

Devices & Services Co.

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AN IMPROVED COPPER OXIDE SELECTIVE COATING PROCESS

INTRODUCTION

This technical note describes a two step conversion process for copper oxide on copper selective coatings, that achieves a dramatic improvement in the optical properties. Using this process the optimum surface properties obtained are a solar absorptivity of 0.93 and an emissivity of 0.04 - 0.05, compared to 0.90 / 0.20 for the usual conversion process.

BACKGROUND

Copper oxide on copper selective absorbers have been in use for many years in flat plate solar collectors, particularly in Australia for hot water heaters. In recent studies [1], it has been shown that the copper oxide surface is susceptible to degradation at elevated temperatures due to further oxidation of the substrate. For low temperature applications such as passive hot water or air heaters, it has proven to be an inexpensive and durable coating.

The black conversion coating is produced by oxidation of the copper surface in a hot sodium hydroxide / sodium chlorite solution for several minutes. One solution used in Australia [2], consists of 0.83 pounds of sodium hydroxide and 0.42 pounds of sodium chlorite per gallon of water. The solution is operated at 140 to 145 C. We have used a similar proprietary solution, Ebonol C [3], that is often used for decorative blackening and corrosion protection for copper and copper alloys.

The selective absorption characteristic of the coating is apparently due to natural absorption of short wavelength solar radiation by the copper oxide, while the oxide layer is relatively transparent at the longer thermal wavelengths. Since the copper substrate has a low emissivity, the oxide layer - copper substrate combination produces a low emissivity and a high absorptivity.

The radiation properties depend on both the thickness and composition of the layer, which are determined by immersion time, temperature, and solution concentration. Figure 1 illustrates the variation of properties with immersion time using the recommended solution concentration of 1.5 pounds of salts per gallon of solution, and a temperature of 140 F.

For the first few minutes absorptivity increases rapidly with only a small change in emissivity. At three to four minutes the layer is thick enough to be opaque to solar radiation so that the absorptivity no longer increases, but the emissivity continues to increase. As the thickness increases the surface finally begins to develop a velvet texture, that further increases solar absorptivity. For this coating process, optimum solar absorber properties occur for immersion times of between two and five minutes. The best properties reported for the copper oxide coating are, 0.90 / 0.15 in reference [1]. For the improved coating process, described below, the best properties obtained were 0.93 / 0.04.

