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STATE HIGHWAY DEPARTMENT
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MEASUREMENT OF THE LINEAR COEFFICIENT OF THERMAL EXPANSION OF

PAVEMENT MARKING PAINT AND A MATHEMATICAL CONSIDERATION

OF THE PHENOMENON OF PAINT PEELING

by

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SYNOPSIS

A series of mathematical relationships were derived from a theoretical treatment of phenomena associated with paint peel. These relationships are expressed in two fundamental equations. On the basis of the equations, a technique was devised for the measurement of the linear coefficient of thermal expansion of dry paint films. This technique was applied in the case of six highway traffic paints of varying durability with results suggesting strongly that the difference in thermal expansion of the paint and the substrate may be an important factor in the production of paint peel.

MEASUREMENT OF THE LINEAR COEFFICIENT OF THERMAL EXPANSION OF PAVEMENT-MARKING PAINT AND A MATHEMATICAL CONSIDERATION OF THE PHENOMENON OF PAINT PEELING

INTRODUCTION

Among the most important of all types of paint failure is adhesion failure, which in the United States is described variously as paint peeling, scaling, or chipping. Many theories have been presented to explain this phenomenon. As yet, none of these has given a complete explanation. This is probably due to the large number of variables which operate on the strength of the adhesion bond. Such factors as moisture, surface roughness, type of substrate, thickness of paint, drying stress, linear coefficient of thermal expansion, surface tension, and many others all affect the adhesion of the paint.

It would be very convenient to be able to predict which paint from a group of paints would be the most durable under a given set of conditions. This would mean that some type of mathematical expression is needed to correlate the bonding forces of the paint with the variables which cause adhesion failure.

It is the objective of this report to give in part a mathematical treatment to the process by which paint peels. The analysis is limited to the effects of the linear coefficient of thermal expansion and the drying stresses which are characteristic of the paint. Also contained in this paper is a method for the measurement of the linear coefficient of thermal expansion of paint. The durability ratings of these paints are known.

Theory of Paint Peeling

In order that the process of paint peeling be understood, the terms "theoretical" and "apparent adhesion" are introduced. The magnitude of the theoretical adhesion bond is determined experimentally at a convenient standard physical and chemical condition (corrections are made for drying stress and surface tension). The standard condition should be maintained from the time of application of the paint to the time at which the numerical value is to be determined. It should be noted that the theoretical adhesion is a function of time, chemical makeup of the paint, substrate material, temperature, thickness of paint, and surface roughness. The apparent adhesion is never equal to the theoretical adhesion, due to the effects of the drying stresses and surface tension of the paint. The apparent adhesion is a function of the theoretical adhesion, linear coefficient of thermal expansion, changes in the chemical environment, drying stresses, and surface tension.

Assumptions. It is conceded by the author that the following assumptions are not necessarily in complete agreement with the conditions of the system in question. They are made to simplify the following analysis.

1. Paint is homogeneous.

2. Substrate will not experience a bending moment due to the difference in the linear coefficient of thermal expansion of paint and substrate.

3. Expansion of substrate is uniform.

4. Adhesion of paint is uniform.

5. Young's modulus of elasticity is applicable to both paint and substrate.

Definitions. The following are the symbols used in the mathematical description of paint peeling as presented in this paper.

a — theoretical adhesion of any given paint (lbs/in.)

A — apparent adhesion of any given paint, determined by experiment (lbs/in.)

x — thickness of paint (in.)

E — modulus of elasticity of any given paint (lbs/in.^{2})

ΔT — temperature change, equal to the temperature of the system minus the reference temperature ($^{\circ}F$)

$\Delta\alpha$ — difference in the linear coefficient of thermal expansion of paint and substrate (in./in. $^{\circ}F$)

K_1 — constant (lbs/in.^{2})

K_2 — constant (lbs/in.^{2})

ds — change in drying stress (in./in.)

t — time

t_o — time of peel

F(p) — paint function (lbs/in.)

In equation 3 the term $E(\Delta T)$ $(\Delta\alpha)$ represents the stress as described in the above paragraph. The term Kx expresses the total stress in a given cross section and that portion which acts on the bond.

Equation 3 only describes the effects of the linear coefficient of thermal expansion.

The Effect of Drying Stress on Adhesion.   Paint films generally undergo a densification in the drying process, even when considering only the non-volatile portion of the applied paint.   When considering a normal paint system of paint film-substrate, as shown in Figure 1,   one can visualize a shrinkage in the Z direction during the densification inherent in drying.   However, during the drying process there can be no noticeable shrinkage at the adhesion interface, i.e., in the X and Y directions of Figure 1. Since the forces causing the densification can be assumed poly-directional, the physical restraint to the shrinkage at the adhesion interface will leave the paint in residual tension and the sub strate in residual compression.   These stresses in the paint film are called drying stresses.

