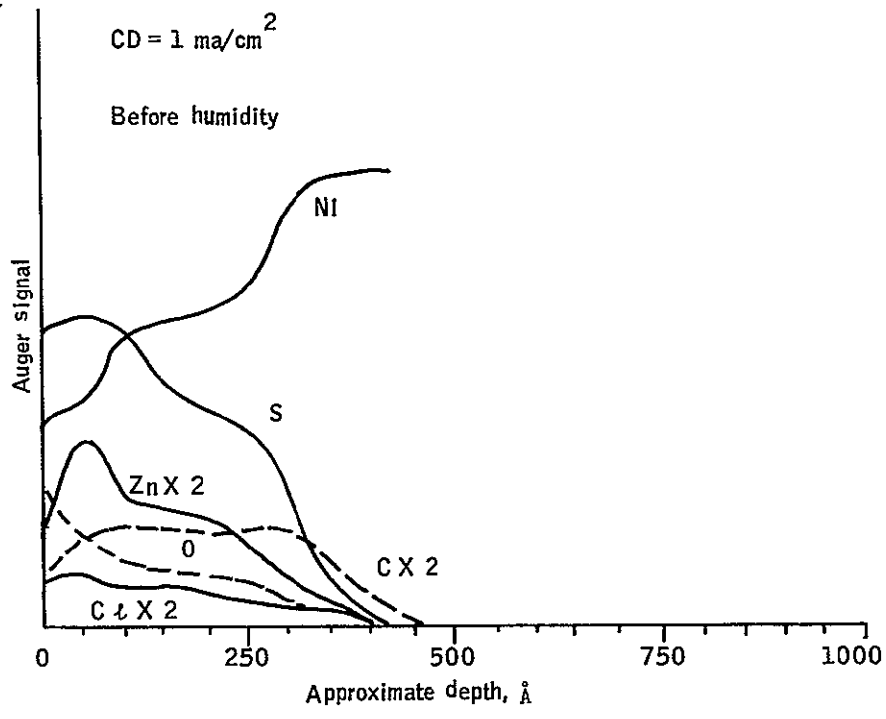


Figure 11.- Effect of current density on the Honeywell formula black nickel.

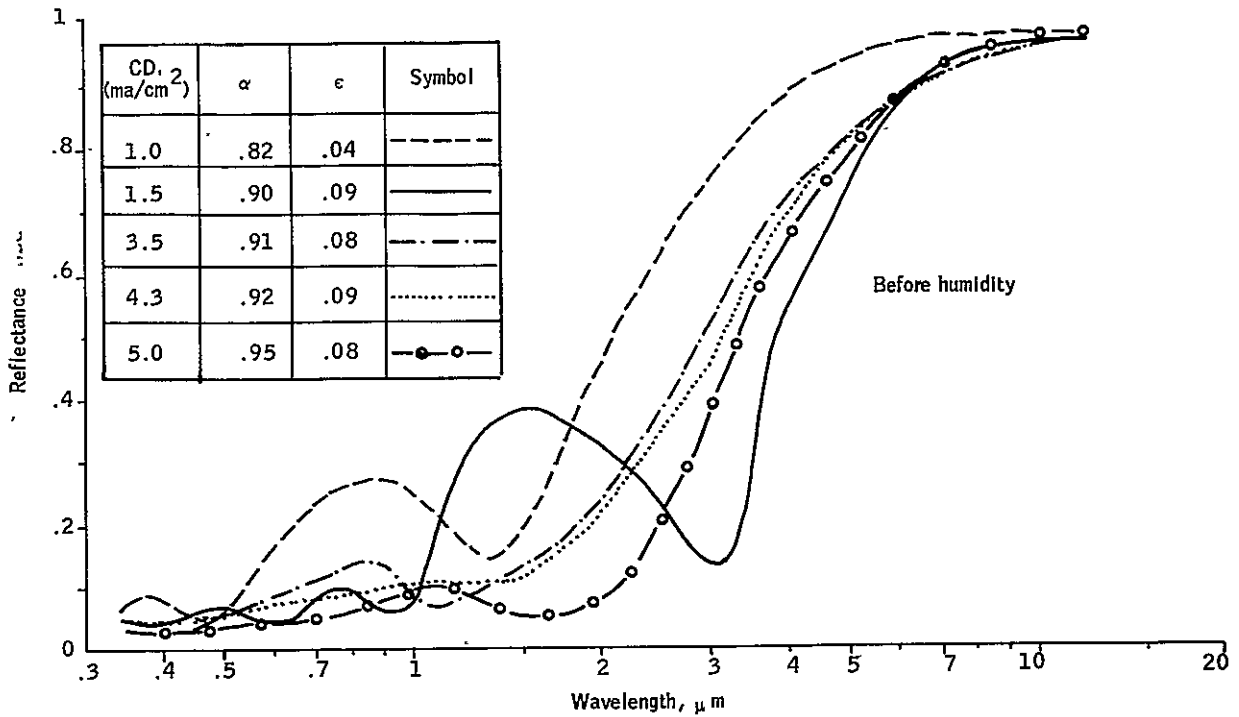


Figure 12. - Effect of current density on the reflectance of NASA black nickel coatings.

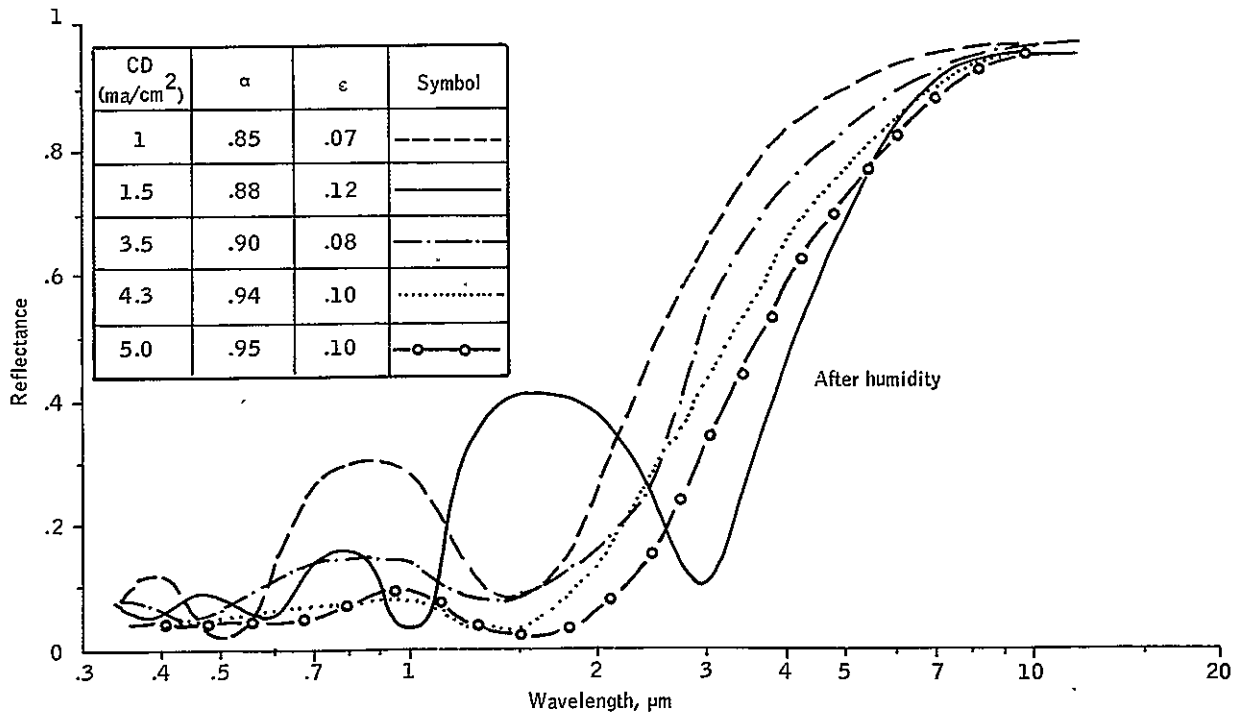


Figure 13. - Effect of current density on the reflectance of NASA black nickel after 2 day humidity test.



Results of the humidity test on solar absorptance and emittance given in Table IV include samples plated at current densities from 0.5 to 5.0 ma/cm<sup>2</sup>. Groups I and II represent tests conducted at different times throughout the program. Group I was given the standard NASA test for one day and Group II underwent prolonged humidity testing. Current densities of 1.5, 4 and 5 ma/cm<sup>2</sup> all gave durable coatings, but the coating plated at 1.5 ma/cm<sup>2</sup> had a slightly higher emittance (12 percent before the humidity test) than the other two coatings which had an initial emittance of 9 to 10 percent. The absorptance of the coating plated at 1.5 ma/cm<sup>2</sup>, which was 88 percent, was also low compared to the 91 to 92 percent absorptance of the other two coatings. After 10 days in the NASA standard humidity, all three of these coatings survived with almost no sign of degradation, especially the coatings plated at current densities of 4 and 5 ma/cm<sup>2</sup>. The absorptance of the sample plated at the NASA standard current density of 4.3 decreased from the original 90.3 percent to 84.4 percent after 10 days in the NASA standard humidity. This drastically different behavior for the 4.3 ma/cm<sup>2</sup> compared to the 4 and 5 ma/cm<sup>2</sup> samples is surprising. Other samples plated using the standard NASA current density at other times in the program had somewhat better humidity resistance but never as good as that of the 4 and 5 ma/cm<sup>2</sup> samples.

Summary of the Effect of Current Density Variations. - For the NASA formula, current density has little effect on coating composition, whereas samples plated from the Honeywell formula are very dependent on a change in current density.

After the humidity test all samples plated at different current densities show a similar increase in oxygen and a decrease in sulfur content near the coating surface.

Despite similarities in the composition profiles, the optical properties were dependent on CD. Coatings plated from baths with CD  $\leq 2.5$  ma/cm<sup>2</sup> show an undamped oscillation in their spectral reflectance curves, have lower solar absorptions and are less stable. Samples with CD's  $\geq 3.5$  ma/cm<sup>2</sup> have reflectance curves damped by absorptions; their optical properties are much better and are more stable. In particular, samples plated at 4 and 5 ma/cm<sup>2</sup> were resistant to prolonged humidity degradation, while absorptance of the sample plated with the standard (4.3 ma/cm<sup>2</sup>) current density decreased about 6 percent after 10 days of the NASA humidity test.

#### Effect of Zn<sup>++</sup>/Ni<sup>++</sup> Ratio on Coating Properties

The great advantage of including zinc ions in solution comes from the high overvoltage of hydrogen on zinc metal, which does not occur on nickel. At the start of plating, zinc or nickel-zinc alloys deposit on the cathode. Due to high overvoltage for hydrogen, the evolution of hydrogen is repressed, and the reduction of nickel and thiocyanate are favored. After the zinc surface is covered with a layer of sulfide, the overvoltage no longer exists, and the plating process goes back to where it started with the deposition of nickel

TABLE IV. - HUMIDITY RESISTANCE OF BLACK NICKEL SAMPLES  
PLATED AT DIFFERENT CURRENT DENSITIES

Current density (ma/cm <sup>2</sup> )	Plating time (sec)	Group I				Group II								
		Days at 38°C and 95% relative humidity												Days in MIL-STD 810B
		0		1		0		4	6	8	10		3	
$\alpha$	$\epsilon$	$\alpha$	$\epsilon$	$\alpha$	$\epsilon$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$		
0.5	344	.81	.05	.86	.03	.81	.05	.68	.63	.63	---	---	---	
1.0	172	.85	.07	.82	.04	.83	.07	.75	.74	.73	.73	.07	.64	
1.5	115	.88	.12	.90	.09	.88	.12	.89	.89	.88	.88	.11	.86	
2.0	86	.85	.06	.84	.05	.86	.06	.78	.79	.79	.78	.06	.74	
2.5	69	.84	.06	.88	.06	.84	.06	.81	.82	.80	.80	.07	.75	
3.5	49	.90	.08	.91	.08	.86	.08	.86	.86	.85	.86	.08	.78	
4.0	43	.93	.09	.94	.07	.91	.09	.92	.92	.91	.91	.08	.95	
4.3	40	.94	.10	.92	.09	.90	.10	.89	.86	.86	.84	.07	.71	
(Standard)														
5.0	34.5	.95	.19	.95	.08	.92	.10	.92	.92	.91	.91	.07	.84	

and zinc or nickel-zinc alloy and the evolution of hydrogen. The cycle is repeated throughout the entire plating process. Thus, the  $Zn^{++}/Ni^{++}$  ratio is expected to have a significant effect on coating composition as well as on coating properties. The standard NASA formula has a  $Zn^{++}/Ni^{++}$  ratio of .364. In the present experiment, the  $Zn^{++}/Ni^{++}$  ratio was varied from .1 to .7; except where otherwise noted,  $Ni^{++}$  was kept at the standard concentration.