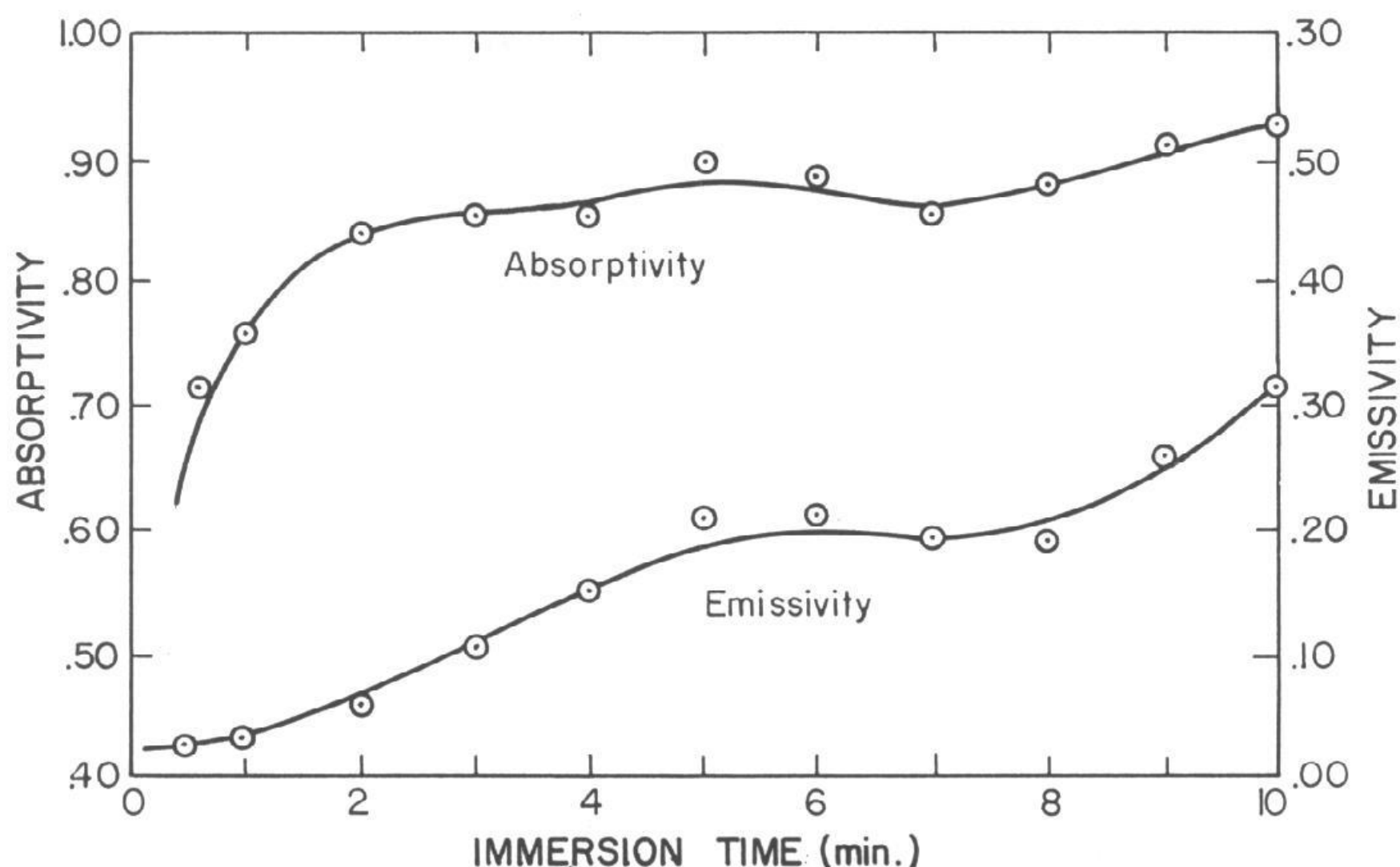


Figure 1. Absorber properties versus immersion time for the standard CuO coating

COATING PREPARATION

Surface Preparation: For all of the samples reported here, the surface was first cleaned with very fine steel wool and a mild detergent, rinsed, dried and then cleaned with dry, oil free steel wool. Consistent coatings can also be produced with chemical cleaning methods.

Initial Immersion: After cleaning, the samples were immersed in the Ebonol solution (1.5 lbs/gallon) at a temperature of 135 F for five to twenty minutes. For immersion times over twelve minutes a yellow green precipitate developed on the surface. If this occurred the precipitate was removed with a soft towel. Following the rinse the sample was blow dried with compressed air. At this point the coating is steel gray in color for the shorter immersion times, to dull gray for the longer times.

Acid Immersion: The sample was dipped in a dilute hydrochloric or sulfuric acid bath for five to fifteen seconds, then rinsed and dried again. The acid dissolves some of the coating leaving a reddish residue with the hydrochloric acid and a reddish brown coating for the sulfuric acid.

Second Immersion: The final step is a second immersion in the Ebonol solution for 10 to 90 seconds. As the immersion time increases, the coating exhibits a transition in color from dark red to blue, indicating that optical interference is responsible for the improved solar absorptivity.

Tables 1 through 4 and Figure 2 describe four of the coating series that were run.

Table 1 Bath Temperature: 135 F
Initial Immersion Time: 5 minutes
Acid Bath: 2% Sulfuric Acid

second immersion time (sec)	solar absorptivity	emissivity
*	0.90	0.15
0	0.84	0.05
10	0.88	0.05
20	0.89	0.06
30	0.93	0.06
50	0.92	0.07
90	0.93	0.14

* prior to acid immersion

Table 2 Bath Temperature: 135 F
Initial Immersion Time: 12 minutes
Acid Bath: 2% Sulfuric Acid

second immersion time (sec)	solar absorptivity	emissivity
*	-	0.24
0	0.88	0.09
10	0.92	0.05
15	0.92	0.04
20	0.93	0.04
30	0.94	0.05
50	0.93	0.06
75	0.93	0.08