Due to the movements which take place in the upper layers of the paint film, as described in the paragraphs above, the stress throughout a given cross section will not be uniform.   The drying stresses in the adhesion interface will be a maximum and the drying stress in the top surface will be a minimum.

In order that paint peel may be initiated, the net bonding forces of the paint must,in respect of time, approach zero.   This would mean that at the time of peel start, there is adhesion failure.   This can be expressed as follows:

1- $F(p) = A$ at any time t .

Therefore at the time of peel,

2- $\lim_{t \to t_0} F(p) = 0$.

The Effect of the Linear Coefficient of Thermal Expansion. Due to the effect of the difference in the linear coefficient of thermal expansion of the paint and substrate, a stress will act upon their bond. This results in a change in the magnitude of the adhesion forces.

This stress is not uniform throughout a given cross section of the paint. In fact, the stress is a maximum at the bonding surface and a minimum at the top surface. This is a result of freedom of movement which the paint has in the upper layers as opposed to that in the bonding surface. The movement alleviates some of the stress.

It follows then:

3- $A = a + K(E) (x) (\triangle T) (\triangle \alpha) = a + K_1 x (\triangle T) (\triangle \alpha).$

Where

K = constant (unitless)
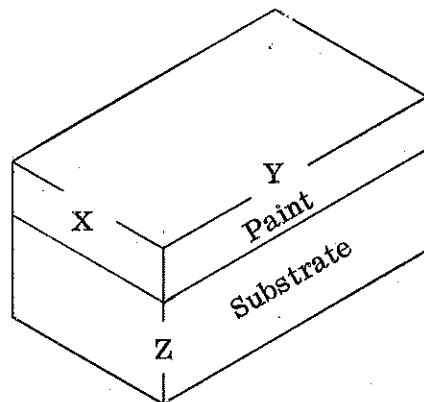
and

$KE = K_1.$

Figure 1

Because of the effect of the densification of the paint film, the thickness of the paint will vary with time. It can also be assumed that the drying stress is a function of time. Therefore, by the same argument used in the development of Equation 3, the effect of the drying stress on the adhesion forces may be described as follows:

$$4- \quad A = a - \int K_s EX \; ds = a - \int K_2 X \; ds \; ,$$

Where

$$K_s = \text{constant (unitless)}$$

and

$$K_s E = K_2 \; .$$

The expression in Equation 4 cannot be integrated at the present time. By combining the equations 3 and 4, an expression for F (p) can be arrieved at.

$$5- \quad F(p) = a + K_1 x (\triangle T) (\triangle \alpha) - \int K_2 x \; ds = A \; .$$

This equation gives a correlation of the properties of any given paint. It is thus shown that no one factor can be specified as the sole agency of paint peel. Each factor must be singled out and measured individually. Then a correlation may be established between the factor measured, and conclusions may be drawn from these correlations. The problem is to measure the individual variables making up the correlation.

Procedure for Measuring Coefficient of Expansion

The method employed for measuring one of these components, the coefficient of thermal expansion, is as follows:

Paint was applied to a wooden block (6" x 6" x 3/4") in layers. After each layer was allowed to dry, successive layers were applied until the paint sample was about 35 mils thick. This was allowed to dry for about 6 months. The sample was removed from the wooden block by means of a band saw. The slab of the wood was cut off, leaving a thin slice between the paint and the saw blade. This method was employed to prevent over-heating of the sample. The remaining wood was sanded off by hand.

One-inch by three-inch samples of paint were then cut off of this sample. These were allowed to dry an additional three weeks to cure the portion of the paint that was in contact with the wood.

Two (A-7) strain gages were attached to the sample with Duco cement, one on each side to compensate for bending strain and also to increase sensitivity by two. A thermocouple was placed in the paint sample, with which to determine average temperature of the paint, as shown in Figure 2.
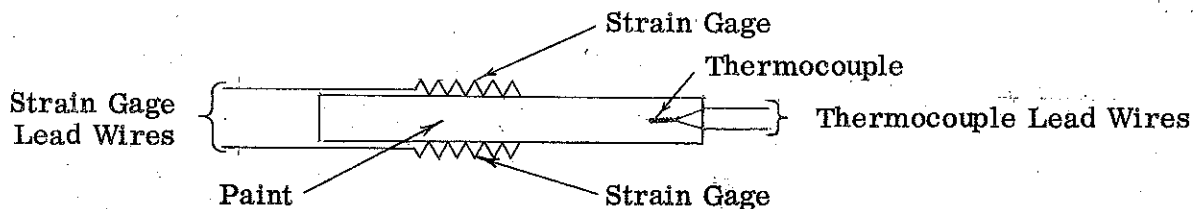

Figure 2

The samples were then put on glass plates mounted on a wooden frame as shown in Figure 3. A lead barrier strip was used to prevent pulling on the gages and thermocouple. The hole shown in Figure 4 in the glass arrangement was made to allow free movement of the lower strain gage.