Effect of  $Zn^{++}/Ni^{++}$  Ratio on Auger Spectra. - The Auger spectra of four samples plated at different  $Zn^{++}/Ni^{++}$  ratios before and after two days in the NASA humidity test are shown in Figures 14 and 15. Before the humidity test, there are significant composition differences among the samples as the  $Zn^{++}/Ni^{++}$  ratio is changed. The amount of oxygen decreases with respect to the sulfur and nickel as the  $Zn^{++}/Ni^{++}$  ratio is increased, which means more sulfides have been formed, and less hydroxides have been deposited. This is consistent with the theoretical prediction that the high overvoltage of hydrogen on zinc represses the evolution of hydrogen and favors the reduction of thiocyanate. Also, at high  $Zn^{++}/Ni^{++}$  ratios, the coating - Ni interface is much less distinct. The reason for this change is uncertain.

During humidity test, the sulfur content decreases, and the oxygen content increases for all of the samples. These composition changes due to the humidity test are greatest for the samples plated at higher  $Zn^{++}/Ni^{++}$  ratios. The greater composition changes become visually very obvious when the  $Zn^{++}/Ni^{++}$  ratio is as high as .7. The scale for the depth of coating has been changed in Figure 15 for the  $Zn^{++}/Ni^{++} = .7$  sample after the humidity test. This spectrum shows that the humidity has penetrated deeply through the coating. The change in composition is great for that sample; very little Ni is left after the humidity test.

Effect of  $Zn^{++}/Ni^{++}$  Ratio on Optical Properties. - The spectral reflectance of the eight samples plated with different  $Zn^{++}/Ni^{++}$  ratios were measured in this program. Four of the reflectance curves are shown in Figure 16.

The spectral reflectances curves of all the samples fall into three distinct groups. For  $Zn^{++}/Ni^{++}$  ratios from .1 to .25, the curves oscillate in the solar region with a high reflectance in the infrared. When the ratio is between .364 and .5, the curves are flat in the solar region, damped by absorption, and have an intermediate reflectance in the infrared. When the  $Zn^{++}/Ni^{++}$  ratio is higher than .5, the spectral curve is very flat in the solar region, but the reflectance increases too slowly in the infrared. There is a sharp change in the shape of the reflectance curves between the  $Zn^{++}/Ni^{++}$  ratio of .25 to .364. For a good combination of solar absorption and low emittance, a  $Zn^{++}/Ni^{++}$  ratio in the range of .25 to .5 is necessary.

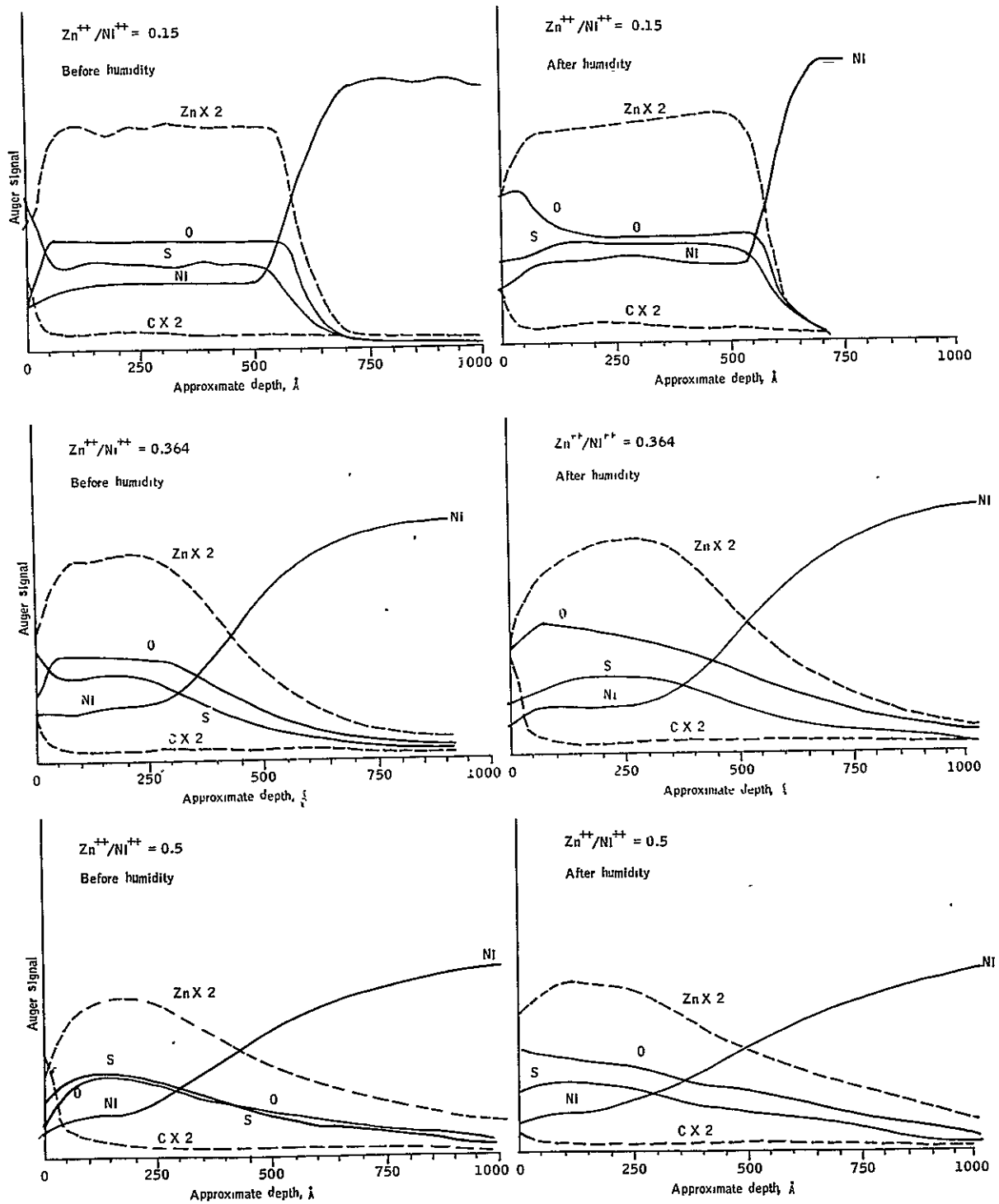


Figure 14. - Effect of Zn<sup>++</sup>/Ni<sup>++</sup> ratio on Auger spectra for Zn<sup>++</sup>/Ni<sup>++</sup> from .15 to .5.

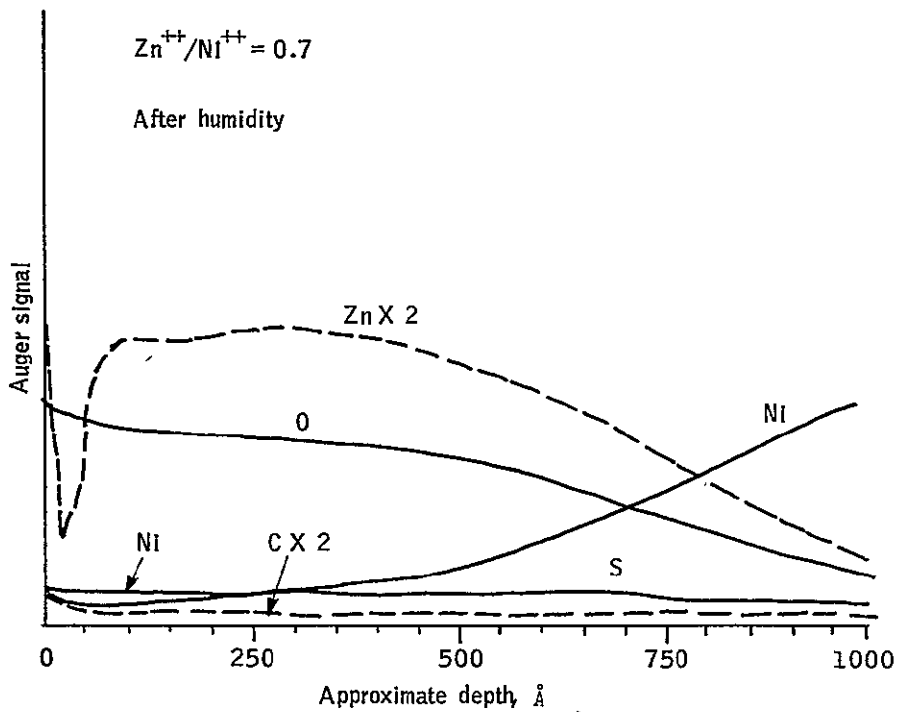
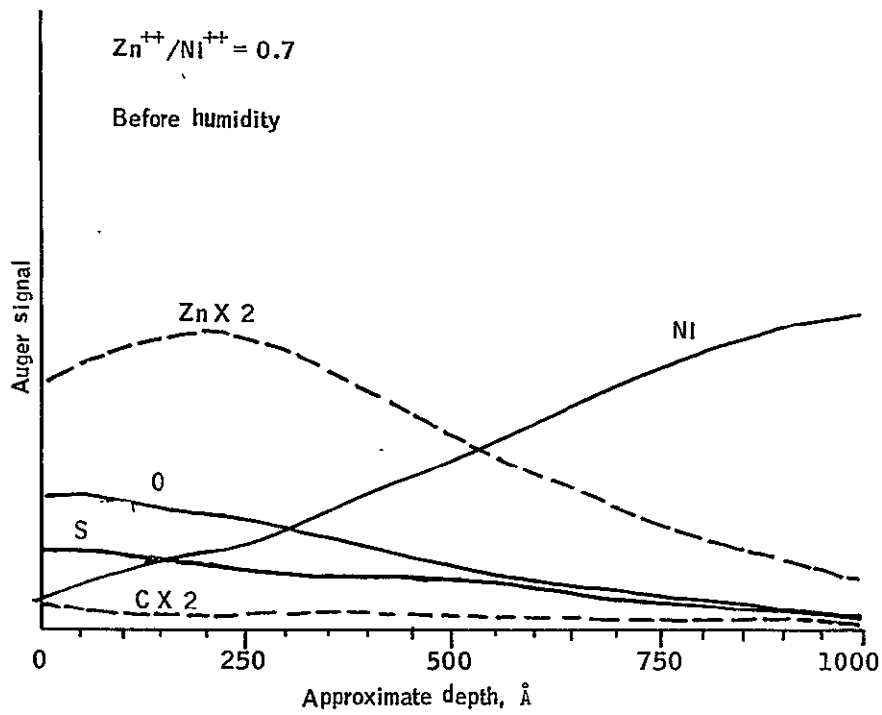


Figure 15.- Effect of  $Zn^{++}/Ni^{++}$  ratio on Auger spectra at  $Zn^{++}/Ni^{++} = .7$ .

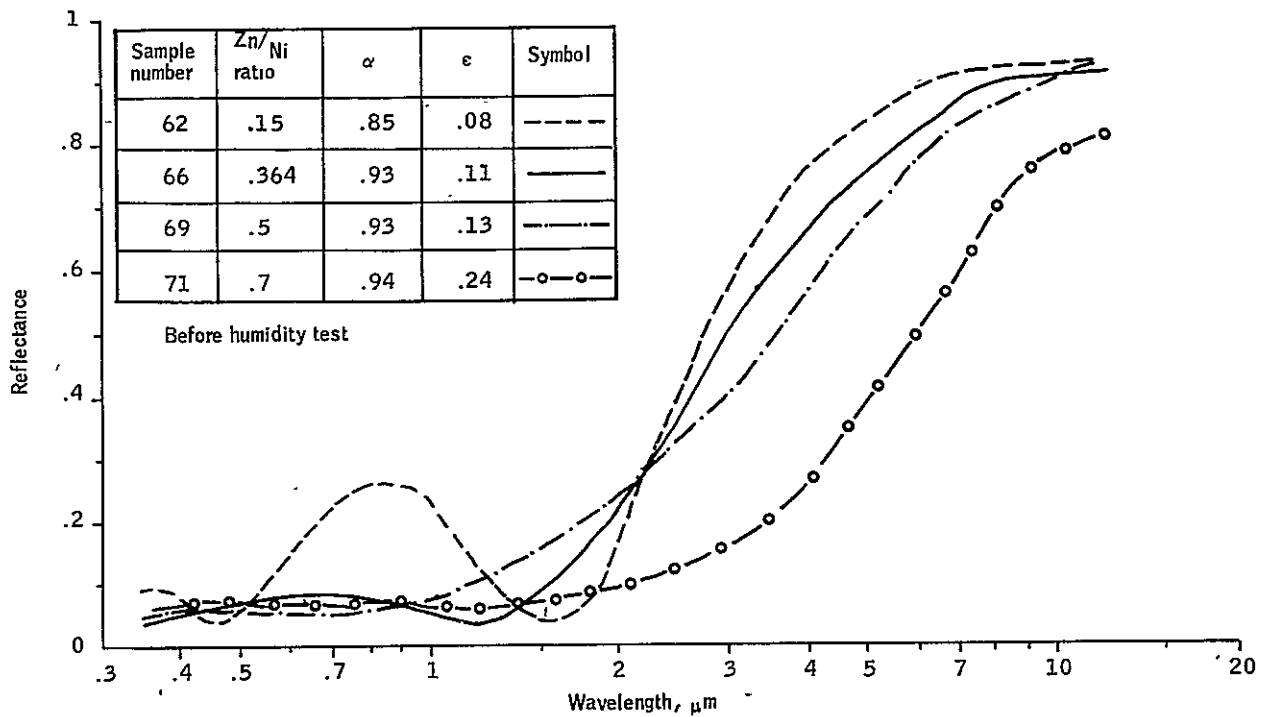


Figure 16. - Effect of  $Zn^{++}/Ni^{++}$  ratio on spectral reflectance.