Table 3 Bath Temperature: 135 F
Initial Immersion Time: 18 minutes
Acid Bath: 2% Sulfuric Acid

second immersion time (sec)	solar absorptivity	emissivity
*	0.90	0.24
0	0.85	0.10
20	0.92	0.08
35	0.93	0.06
45	0.94	0.09
60	0.93	0.09

Table 4 Bath Temperature: 135 F
Initial Immersion Time: 12 minutes
Acid Bath: 2.8% HCL

second immersion time (sec)	solar absorptivity	emissivity
0	0.50	0.02
10	0.63	0.02
20	0.78	0.02
30	0.81	0.02
40	0.84	0.02
50	0.84	0.03
60	0.86	0.03
80	0.90	0.04
90	0.90	0.05
100	0.90	0.13

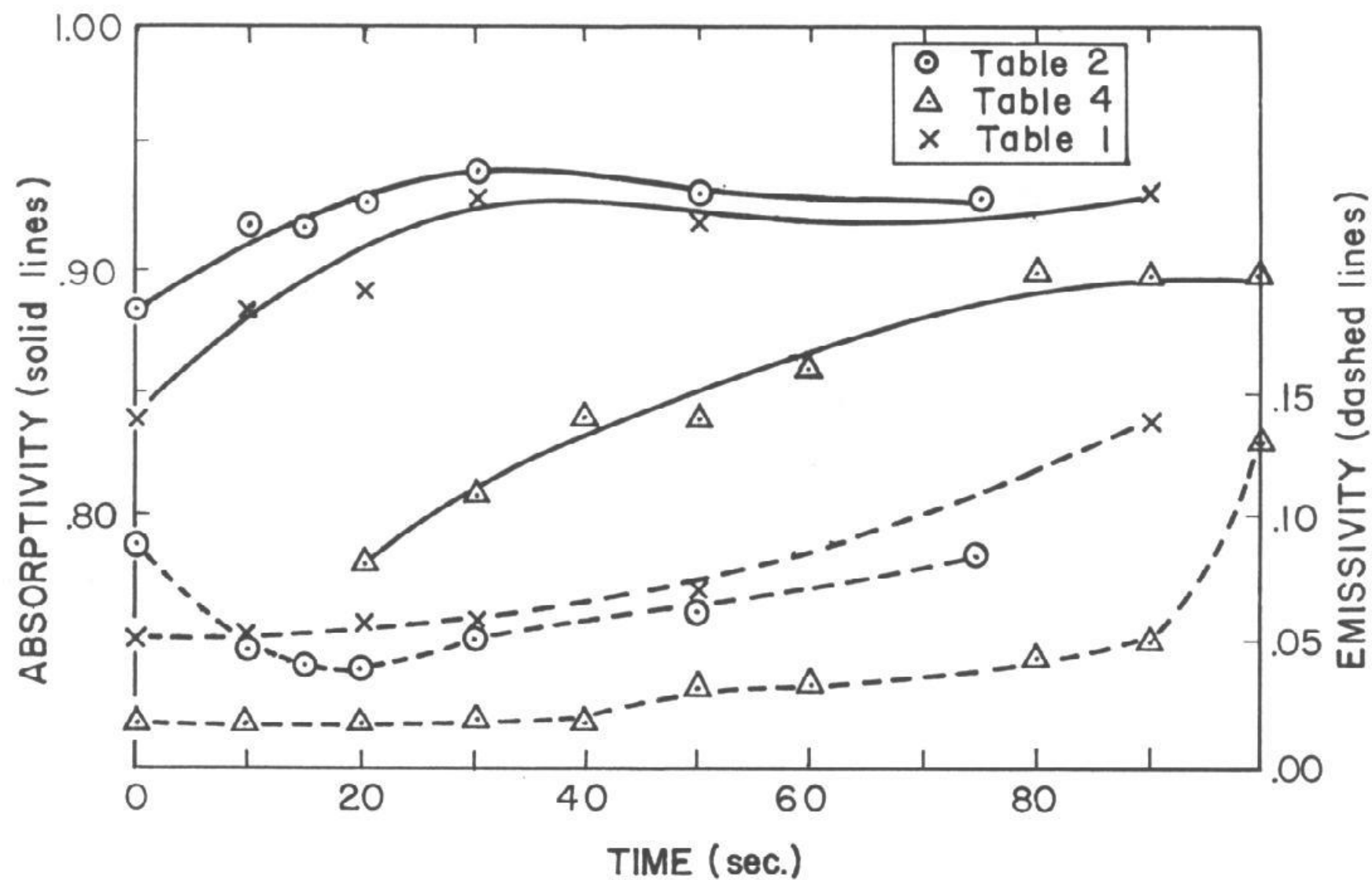


Figure 2. Variation of absorber properties with second immersion time

Based on these four coating series some observations were made about the coating process. First, unlike most other chemical immersion or conversion coatings, in some cases the emissivity actually decreases with immersion time in the second immersion step. This produces a minimum in the emissivity curve at about the same time that a maximum occurs in the absorptivity.

Using the hydrochloric acid the resulting surfaces exhibited intense colors of red or blue indicating that the interference minimum in the visible is narrow. With the sulfuric acid the colors were much darker indicating a broader minimum and therefore resulting in higher solar absorptivities. The longer the initial immersion time, the broader the interference minimum. For the 18 minute initial immersion, the surfaces were very dark violet to almost black.

As the second immersion time increases beyond about 45 seconds, the surface colors begin to disappear and the steel gray color of the copper oxide reappears. This results in a higher reflectivity in the visible portion of the spectrum and the solar absorptivity decreases slightly.

EVALUATION OF SELECTIVE COATINGS