A compensating gage was made by placing two (A-7) strain gages on a steel bar, 1/4" x 1" x 2", in a series fashion, after which it was waterproofed.

An automatic temperature recorder was used to record temperatures; and a dynamic strain analyzer and oscillograph were used to record strain changes. The compensating gage was kept at 32 degrees F by placing it in a thermos containing ice water. Seventy degrees F was taken as the zero stress point.

When the curve below 70 degrees F was run, the temperature of the freezer was at 0 degree F, and the test sample was then placed in it. When the upper part of the curve was run, the oven was at 160 degrees F. In both cases, recordings were also made as the sample returned to 70 degrees F.

The purpose of having the freezer and the oven at these temperatures when the samples were placed in them was to eliminate the drying error which occurs when a test takes a long time to run.

In the running of the test, two operators are required; one to read the temperatures as they are recorded, and one to mark the place on the oscillograph which will correlate strain and temperature. Only one paint was run at a time.

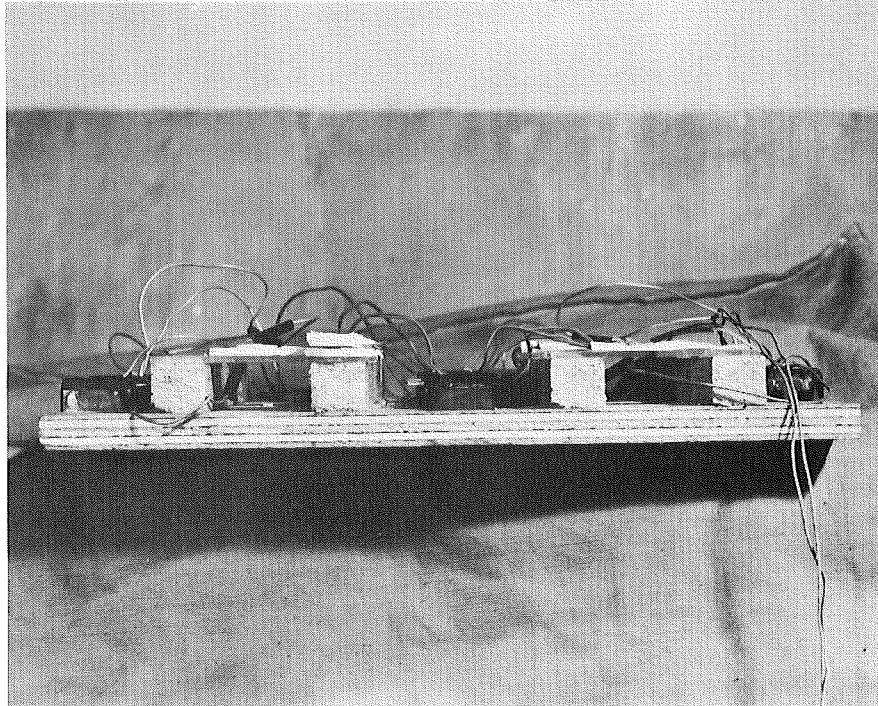Figure 3
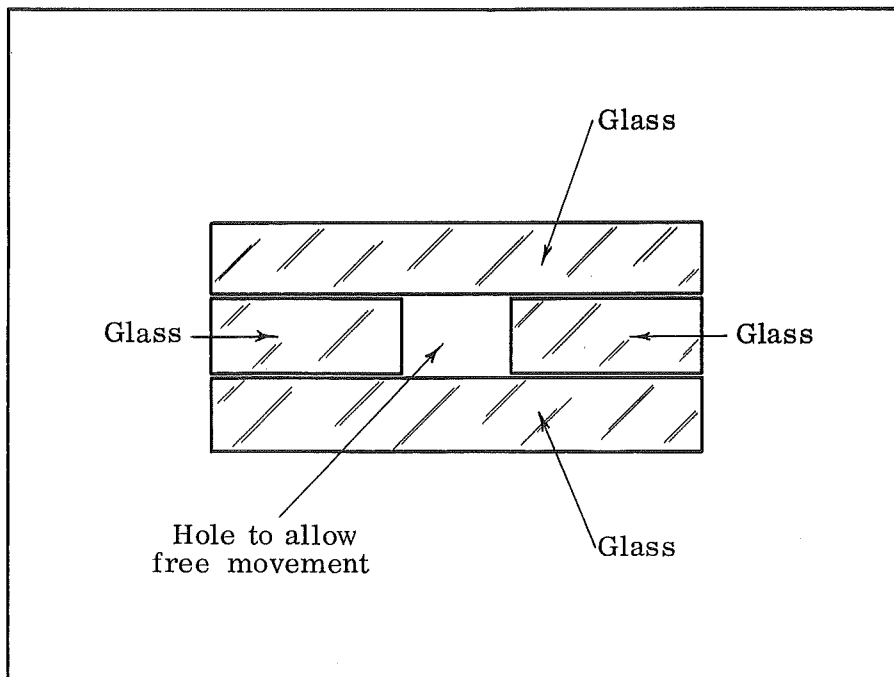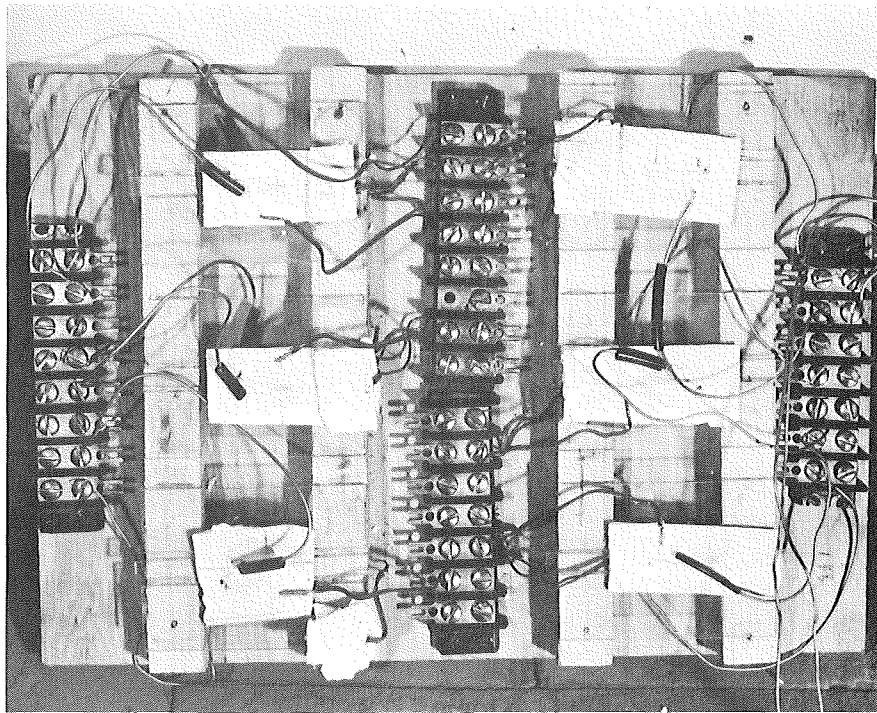