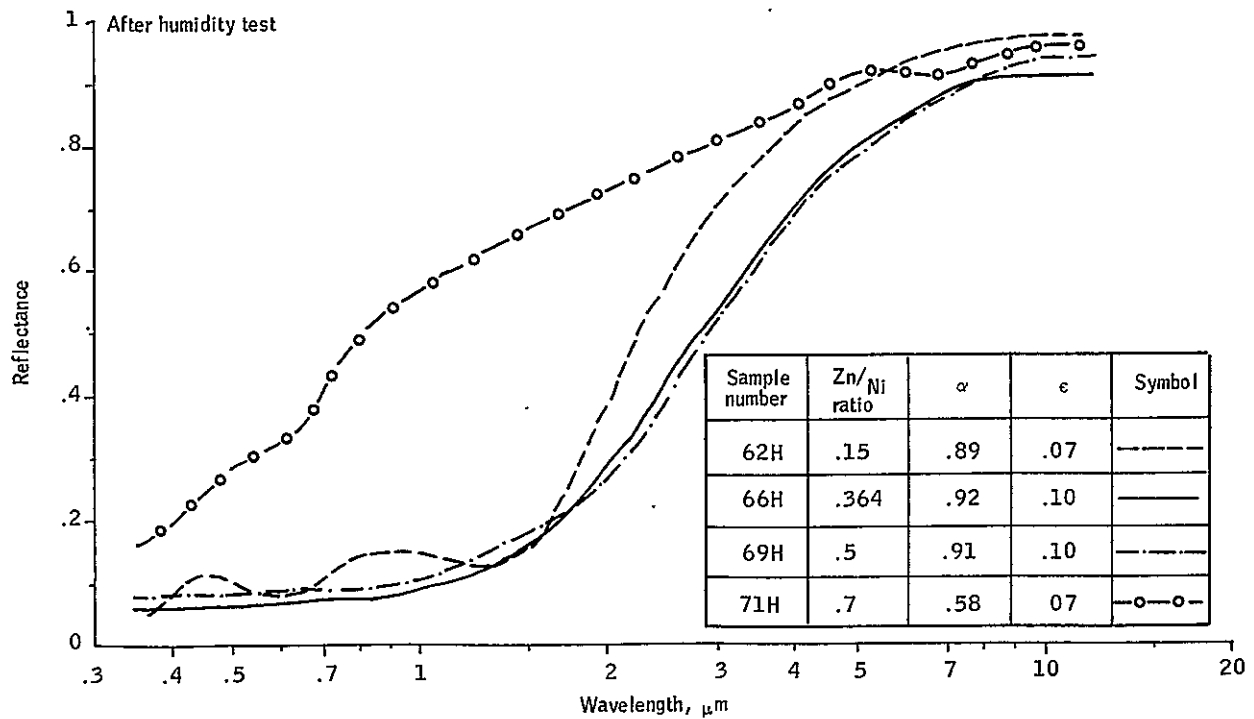


Figure 17. - Effect of  $Zn^{++}/Ni^{++}$  ratio on spectral reflectance after humidity.

At high zinc ion concentration, or when the  $Zn^{++}/Ni^{++}$  ratio is greater than .5, the coating looks gray. This is probably due to too much free nickel metal in the coating, which also accounts for the very flat spectral curve and the high emittance (24 percent). This free Ni can be seen in the Auger spectra (Figures 14 and 15) as the indistinct Ni-coating interface.

The reflectances of the same coatings after 48 hours in the NASA standard humidity test are given in Figure 17. A reflectance increase in the 1-2  $\mu m$  wavelength region can be seen for most of the samples. This change is more pronounced for the low and very high  $Zn^{++}/Ni^{++}$  ratio and is not as significant for the  $Zn^{++}/Ni^{++}$  ratio between .25 and .5. The oscillation of the low  $Zn^{++}/Ni^{++}$  ratio curve is damped by absorption after the humidity test. The coating with  $Zn^{++}/Ni^{++} = .7$  was almost completely degraded by the humidity; its solar absorption decreased from 94 percent to 58 percent. This coating could be wiped off by rubbing gently after the humidity test.

The results for samples plated at  $Zn^{++}/Ni^{++}$  ratios from .1 to .7 with  $Ni^{++}$  kept at the standard concentration are summarized in Table V. Samples plated at a  $Zn^{++}/Ni^{++}$  ratio higher than the standard ratio had a high initial absorptance, but they degraded badly. The degradation increased as the ratio was increased. Samples plated at a  $Zn^{++}/Ni^{++}$  ratio lower than the standard (.364) had a low absorptance initially; after ten days of the NASA humidity test, their absorptances were either increased or about the same; after another three days of 810B humidity test, their absorptances were only slightly decreased. The  $\alpha$  changes are probably strongly dependent on the exact position of minimums in the reflectance spectrum for these samples. At the initial stage of humidity degradation, samples plated at the lower  $Zn^{++}/Ni^{++}$  ratios changed their colors from an original gold or yellowish blue to a blue or dark blue. Further humidity exposure changed the colors only slightly. This indicates that the initial humidity exposure probably oxidized or hydrolyzed the coatings near the surfaces and that protected somewhat the coatings underneath. Note that the solar absorptance of all of the  $Zn^{++}/Ni^{++} = .364$  samples stabilized at about the same level of  $\alpha \sim .82$ . Considering the low initial of  $\alpha$  of the  $Zn^{++}/Ni^{++} \leq .25$  samples, and the poor durability of high ratio samples, it is probably best to use the standard NASA  $Zn^{++}/Ni^{++}$  ratio of .364.

Effect of  $Ni^{++}$  Variations from Standard NASA Formula. - To determine effects of  $Ni^{++}$  concentration, a limited test program was undertaken. The properties of samples prepared using the NASA standard formula, but with variation from the recommended  $Ni^{++}$  content ( $Zn^{++}$  content held constant), are shown in Table VI. The test procedure used for these samples is as follows:

Solar reflectance and IR emittance of freshly prepared samples were measured. A MIL-STD-810B humidity test was then given to one sample for one day, and the solar reflectance was measured.

TABLE V. - HUMIDITY RESISTANCE OF BLACK NICKEL SAMPLES PLATED AT DIFFERENT Zn<sup>++</sup>/Ni<sup>++</sup> RATIOS

[Zn <sup>++</sup> ] [Ni <sup>++</sup> ]	Plating Time (S)	Days at 38°C and 95% relative humidity							Days in MIL-STD 810B
		0		4	6	8	10		3
		$\alpha$	$\epsilon$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$
0.10	40	.82	.08	.88	.88	.86	.86	.07	.81
0.15	40	.79	.08	.84	.82	.80	.82	.07	.78
0.20	40	.79	.08	.81	.78	.78	.76	.06	.70
0.25	40	.81	.06	.84	.83	.80	.81	.07	.79
0.364 (Standard)	40	.93	.11	.88	.84	.82	.82	.08	.80
0.40	40	.92	.11	.85	.81	.78	.77	.08	.75
0.50	40	.92	.13	.86	.82	.80	.78	---	.80
0.70	40	.93	.24	.43	---	---	---	---	---

TABLE VI. - EFFECT OF Ni<sup>++</sup> CONCENTRATION CHANGE ON HUMIDITY OF NASA STANDARD FORMULA COATINGS

[Ni <sup>++</sup> ] (g/l)	Sample number	Before humidity		After 1 day 810B humidity	After 4 days NASA test + 1 day 810B	
		$\alpha_s$	$\epsilon$	$\alpha_s$	$\alpha_s$	$\alpha_s$
		20	72	0.886	0.06	0.673
22	74	0.909	0.06	0.839	0.901	0.745
23.45 (Standard)	77	0.906	0.08	0.876	0.895	0.735
24.5	79	0.911	0.07	0.792	0.908	0.784
26	81	0.918	0.08	0.849	0.891	0.690
30	82	0.908	0.07	0.862	0.874	0.708
50	83	0.919	0.07	0.828	0.917	0.793
80	84	0.900	0.07	0.865	0.900	0.811



A second sample was given four days exposure to the NASA humidity test, and the solar reflectance was measured. That sample was then given the MIL-STD-810B test for one day, and the solar reflectance was measured again.

There is no spectacular improvement in the humidity resistance for any of these samples; they all degrade substantially in the 4-day NASA + 1-day 810B tests. However, samples prepared with high  $\text{Ni}^{++}$  content seem to be somewhat more durable than the low  $\text{Ni}^{++}$  content samples.

Summary of the Effects of  $\text{Zn}^{++}/\text{Ni}^{++}$  Ratio. - As the  $\text{Zn}^{++}/\text{Ni}^{++}$  ratio is increased, the amount of oxygen decreases with respect to sulfur and nickel concentration. This implies that more sulfides have been formed, and less hydroxide has been deposited. At high  $\text{Zn}^{++}/\text{Ni}^{++}$  ratios, free metallic nickel is present in the coating, especially near the coating-Ni substrate interface.

After humidity testing, the sulfur content decreased, while the oxygen content increased. This occurred for all the samples but was greatest for the higher  $\text{Zn}^{++}/\text{Ni}^{++}$  ratios.

$\text{Zn}^{++}/\text{Ni}^{++}$  ratios in the range of .364 to .5 gave the best combination of solar absorption and low emittance. If the ratio is too low, the curves oscillate in the solar region with a high reflectance in the infrared. If the ratio is too high, the reflectance increases too slowly in the infrared, and the emittance is high.

Although they have a high initial absorptance, the samples plated at a  $\text{Zn}^{++}/\text{Ni}^{++}$  ratio higher than the standard degraded badly after the humidity test. Samples plated at a lower  $\text{Zn}^{++}/\text{Ni}^{++}$  ratio had a low absorptance initially, but after humidity testing, either increased their absorptance or remained constant. A  $\text{Zn}^{++}/\text{Ni}^{++}$  ratio near the NASA recommended value of .364 gives about the best combination of durability and optical properties.

Increasing only the  $\text{Ni}^{++}$  content of the bath while keeping the  $\text{Zn}^{++}$  content constant increases coating stability slightly.

Effect of Temperature on Coating Properties. - Since the rates of different reactions are affected differently by increasing the temperature, coating compositions will be affected by the bath temperature. Another effect the temperature may have is to change the solubility of sulfides and hydroxides of nickel and zinc. No attempt was made to compute these changes theoretically. Samples were prepared at  $\sim 10$  different temperatures in the experimental study. The NASA standard formula recommends that the temperature be kept in the range 21 to 26.7°C.

Effect of Temperature on the Auger Spectra. - Samples were plated at temperatures from 18°C (65°F) to 52°C (125°F) in 5.6°C (10°F) intervals at both the standard high current density (4.3 ma/cm<sup>2</sup>) and at a lower current density (2.15 ma/cm<sup>2</sup>). Since the low current density samples gave essentially the same results as the high current density samples, those results will not be presented. The Auger spectra of four of the samples before and after the humidity test, are given in Figures 18 and 19. Since chemical reactions generally proceed at a faster rate as temperature is increased, the plating times in the depositions were varied in an attempt to keep the coating thicknesses constant. The rule we used to calculate the plating times was that reaction rates double for every 10°C temperature increase. This rule did not work well for the black nickel plating reactions as can be seen from Figures 18 and 19, which show different thicknesses for different temperature samples. At higher temperatures, the coatings are thinner since the reaction rates did not increase as rapidly as expected with temperature.

The composition of samples before the humidity test are similar except that the sulfur increases slightly toward the coating surfaces as the plating temperature increases. This sulfur increase resulted in less stable coatings as evidenced by larger changes in the Auger spectra (note especially the change in zn content) and decreases in solar absorptance after the humidity test. The oxygen content was more strongly affected at lower temperatures, but this change did not affect optical properties as much.

