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A New Method of Moisture Penetration Measurement in Protective Coatings

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Synopsis

Various methods are used by the paint and coating technologists to evaluate the resistance of protective coatings to penetration of water through them. This article intends to introduce a new, simple method for the moisture resistance evaluation. The method uses thin metal films as the sensor and is not absolute. However, it may be very useful for comparative experiments when the paint formulator seeks an optimum performance of coating developed for moisture protection.

INTRODUCTION

The rate at which water permeates the protective film is of particular interest in the coating industry. Results of water permeation tests performed with coating materials determine their suitability for various applications. When a formulation of a coating to be used as a barrier to moisture penetration is being developed, moisture tests direct the formulator to an optimum composition and cure schedule.

Several methods have been developed to evaluate performance of protective coatings, films, and plastics material with respect to their ability to resist the permeation of water. Basically, two sections of a chamber are separated by the sample to be tested and a concentration gradient of water is applied across the membrane. The most often used method for determining the water permeability through polymer films is the "cup" method.[1-10] The film is prepared separately and then transferred to, and sealed over, the top of a cylindrical dish containing dry desiccant. The assembly is placed in an atmosphere of a constant humidity, and the gain in weight is recorded over an interval of time. A review of this and other methods was presented by Stannett and Yasuda[11] and, recently, by Lever and Rhys.[12]

The cup method, often referred to as the Payne cup method after its developer H. F. Payne, is a very useful, absolute method for determining the amount of water which has penetrated through the film in a given time. However, in many, if not most cases, it is not the absolute value which one needs to evaluate; relative values of the water penetration through coating are sufficient whenever an improvement and the optimum formulation of paint are being sought. A simple and unpretentious method would be appreciated in these cases.

We have found that electrolessly deposited nickel–phosphorus (Ni–P) thin films[13] are a good tool for determining the resistance of coating to moisture for comparative purposes. The Ni–P deposit is extremely sensitive to the presence of moisture when it is under load, i.e., when the electrical potential is applied between two areas of the film. It is probably an electrolytical process that takes place in the Ni–P layer and results in the destruction of the original structure. In the absence of water, the electrical resistance value of the film changes insignificantly. However, in the presence of a minute amount of water, the Ni–P film increases its resistance value, and in the limit it may become an open circuit. The resistance change is proportional to the voltage applied, the time for which it is applied, and the amount of water which is present. The sensitivity of the detection is so high that even the best protective coatings will be found permeable to moisture. There is no correlation between the resistance change and the original resistance, and for this reason the same resistance films should be used in comparative experiments. However, it should be noted that the higher the original resistance, the higher the sensitivity of the resistor to moisture.

RESULTS

We demonstrate the technique of the moisture test on several studies. The first study compares the moisture resistance of protective coating based on diallyl isophthalate polymer (DAIP) with that of a special sili-

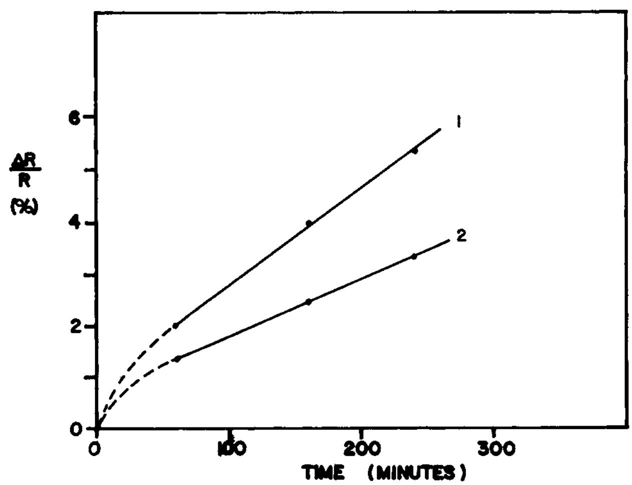

Fig. 1. Typical changes of resistance of DAIP-coated metal films under test. Dotted portions represent a transient process, and solid portions demonstrate a constant rate of water diffusion through the protection. Curve 1 is a single DAIP coat 0.1 mm thick, and curve 2 is a double coat 0.2 mm thick.

TABLE I
Determination of Resistance to Moisture Penetration.
Comparison of Two Different Coatings.

Coating	$R_0 \times 10^{-4}$, ohms	$\Delta R/R_0$,[a] %	Mean $\Delta R/R_0 \pm$ S.D., %
Special silicone	400	4.5	4.14 ± 0.42
	398	4.0	
	398	4.0	
	401	4.7	
	400	3.5	
DAIP			
200°C	397	1.0	1.52 ± 0.40
	397	1.0	
	398	1.5	
	397	1.3	
	400	1.5	
	393	1.3	
	394	2.0	
	404	2.2	
	398	1.8	
215°C	398	1.0	1.40 ± 0.37
	396	1.0	
	397	2.0	
	393	1.5	
	397	1.5	
230°C	399	1.5	1.34 ± 0.39
	397	1.0	
	393	0.8	
	394	1.3	
	400	1.3	
	391	1.8	
	396	1.0	
	400	2.0	

[a] ΔR is change of resistance after 1-hr exposure of the resistors to 100% humidity at 100°C under potential of 40 V.

cone-based coating. Different temperature of cure and thickness of DAIP coating were employed. The contribution of this part to the introduction of the new method is to show its reproducibility by means of the standard deviation from the mean value. The second study follows the quantity of the resistance change as a function of time. It demonstrates achievement of the equilibrium rate of penetration of water through the protective coating after a short time period of the rate adjustment. In the third study, various polymer films were tested and compared in order to see if the resistance changes appeared to be in the order of the expected relative permeabilities of the coatings to water.