The best solar selective properties were obtained for the twelve minute initial immersion and the sulfuric acid intermediate dip. For this process, the solar absorptivity reaches a maximum, 0.93 - 0.94 and the emissivity reaches a minimum, 0.04 - 0.05, at the about the same time during the second immersion. For this process these are obviously the optimum properties. In general the optimum depends on the anticipated operating conditions for the absorber, since both the absorptivity and emissivity usually increase with coating time. A criterion for choosing the optimum properties is presented in reference [4] and was originally derived by Tabor in reference [5]. The result of the derivation is given in the equation below.

$$da/de = bs(T^{**4} - T_c^{**4}) / tQ$$

where, a is the solar absorptivity

e is the emissivity

s is the Stephan-Boltzman constant

T is the absorber operating temperature

T_c is the average temperature surrounding the exposed absorber surface, ie, the cover temperature in a flat plate collector

t is the transmissivity of the cover, or the concentration ratio for a concentrating collector

Q is the average incident solar energy

b is a constant that corrects for thermal transients (typically 0.80 to 0.95)

This ratio of terms has been designated the Tabor number, and describes the operating condition for the absorber. If T_a is greater than one, a decrease in emissivity is of greater benefit than a similar increase in absorptivity. For a given coating process, the optimum properties can be determined from a plot of absorptivity versus emissivity. The processes described in Tables 2 and 4 are plotted in Figure 3.

The numbers plotted along the curves are the slopes, and represent optimum properties for the different values of T_a. Notice that if a line is drawn tangent to the curve at any point, all other points on the curve lie below and to the right of the line. Points to the left and above the line represent better properties for the particular value of T_a.