Effect of Temperature on Optical Properties. - Spectral reflectances of samples plated at different temperatures before the humidity test are shown in Figure 20. Those after a 48-hour NASA humidity test are shown in Figure 21.

The wavelength at which reflectance curves rise (a rough indication of coating thickness) decreases as the temperature is increased, which again shows that the usual rule used to calculate plating times did not work in this case. This result is probably due to the fact that all reactions, including both those favoring the deposition and those preventing the deposition, became faster as temperature was increased.

The most significant result of this experiment is the distinct change in shape of the spectral curves as the temperature changes from 18 to 29°C. See Figure 20. At 18°C and 24°C, the curve is flat in the solar region, damped by absorption, whereas at 29°C, the reflectance curve has a distinct oscillation. Since the flat spectral shape has higher absorption and is less sensitive to thickness errors, keeping the temperature at or below 24°C is quite important.

Among these samples, the ones plated at lower temperatures were more stable, showing smaller changes in spectral reflectance. The sample plated at 18°C was the most stable.

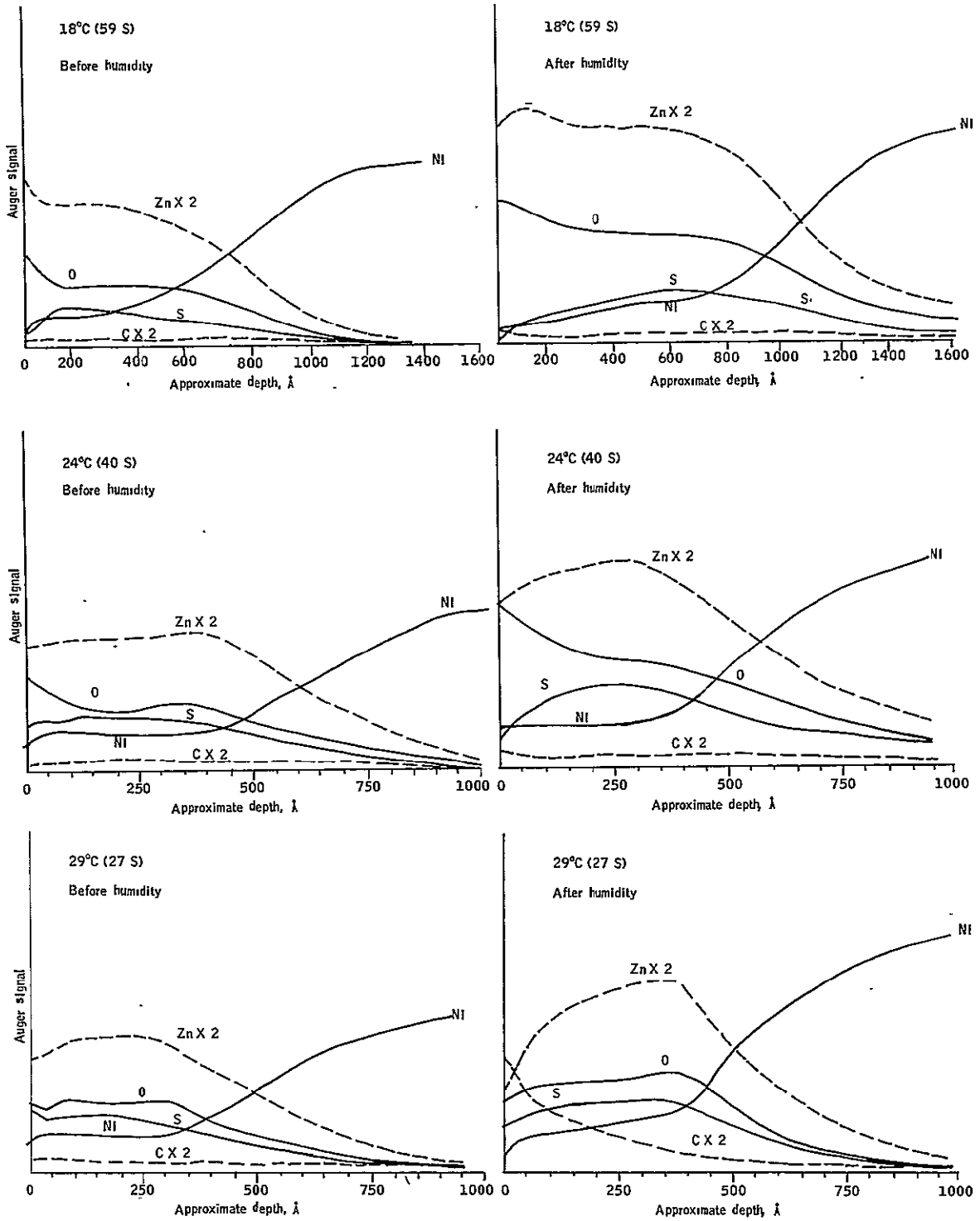


Figure 18. - Effect of temperature on Auger spectra, from 18°C to 29°C.

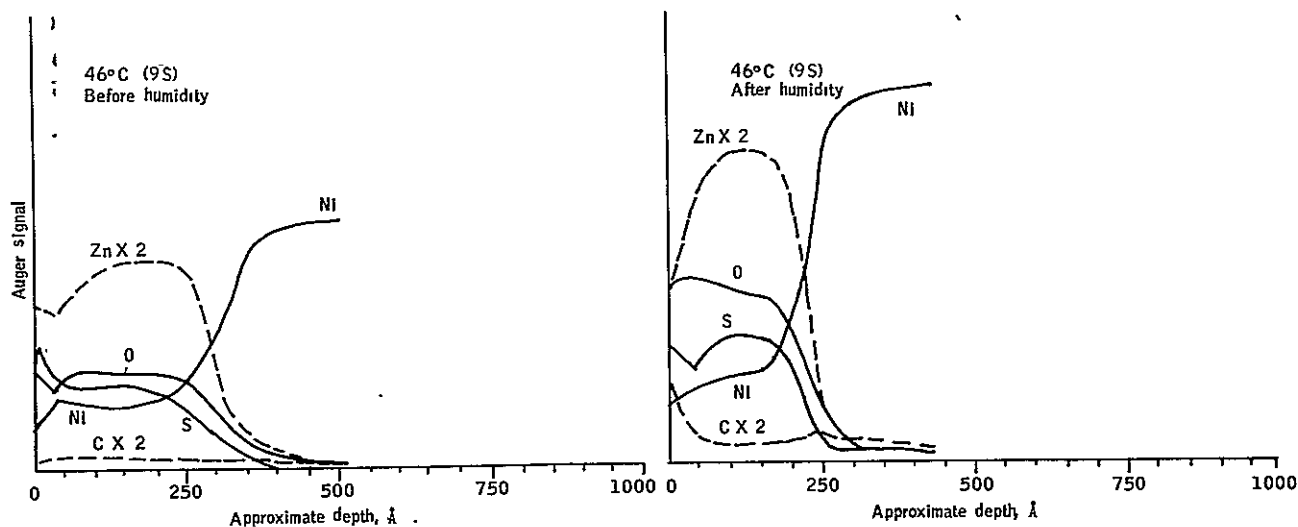


Figure 19. - Effect of temperature on Auger spectra, 46°C

As previously mentioned, the coatings plated at high temperatures were thinner because we overcorrected for the expected change in reaction rates. Hence, the high temperature samples may have been less desirable because they were thinner. To eliminate this factor, another set of samples was prepared for which the thicknesses were nearly the same at various plating temperatures. The spectral reflectances of these samples are shown in Figure 22. A significant oscillation in the reflectance curve begins at 27°C and increases as the temperature is increased. The result is that samples plated at higher temperatures have lower solar absorptance.

Reflectance curves of the same samples after the humidity test are shown in Figure 23. After the humidity test, all reflectance curves are flattened in the solar region, damped by absorption, and the reflectance cut-off points are pushed toward shorter wavelengths. Results of these two effects are a higher absorption with a lower emittance. These results are usually observed for samples subjected to a short and less severe humidity test, e. g., 48 hours at 38°C and 95 percent humidity. Longer or more severe humidity tests usually cause a decrease in absorption as will be discussed below. Among the sample reflectance curves shown in Figures 22 and 23, the lower plating temperatures again displayed the smallest changes, even though the coatings were of roughly equal thickness.

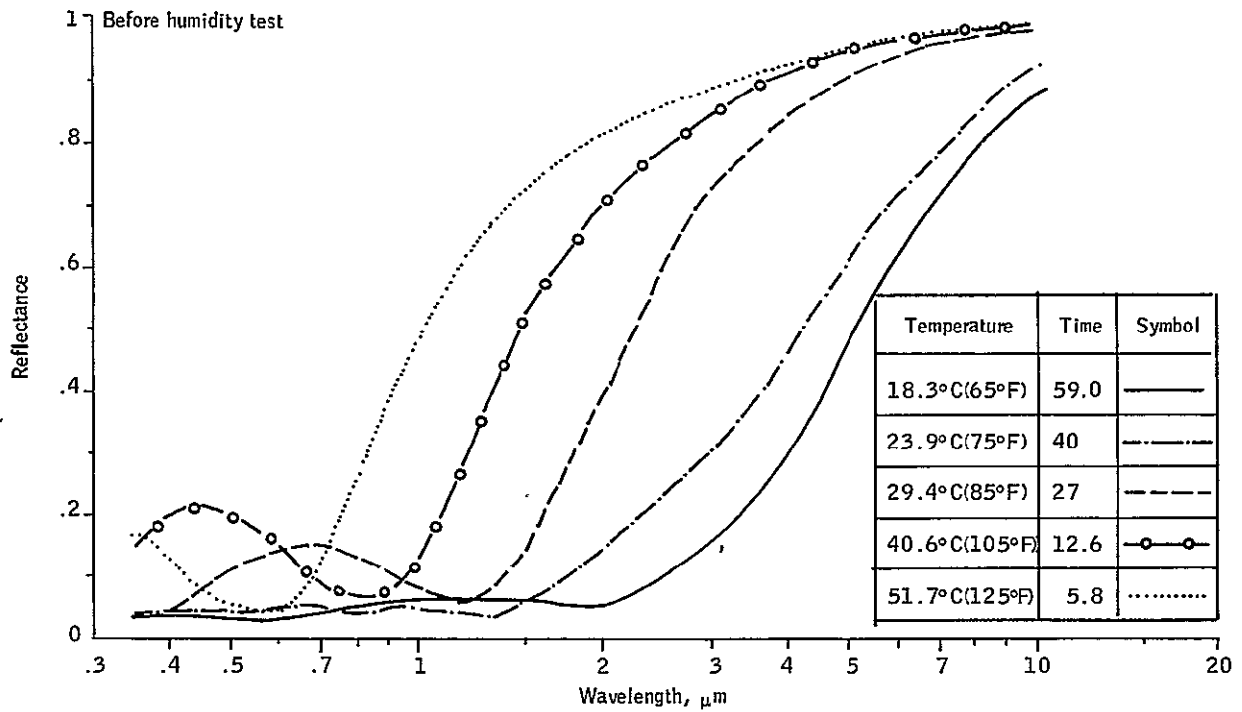


Figure 20. - Effect of temperature on spectral reflectance before humidity test.

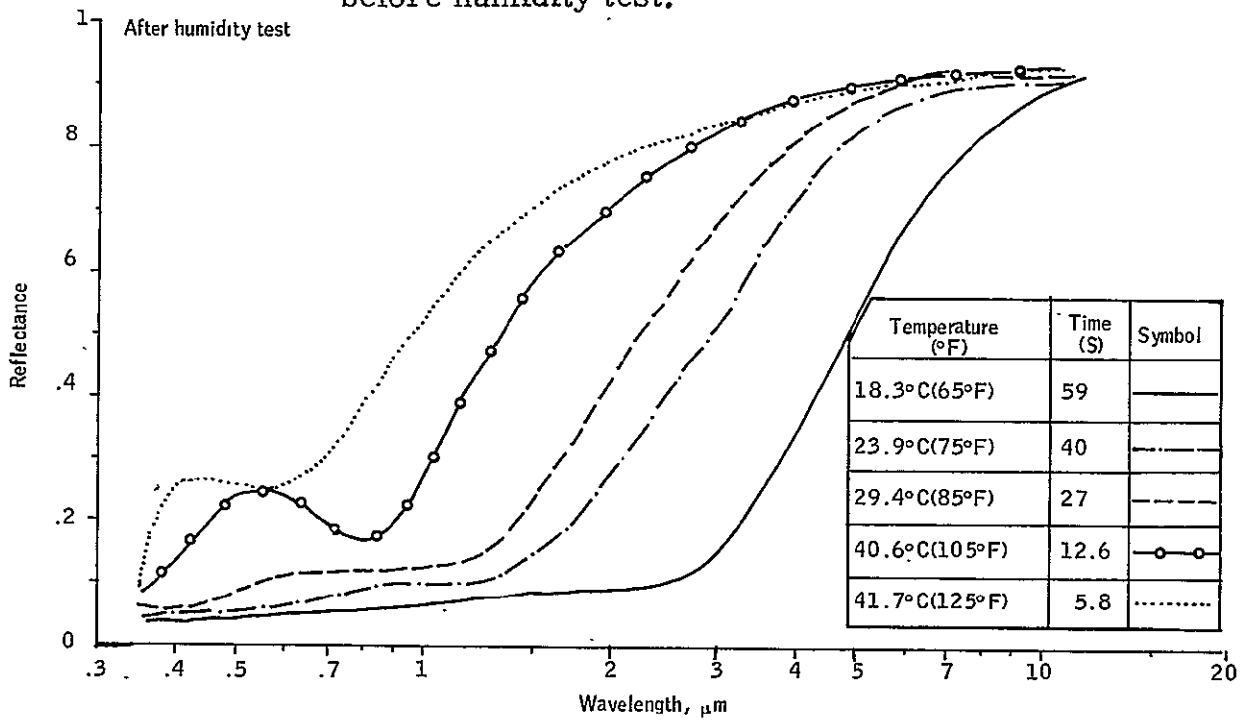


Figure 21. - Effect of temperature on spectral reflectance after humidity test.