The experimental arrangement was as follows. Uncoated Ni–P films were coated with films of the protective materials to be tested. After cure procedure, the films were exposed to 100% humidity at 100°C at atmospheric pressure under a potential of 40 V. Initial film resistance was between 4 and 4.5 Megohms. The heat produced in the film due to Joule

TABLE II
Determination of Resistance to Moisture Penetration.
Comparison of One and Two Coats of DAIP.

Thickness × 10, mm	$R_0 \times 10^{-4}$, ohms	$\Delta R/R_0$,[a] %	Mean $\Delta R/R_0 \pm$ S.D., %
1.3 ± 0.1	448	1.6	1.62 ± 0.53
1.3 ± 0.1	446	1.3	
1.3 ± 0.1	443	1.8	
1.3 ± 0.1	448	0.9	
1.3 ± 0.1	446	2.5	
2.0 ± 0.2	456	0.9	0.98 ± 0.10
2.0 ± 0.2	444	0.9	
2.0 ± 0.2	436	1.1	
2.0 ± 0.2	446	1.1	
2.0 ± 0.2	441	0.9	

[a] ΔR is change of resistance after 1-hr exposure of the resistors to 100% humidity at 100°C under potential of 40 V.

TABLE III
Determination of Resistance to Moisture Penetration.
Comparison of Various Materials.

Material	Thickness × 10, mm	$R_0 \times 10^{-4}$, ohms	$\Delta R/R_0$,[a] %
Heat-shrinkable sleeve[b]	3	480	0.0
Poly-DAIP[c]	1	480	1.1
Fluorocarbons[d]	1	446	1.3
Silicone[e]	1	478	1.8
Polystyrene[f]	0.3	478	2.2
Chlorinated polyethylene[g]	0.5	480	3.6
Pigmented silicone[h]	1	472	6.8
No coat	0	480	∞

[a] ΔR is change of resistance after 15-min exposure of the resistors to 100% humidity at 100°C under potential of 40 V.
[b] RNF 100, Raychem Ltd.
[c] DAPON M, FMC Corporation.
[d] EMRALON 333, resin-bonded tetrafluoroethylene, Acheson Colloids Ltd.
[e] DC 630, Dow Corning.
[f] Solution of conventional polystyrene foam.
[g] Polysciences, Inc.
[h] High-temperature grade, Midland Industrial Finishes.

heating was not significant. This can be calculated from $W = V^2/R$, where W is in watts, V is in volts, and R is in ohms. Resistance readings were taken on a Wheatstone bridge before and after the foregoing treatment, and a resistance change was evaluated. It must be noted that after the moisture treatment, the resistors should be dried for a short period (e.g., 95°C for 10 min) in order to avoid the passage of electric current through the wet coating.

The results of our comparative tests are shown in Tables I, II, and III, and in Figure 1.

DISCUSSION AND SUMMARY

Ni–P thin films provide an easy and elegant method for evaluating protective coatings in terms of protection against penetration of water whenever two or more samples are to be compared.

Using the metal film technique, we readily established the superiority of DAIP coating to our special silicone coating (Table I), and evaluated the effect of temperature of cure (Table I) and of thickness of the coat (Table II) on the moisture resistance. In Figure 1, we show the time function of the resistance change during the test. After an adjustment period, the rate of the change attains a constant value which presumably is a result of a constant rate of permeation of water through the protective coating.

Finally, we performed the test with various protective coatings and summarize the results in Table III. As expected, the poly(diallyl isophthalate) is superior to other conventional coatings. The best, of course, appeared to be the heat-shrinkable sleeving. The highly pigmented silicone, flame-retardant grade, was much more permeable to water than the clear silicone. Polystyrene and chlorinated polyethylene were graded less protective than the other samples (except the pigmented silicone). However, it should be noted that the thickness of the former was from 3 to 5×10^{-2} mm, whereas the thickness of the latter was from 10 to 12×10^{-2} mm.

We conclude that the method shows a good reproducibility and provides the advantage of an adjustable sensitivity by selecting the right resistance value. For our experiments, we choose metal films with a high resistance value of 4–5 Megohms in order to achieve the high sensitivity to the presence of moisture under the protective coat. Thin films with values in a range of kilohms would presumably be better for testing coatings with poor moisture protection characteristics. Of course, other alternatives when working with such materials could be to use less severe humidity conditions and/or shorten the time of the test.

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