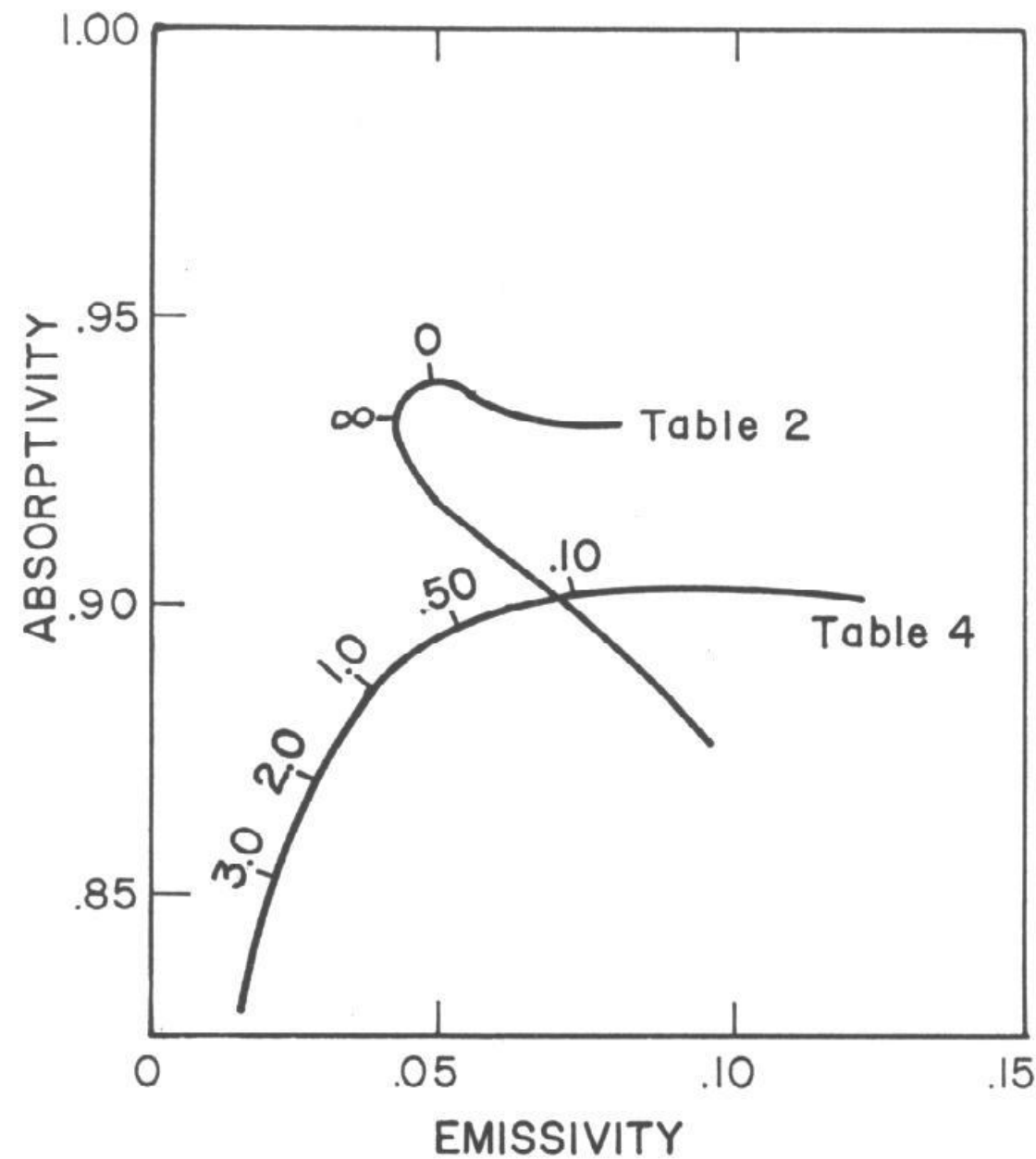


Figure 3. Absorptivity versus emissivity curves

The Tabor criterion can also be used to compare any two selective surfaces by defining an effective absorptivity as shown below.

$$A_o = a - T_a(e)$$

The effective absorptivity " A_o " is the absorptivity that a zero emissivity surface would have, to be equivalent for the given operating conditions. Therefore once T_a is determined for a particular operating condition the surface with the larger value of A_o is the better surface.

References

- [1] H.Y.B. Mar, J.H. Lin, P.B. Zimmer, R.E. Peterson and J.S. Gross, "Optical Coatings for Flat Plate Solar Collectors," Final Report for ERDA under Contract No. NSF-C-957 (AER-74-09104), September 1975.
- [2] D.J. Close, CSIRO Eng. Sec., Report E.D.7, Melbourne, June 1962.
- [3] Ebonol C, a product of Enthone, Inc.
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- [5] H. Tabor, "Selective Surfaces for Solar Collectors," in Low Temperature Engineering Applications of Solar Energy, ASHRAE publication, 1966.