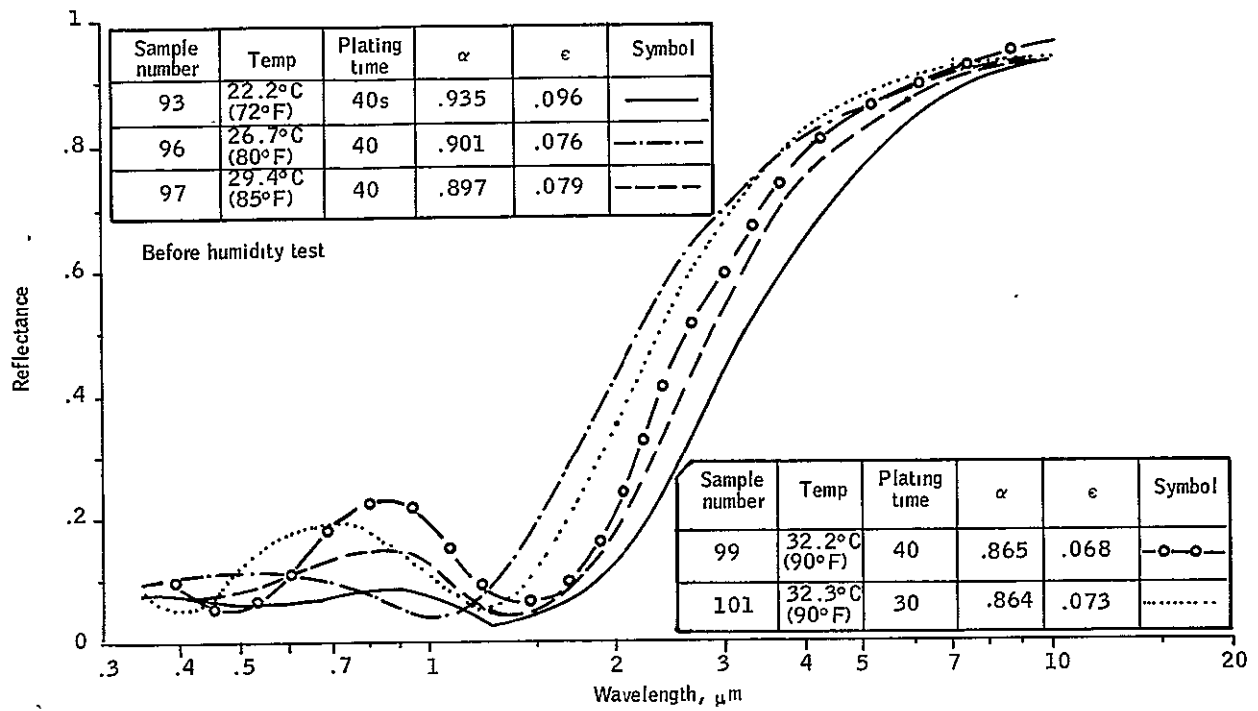


Figure 22.- Effect of temperature on spectral reflectance.

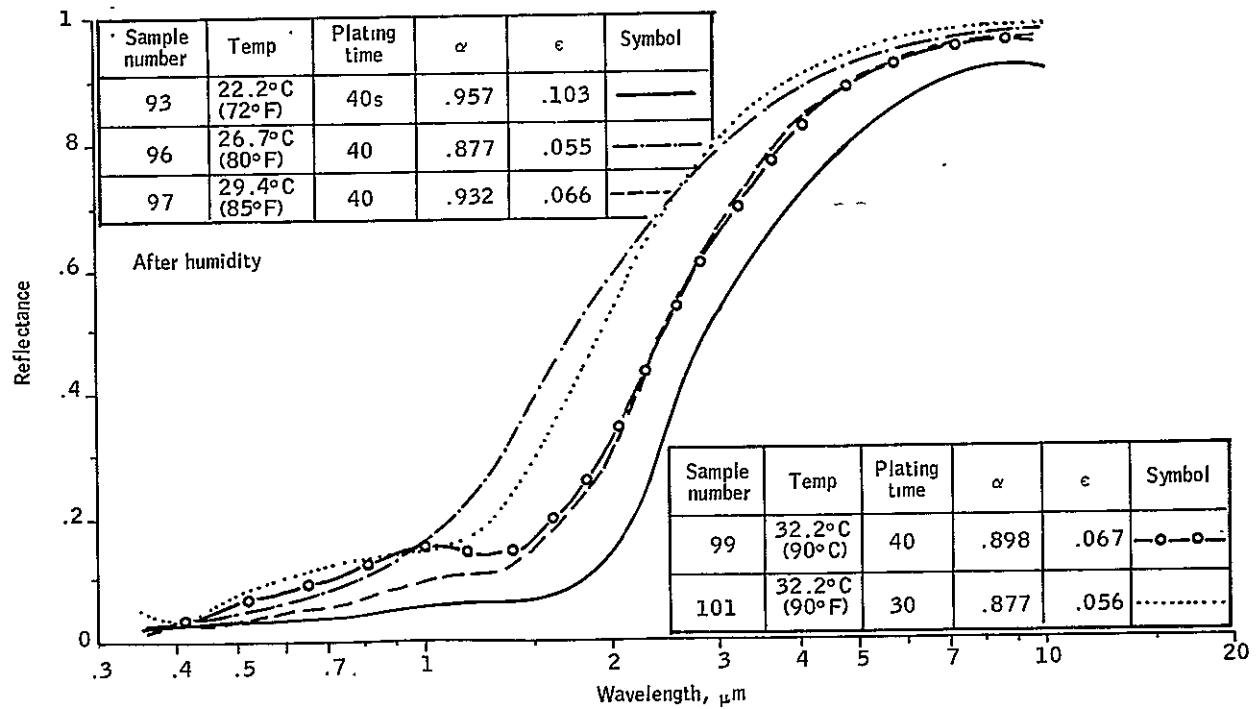


Figure 23.- Effect of temperature on spectral reflectance.

The results of both short and prolonged humidity tests on  $\alpha$  and  $\epsilon$  for samples plated at temperatures from 18°C to 52°C are listed in Table VII. The suggested plating temperature range in the NASA formula is from 21°C to 27°C. The most stable samples in Table VII were those plated at 22°C, 24°C, 29°C and 35°C for 40 seconds. The samples plated at the higher temperatures, 29°C and 35°C, were thicker than those samples plated at lower temperatures with the same plating time. The good humidity resistance of the samples plated at 29°C and 35°C was probably due to this greater thickness. However, the solar absorptance of these thick coatings plated at high temperatures was too low ( $\alpha = 80$  to 85 percent). Thus, to obtain durable coatings with good optical properties it is important to keep the plating temperature between 22°C and 24°C.

Summary of Effects of Temperature on Coating Properties. - As the temperature is increased, the sulfur content increases near the coating surface, resulting in a less chemically stable coating.

Before humidity testing, samples plated at 18 to 24°C have reflectance curves that are flat in the solar region. For samples plated at or above 27°C, the reflectance curves have a distinct oscillation in the solar region, and the samples have a lower solar absorptance.

After short term humidity testing, samples from 18°C to 35°C have reflectance curves flattened in the solar region, while those above 35°C still have the oscillation.

In long term humidity tests, the 18°C sample also degraded. Hence, to obtain durable coatings with good optical properties, the temperature should be between 22°C and 24°C.

#### The Effect of Thiocyanate Concentration on Coating Properties

The  $\text{SCN}^-$  ion provides the sulfur which allows the deposition of nickel and zinc sulfides in the plating process. Notice in Figure 24 that higher concentrations of thiocyanate ions enhance the reduction reactions. Thus, the  $\text{SCN}^-$  concentration is expected to have a significant effect on coating properties. In this experiment, plating solutions with ten different concentrations of NaSCN covering the range 3 to 30 g/l were used to produce black nickel coatings. The standard NASA formula was 15 g/l of NaSCN.

Effect of  $\text{SCN}^-$  Concentration on Auger Spectra. - The Auger spectra of four representative samples plated at different NaSCN concentrations before and after a two-day NASA standard humidity test are shown in Figure 24. The most significant effect of thiocyanate concentration on the coating composition is the increase in sulfur content as the thiocyanate concentration increases. The sulfur increase is most obvious when the sodium thiocyanate increases from 15 g/l, the NASA standard formula,

TABLE VII.- HUMIDITY RESISTANCE OF BLACK NICKEL SAMPLES  
PLATED AT DIFFERENT TEMPERATURES

Temperature		Plating time (s)	Days at 38°C and 95% relative humidity						Days in MIL-STD 810B	
			0		4	6	8	10		3
°C	°F		$\alpha$	$\epsilon$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$
18.3	65	59	.95	.19	.80	.74	.72	.70		
22.2	72	40	.92	.10	.91	.92	.91	.89	.08	.80
23.9	75 (standard)	40	.91	.10	.90	.89	.85	.86	.08	.78
26.7	80	40	.90	.08	.86	.85	.81	.80	.06	.67
29.4	85	40	.85	.08	.89	.89	.87	.87	.07	.77
29.4	85	33	.88	.08	.88	.85	.86	.84	.06	.75
29.4	85	27	.88	.06	.83	.81	.79	.78	.06	.67
35.0	95	40	.80	.08	.83	.84	.84	.85	.07	.82
35.0	95	18	.86	.05	.77	.78	.72	.71	.06	.60
40.6	105	13	.83	.05	.67	.67	.63			
46.1	115	9	.77	.05	.56	.55				
51.7	125	6	.67	.04	.52	.50				



to 21 g/l. At low SCN<sup>-</sup> concentration, the coating S content is low, but the O and both Ni and Zn are at about the same level as coatings produced at high SCN<sup>-</sup> concentration. This indicates that, at low SCN<sup>-</sup> concentration, there may be more free metals in the coating, resulting in flatter reflectance curves and higher emittance.

After the two-day humidity test, an increase in oxygen and a decrease in sulfur near the coating surface occurred for all the samples can be seen on the Auger spectra in Figure 24. A slight decrease in nickel near the coating surface can also be seen on Figure 24. Based on the Auger data, no particular NaSCN concentration appears to offer greatly enhanced humidity resistance.

Effect of NaSCN Concentration on Optical Properties. - The effect of the variation of SCN content, keeping all other variables constant, on the spectral reflectance of the coatings is shown in Figure 25. The curves are flatter at low SCN<sup>-</sup> concentrations, also, at very low NaSCN concentration (3-6 g/l), the emittance has increased to 12 to 15 percent. Both of these effects are probably due to the presence of uncombined metals in the coating as was also suggested from the Auger data.

At high NaSCN concentrations (greater than 15 g/l), oscillations begin to appear in the spectral reflectance curves. The oscillations become very large at NaSCN = 25 g/l. Such oscillations indicate insufficient absorption in the solar region, so that a NaSCN concentration below 24 g/l may be necessary.

The reflectance curves of the same samples after 48 hours in the NASA standard humidity chamber test (38°C and 95 percent relative humidity) are shown in Figure 26. An important effect is an increase in reflectance of some of the samples in the 1 to 2 μm wavelength region compared to samples before the humidity test. This effect is more pronounced for the high NaSCN concentration and is not very significant for NaSCN less than 24 g/l. Thus, for greater stability, concentrations of NaSCN greater than 21 g/l should be avoided.

The effect of the prolonged humidity test on  $\alpha$  and  $\epsilon$  values for samples plated at all the different NaSCN concentrations are listed in Table VIII. NaSCN concentrations that gave durable coatings were scattered in the range of 6-21 g/l. The results in the table do not show a clear pattern for coating durability. Samples plated at the NaSCN concentrations of 6 g/l and 21 g/l had the best humidity resistance. It is likely that any concentration in the range of 6 to 21 g/l would give roughly equivalent durability properties.

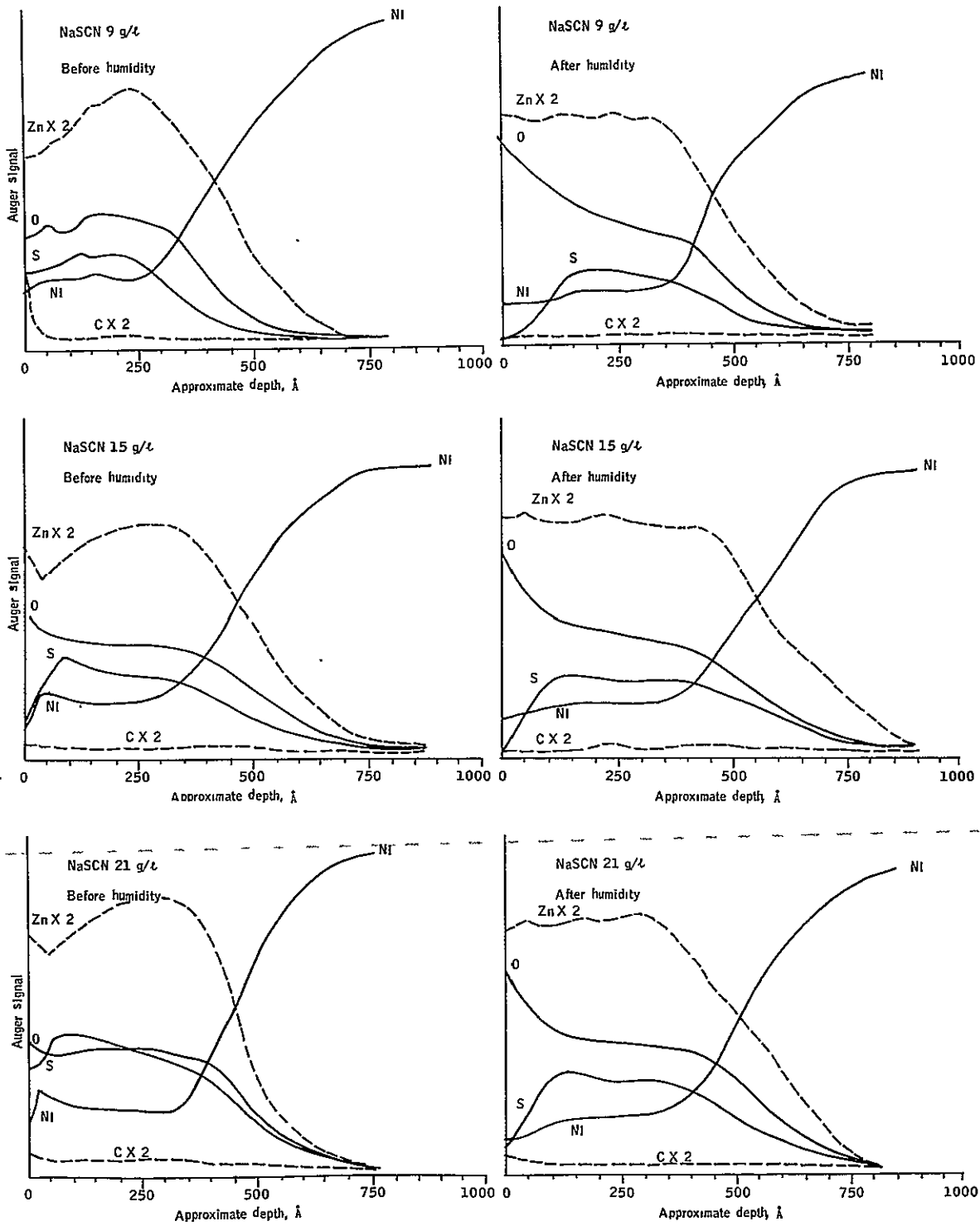


Figure 24. - Effect of NaSCN concentration on Auger spectra.

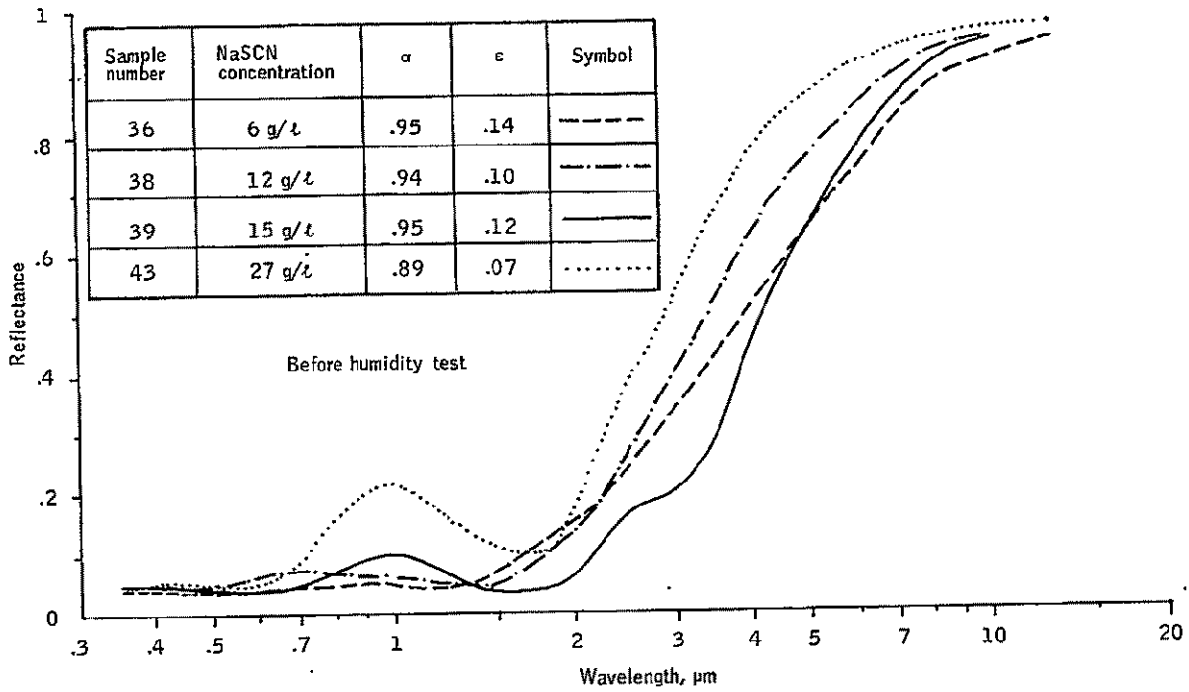


Figure 25.- Effect of sodium thiocyanate concentration on spectral reflectance.

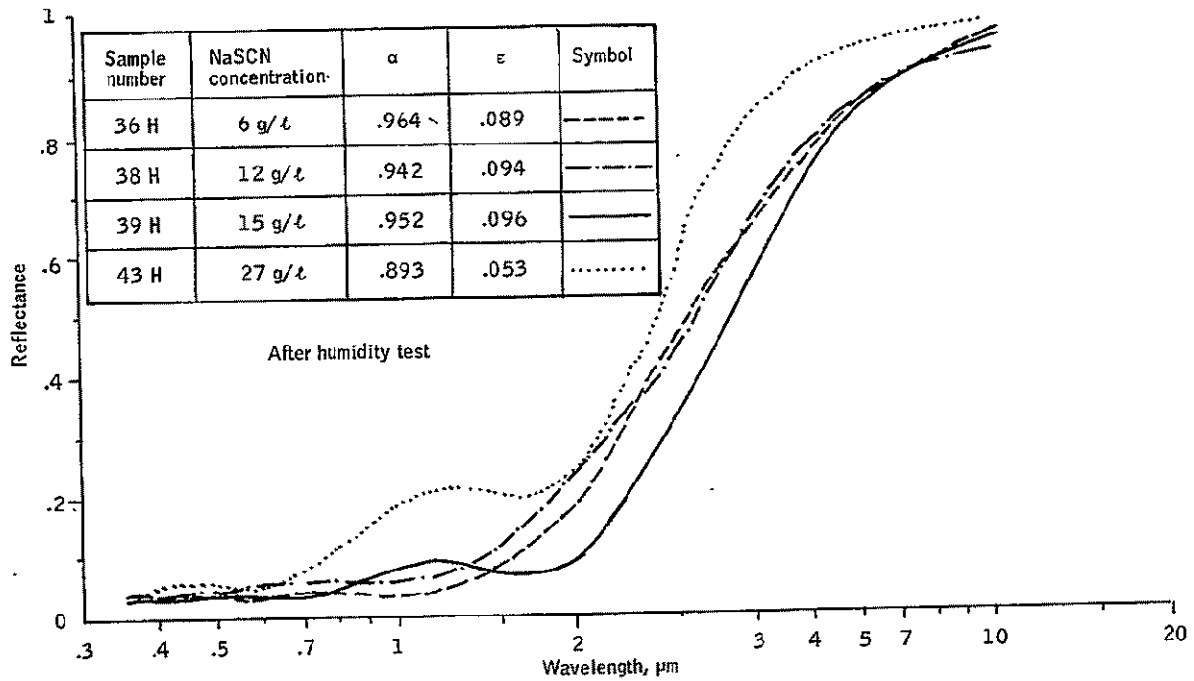


Figure 26.- Effect of sodium thiocyanate concentration on spectral reflectance after humidity test.

TABLE VIII. HUMIDITY RESISTANCE OF BLACK NICKEL SAMPLES  
PLATED AT DIFFERENT NaSCN CONCENTRATIONS

NaSCN (g/l)	Plating time (s)	Days at 38°C and 95% relative humidity									Days in MIL-STD 810B
		0		2		4	6	8	10		3
		$\alpha$	$\epsilon$	$\alpha$	$\epsilon$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$
3.0	40	.93	.12	.93	.11	.84	.84	.86	.80	.09	.73
6.0	40	.95	.14	.96	.09	.93	.92	.91	.90	.13	.88
9.0	40	.94	.11	.96	.12	.92	.91	.88	.88	.10	.80
12.0	40	.94	.10	.94	.09	.91	.88	.85	.84	.10	.80
15.0 (standard)	40	.93	.12	.93	.10	.92	.93	.91	.91	.09	.83
18.0	40	.91	.09	.90	.08	.91	.90	.88	.90	.09	.80
21.0	40	.92	.10	.92	.08	.91	.91	.89	.89	.08	.86
24.0	40	.89	.11	.89	.08	.89	.89	.86	.86	.08	.81
27.0	40	.89	.07	.89	.05	.85	.80	.79	.76	.06	.65
30.0	40	.87	.07	.89	.07	.83	.83	.80	.81	.07	.78

Summary of the Effects of Thiocyanate Concentration. - As the thiocyanate concentration is increased, sulfur content in the coating increases. After humidity testing, the usual increase in oxygen and decrease in sulfur content can be seen near the coating surface.

At low SCN concentrations, the reflectance curves are flatter and have higher emittances, probably due to free metal in the coatings. At high SCN<sup>-</sup> concentrations, oscillations appear in the spectral reflectance curves. After humidity testing, there is an increase in the solar reflectance for high NaSCN concentrations of greater than 21 g/l. Coatings in the range 6 to 21 g/l have the best prolonged humidity resistance.

#### Effect of Ammonium Ion on Coating Properties

Presence of the ammonium ion is very important in black nickel plating. Without ammonium ion, the coating will be nonadherent and smutty<sup>3</sup>. The functions of ammonium ion are summarized as follows:

- Prevents too great a rise in pH by buffer action and thus favors the reduction of thiocyanate, and hence metal sulfide formation.
- Suppresses the formation and precipitation of hydroxide salts of both nickel and zinc.
- Reduces the metallic nickel and zinc contents in the coating by forming ammonia complexes of nickel and zinc which are more difficult to reduce into free metals than uncomplexed nickel and zinc ions.
- The suppression of metallic ion reduction permits the reduction of thiocyanate to proceed.

In this experiment, six NH<sub>4</sub><sup>+</sup> concentrations in the range 3 to 8 g/l were investigated. The NH<sub>4</sub><sup>+</sup> concentration of the standard NASA formula is 5-6 g/l.

Effect of NH<sub>4</sub><sup>+</sup> Concentration on Auger Spectra. - The Auger spectra of three representative samples plated at different ammonium concentrations are shown in Figure 27. No significant difference was found among the Auger spectra either before or after the two-day NASA standard humidity test. Although production of good coatings requires the presence of NH<sub>4</sub><sup>+</sup> ions, the coating composition is not very dependent on the exact concentration.

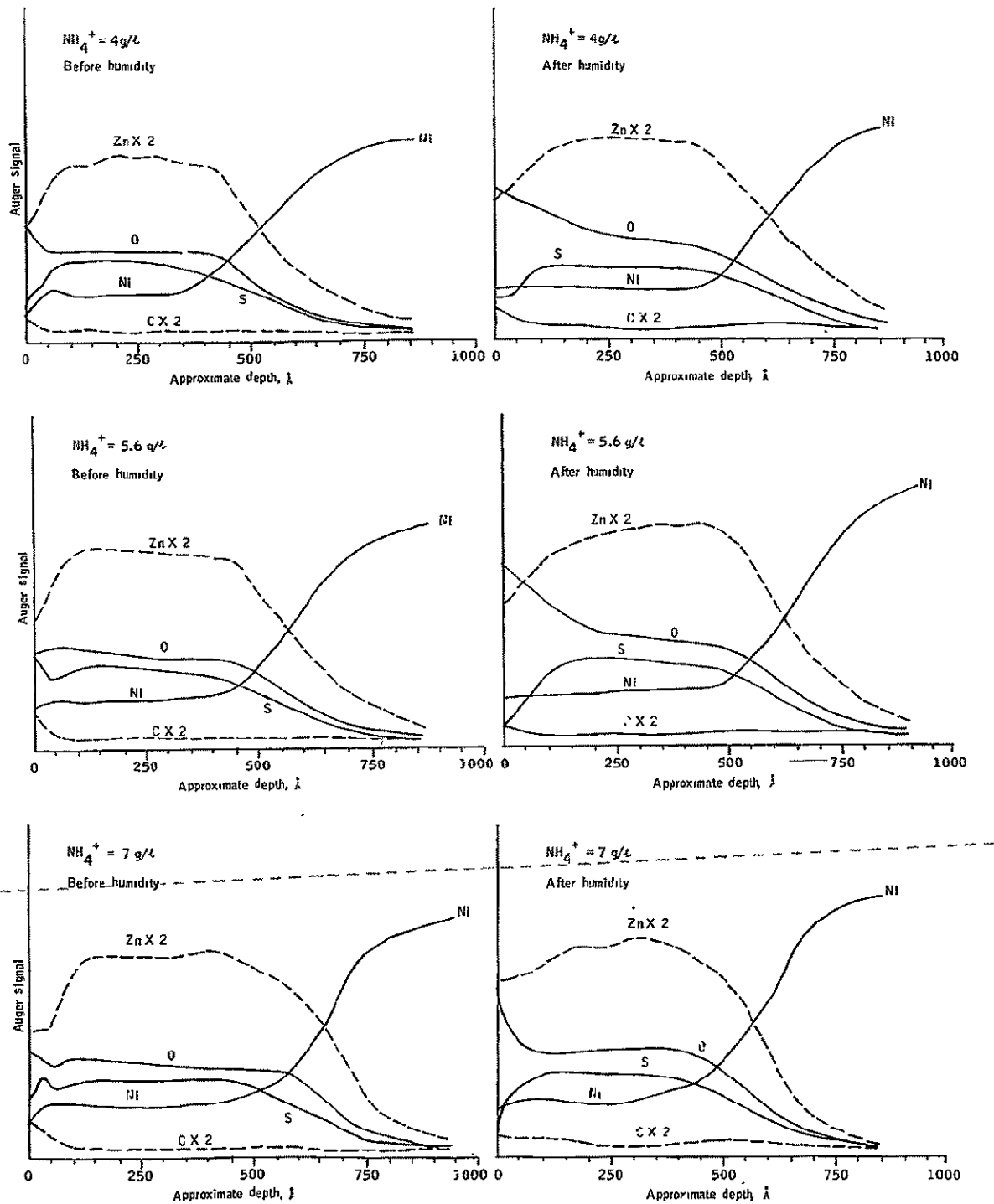


Figure 27. - Effect of  $\text{NH}_4^+$  concentration on Auger spectra.

Effect of  $\text{NH}_4^+$  Concentration on Optical Properties. - Coating insensitivity to the level of  $\text{NH}_4^+$  concentration is also apparent from the optical properties. The small effect of  $\text{NH}_4^+$  concentration on the spectral reflectance of three coatings is shown in Figure 28. All the curves are similar.

The spectral reflectance of the same samples after the 2-day NASA humidity test are shown in Figure 29. A similar increase in reflectance in the 1 to 2  $\mu\text{m}$  region and a decrease of the bump at 0.9  $\mu\text{m}$  is observed for all the samples. The overall solar absorption is actually increased in this short humidity test. However, degradation of  $\alpha$  results from the long-term humidity test for all samples plated at various  $\text{NH}_4^+$  concentrations, as given in Table IX. Table IX again shows that  $\text{NH}_4^+$  concentration has very little effect on the coating optical properties and humidity resistance.

Summary of the Effects of  $\text{NH}_4^+$  Concentration. - If the  $\text{NH}_4^+$  concentration is at least 3 g/l (the smallest concentration tested), further increases in  $\text{NH}_4^+$  concentration have little effect on coating optical properties or humidity resistance.

TABLE IX.- HUMIDITY RESISTANCE OF BLACK NICKEL SAMPLES PLATED AT DIFFERENT  $\text{NH}_4^+$  CONCENTRATIONS

$\text{NH}_4^+$ g/l	Plating Time (s)	Days at 38°C and 95% relative humidity						Days in MIL-STD	
		0		4	6	8	10		810B
		$\alpha$	$\epsilon$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$
3.0	40	.88	.09	.88	.89	.87	.88	.09	.81
4.0	40	.88	.08	.89	.90	.87	.90	.09	.82
5.0	40	.84	.08	.87	.87	.86	.86	.07	.76
5.6	40	.86	.08	.88	.88	.86	.87	.07	.84
(Standard)									
7.0	40	.86	.08	.88	.89	.88	.89	.07	.83
8.0	40	.86	.08	.88	.90	.87	.88	.08	.81

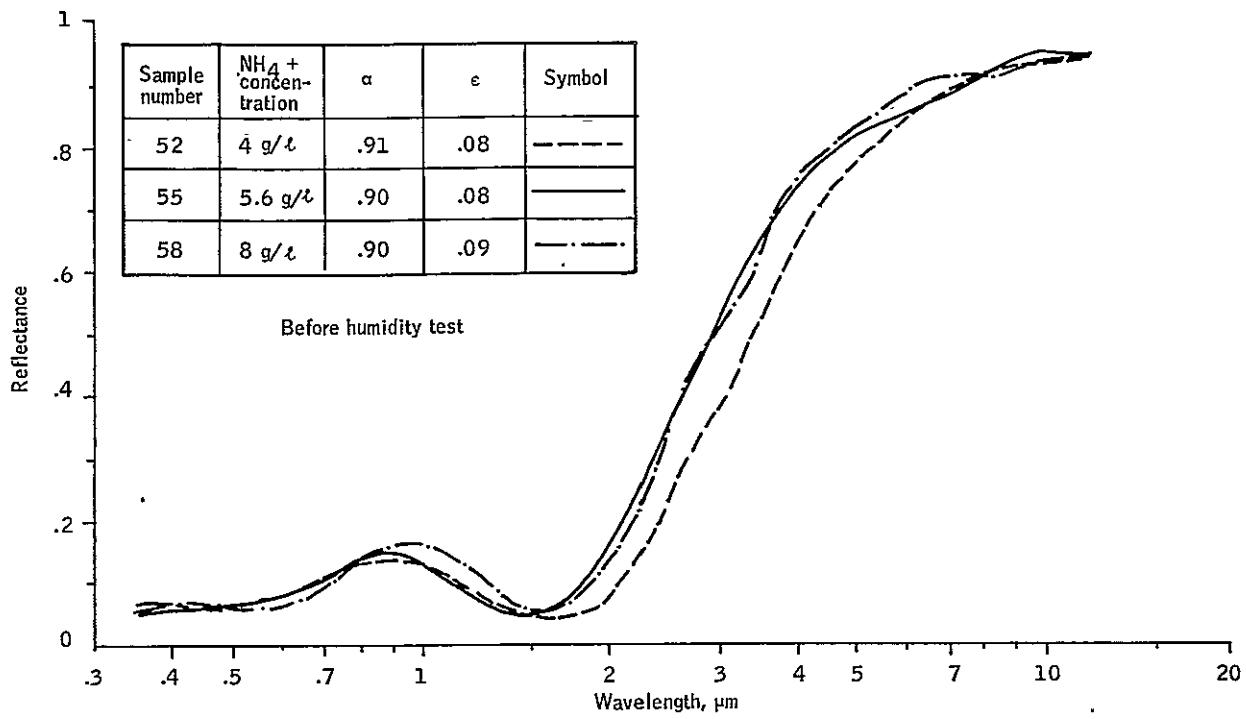


Figure 28.- Effect of ammonium ion concentration on spectral reflectance before humidity test.

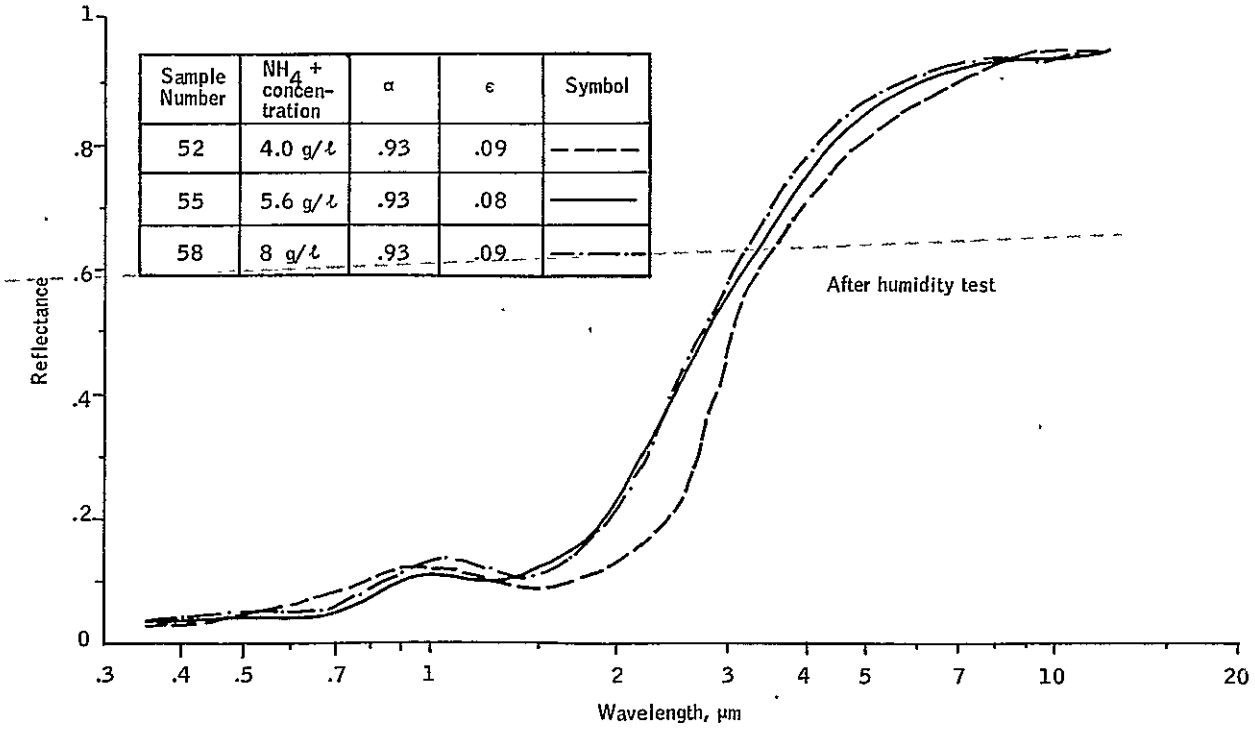


Figure 29.- Effect of ammonium ion concentration on spectral reflectance after humidity test.



## Summary of the Parameter Study and Improved Black Nickel Formulas

Auger analysis of nearly all the samples exposed to humidity showed the conversion of metal sulfides to metal oxides or hydroxides near the coating surface with a corresponding degradation in solar absorptance. In this process the sulfide is washed from the surface by the humidity which is probably the source of the optical degradation. This process can be greatly impeded by depositing coatings which are initially rich in hydroxides and which have a minimum amount of sulfur. This was the basic strategy used to obtain more humidity resistant coatings. Based on the parameter study, it was found that an increase in oxygen and decrease in sulfur content could be accomplished by increasing the bath pH (and possibly current density) or by decreasing the  $Zn^{++}/Ni^{++}$  ratio (or  $Zn^{++}$  concentration), the temperature, or the  $SCN^-$  concentration. Within certain limitations (namely, the maintenance of good optical properties) these changes were incorporated in the improved plating formulas to be described below.

A second general strategy which can be used to improve the coating is to simply plate thicker black nickel coatings. Although in the initial stage of humidity exposure most of the coatings seemed to be oxidized or hydrolyzed by the humidity, beyond that stage further humidity exposure degraded the coatings less severely and more slowly. Thus the degradation stabilized near the coating surface. As a result, thick coatings had significantly better humidity resistance although they also usually had an undesirable higher emittance. However, it is possible to adjust the coating thickness along with other favorable parameters to optimize both the optical properties and humidity resistance.

The improved plating formulas were actually derived through an iterative process using as general guidelines the desire to reduce the sulfur content and to increase the coating thickness. The stability of optical properties under humidity exposure for all of the coatings studied in this development phase are given in Table X. In each case the variations from a basic formula are indicated. Also the average properties obtained with the NASA standard solution are shown for comparison. The composition of the three new solutions studied are listed in Table XI along with the composition of the NASA standard solution.

Among all of the bath compositions and plating conditions studied, the two indicated by the asterisk on Table X gave the best combination of humidity resistance and optical properties. Note that after 14 days in the NASA standard humidity chamber the absorption for both of these samples was better than 0.91. Among these two samples the one plated for 45 seconds had considerably better resistance to the severe MIL-STD-810-B humidity test, but its initial optical properties are not quite as good as those for the sample plated for 40 seconds. Since we feel that the 810B test is

TABLE X. -HUMIDITY RESISTANCE OF IMPROVED BLACK NICKEL COATINGS

(a) Solution 1										
Current density (ma/cm <sup>2</sup> )	Time (S)	Before humidity		810 B humidity		NASA standard humidity				
		α	ε	1 day	4 days	4 days	10 days	14 days		20 days
				α	α	α	α	α	ε	α
4.0	40	.882	.07	.694	---	.883	---	---	---	---
4.0	45	.849	.07	.821	---	.887	---	---	---	---
4.0	50	.812	.09	.834	---	.864	---	---	---	---
5.0	40	.865	.07	.835	---	.876	---	---	---	---
5.0	45	.791	.13	.865	---	.845	---	---	---	---
5.0	50	.814	.12	.832	---	.853	---	---	---	---
6.0	40	.797	.09	.841	.772	.872	---	---	---	---
6.0	45	.822	.11	.859	.789	.820	---	---	---	---
6.0	50	.794	.13	.819	---	.855	---	---	---	---
(b) Solution 2										
4.0	40	.911	.07	.888	---	.908	---	---	---	---
4.0	45	.918	.07	.745	---	.912	---	---	---	---
4.0	50	.913	.09	.755	---	.884	---	---	---	---
5.0	40	.930	.10	.665	---	.892	---	---	---	---
5.0	45	.896	.09	.817	---	.914	---	---	---	---
5.0	50	.904	.11	.893	---	.926	---	---	---	---
6.0	40	.904	.10	.905	.775	.937	---	.839	---	.786
6.0	45	.896	.11	.946	.856	.946	.890	.848	.10	.832
6.0	50	.906	.21	.908	---	.929	---	---	---	---
(c) Solution 3										
5.0	43	.898	.07	.856	.786	---	.855	.813	---	.805
5.0	48	.877	.10	.877	.821	---	.927	.898	---	.897
6.0	37	.892	.08	.901	.838	---	---	---	---	---
*6.0	40	.907	.10	.842	.751	---	.924	.917	.10	.906
*6.0	45	.885	.12	.902	.867	---	.928	.913	.14	.886
6.0	47	.890	---	.834	.754	---	---	---	---	---
7.0	35	.899	.10	.588	.485	---	.868	.814	---	.806
7.0	43	.896	.13	.785	.649	---	.921	.902	---	.884
7.0	48	.880	.22	.866	.795	---	.916	.891	---	.885
(d) Standard NASA solution average										
4.3	40	.900	.097	.846	---	.891	.783	.721	---	.670

TABLE XI.- COMPARISON OF NASA STANDARD FORMULA AND NEW BATHS

Plating/bath parameter	NASA standard bath	New bath # 1	New bath # 2	New bath # 3
pH	5.6-5.7	6.0	6.0	6.0
Temperature (°C)	22.2	22.2	22.2	22.2
Current density (ma/cm <sup>2</sup> )	4.3	---	---	---
[NH <sub>4</sub> <sup>+</sup> ] (g/l)	5.6	7.0	7.0	7.0
NaSCN (g/l)	15.0	15.0	15.0	6.0
Zn <sup>++</sup> /Ni <sup>++</sup>	0.346	0.10	0.30	0.30
[Ni <sup>++</sup> ] (g/l)	23.45	23.45	23.45	23.45
Time (S)	40.0	---	---	---

more severe than necessary to simulate long-term humidity effects, the thinner (40 second) coating would probably be satisfactory.

Thus the recommendation of this program is that the formula given in Table XII be used for solar absorber applications of black nickel coatings.

TABLE XII.- RECOMMENDED SOLUTION

Nickel sulfate (NiSO <sub>4</sub> ·6H <sub>2</sub> O)	53.9 g/l
Nickel ammonium sulfate [NiSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O]	76.7 g/l
Ni <sup>++</sup>	23.45 g/l
NH <sub>4</sub> <sup>+</sup>	7.0 g/l
Zinc sulfate (ZnSO <sub>4</sub> ·7H <sub>2</sub> O)	30.9 g/l
Zn <sup>++</sup> /Ni <sup>++</sup>	0.30
Sodium thiocyanate (NaSCN)	6 g/l
pH	6.0
Temperature	22.2°C (72°F)
Current density	6.0 (ma/cm <sup>2</sup> )
Time	40 seconds

Note: The time can be increased to 45 seconds if greater humidity resistance is shown to be needed in long term tests, but this would degrade the optical properties somewhat.

## Polymeric Overcoats to Protect Black Nickel

An alternative approach which was investigated briefly in the program was the use of polymeric overcoat materials to protect underlying black nickel coatings. A key requirement for such a polymeric coating is high transparency in the infrared so that the low emittance of the black nickel coating is not increased. Three polymeric materials, which in previous work<sup>1</sup> were found to be very transparent in the infrared, were investigated. The three materials were: ethylene propylene material (EPM), ethylene propylene diene material (EPDM), and a silicone-based polymer. All three were shown to adhere well to black nickel coatings. Thickness for the polymeric coatings was  $\sim 10^{-2}$  cm. The silicone coating was found to drastically increase the emittance for coatings of this thickness, to over 0.60 in most cases. The EPM and EPDM materials have nearly identical IR absorption spectra and both increased the emittance by  $\sim 8$  percent when used at the 0.01 cm thickness. Thinner coatings could not be made without pinholes. At 0.01 cm, however, these coatings did give a considerable degree of humidity protection to the black nickel coating. EPDM coating on the NASA standard black nickel was subjected to three days in the 810B humidity test with minimal effects, as shown in Figure 30.

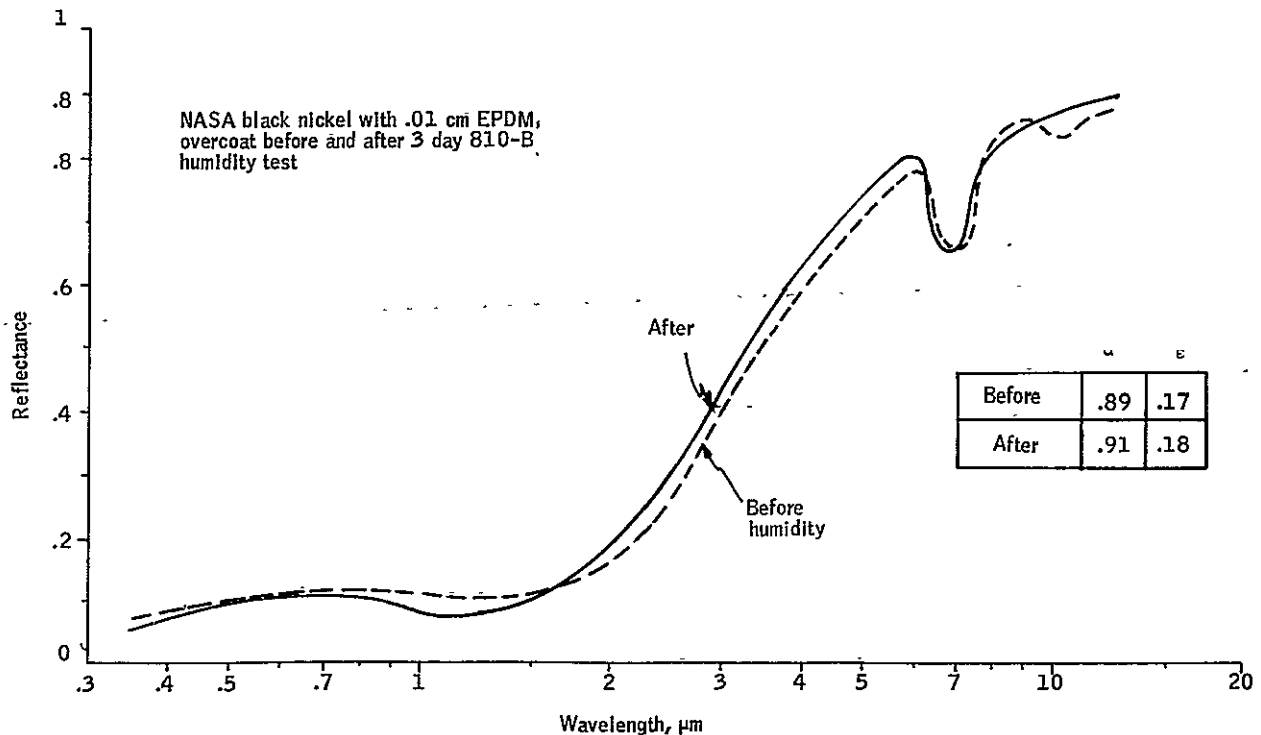


Figure 30. - Effect of humidity on a black nickel coating  
with EPDM overcoat.

In addition to the increased emittance, there are several other problems associated with practical use of polymeric overcoats on a flat-plate collector. The EPDM material has double-bonded molecular structure which may be susceptible to UV degradation. The EPM has no double bonds, but it may have the disadvantage of flowing slightly if used on a warm inclined plane, such as a flat-plate collector. Another serious problem is the lack of stability for both the EPM and EPDM at the elevated temperatures which may temporarily result when cooling fluid is not circulating in a flat-plate collector. Both materials were found to burn off in less than one hour at 232°C (450°F) which is a temperature that may be achieved under thermal runaway conditions.

In summary, none of the polymeric material investigated in this program, or others that we are aware of, can fulfill all the requirements which would be needed as a practical polymeric protective coating.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

The objective of this program was to determine an improved technique for electroplating of black nickel coating which would increase the coating resistance to humidity without sacrificing its excellent selective absorbing optical properties. The optical properties of the best new coatings before and after various humidity exposures are compared in Table XIII to that of the NASA standard formula, which served as the baseline for the program.

TABLE XIII.- HUMIDITY RESISTANCE OF OLD AND NEW FORMULAS

	Before humidity		MIL-STD 810B humidity		NASA standard humidity				
	$\alpha$	$\epsilon$	1 day	4 days	4 days	10 days	14 days		20 days
			$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\epsilon$	$\alpha$
NASA standard	0.900	0.097	0.846	---	.891	.783	.721	---	.670
New formula:									
40 second electroplate	.902	.10	.842	.751	---	.924	.917	.10	.906
45 second electroplate	.885	.12	.902	.867	---	.928	.913	.14	.886

The new formula, plated for 40 seconds, is more susceptible to the severe MIL-STD-810B humidity test than is the 45-second coating, but in the NASA standard test (38°C at 95% RH) both coatings do equally well. The thinner coating has the advantage of somewhat better optical properties. Both new coatings do substantially better than the baseline NASA black nickel coating.

### Recommendations

It is recommended that the new solution formula developed in this program be used for a flat-plate solar demonstration program. A critical need exists for long-term field condition testing of black nickel coatings.

It is likely that more small-scale experimental work involving iterations of the plating variables could further enhance both optical and humidity resistance of black nickel coatings. In other words, although the coating properties were greatly improved during this program, they have not been totally optimized. In particular the better solar properties obtained in some previous work ( $\alpha \sim 0.96$  and  $\epsilon \sim 0.07$ ) might be approached through further effort.

The use of polymeric overcoats to protect black nickel coatings cannot be recommended at this time. Suitable materials which simultaneously fulfill the requirements for low IR absorption, high temperature stability, and the ability to provide humidity protection have not been identified.

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