Figure 4

Figure 5
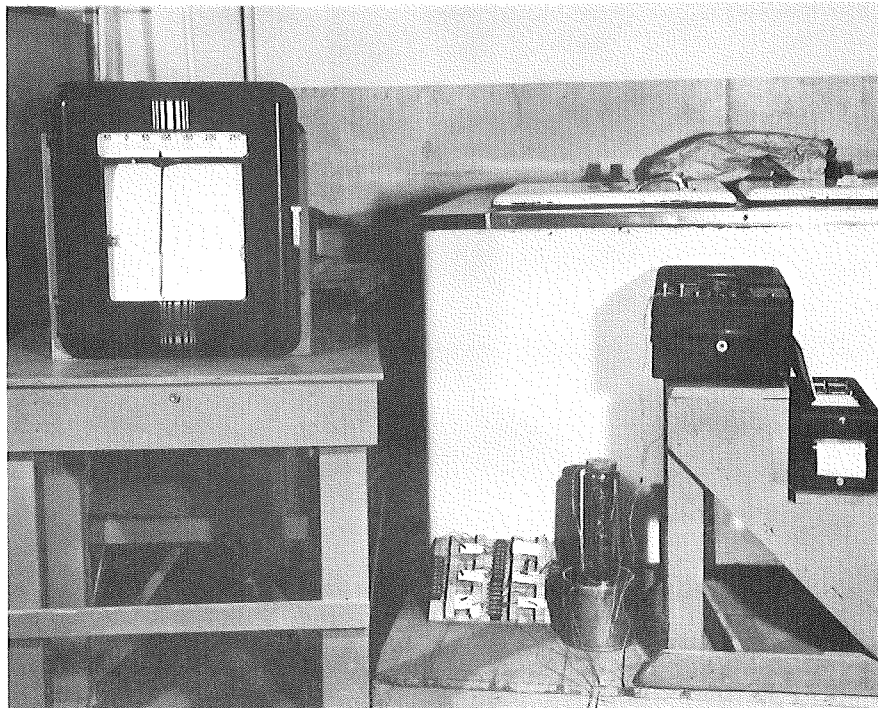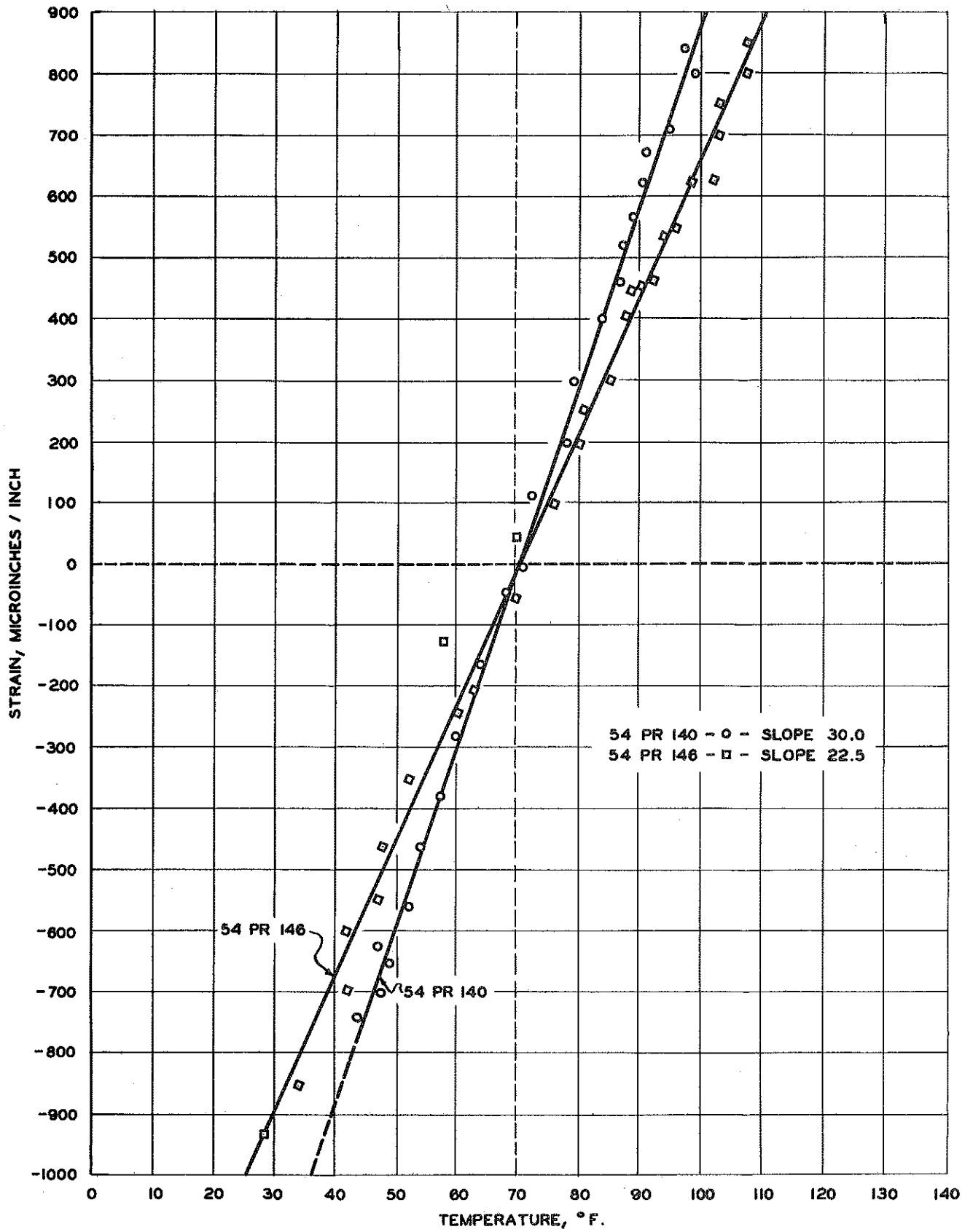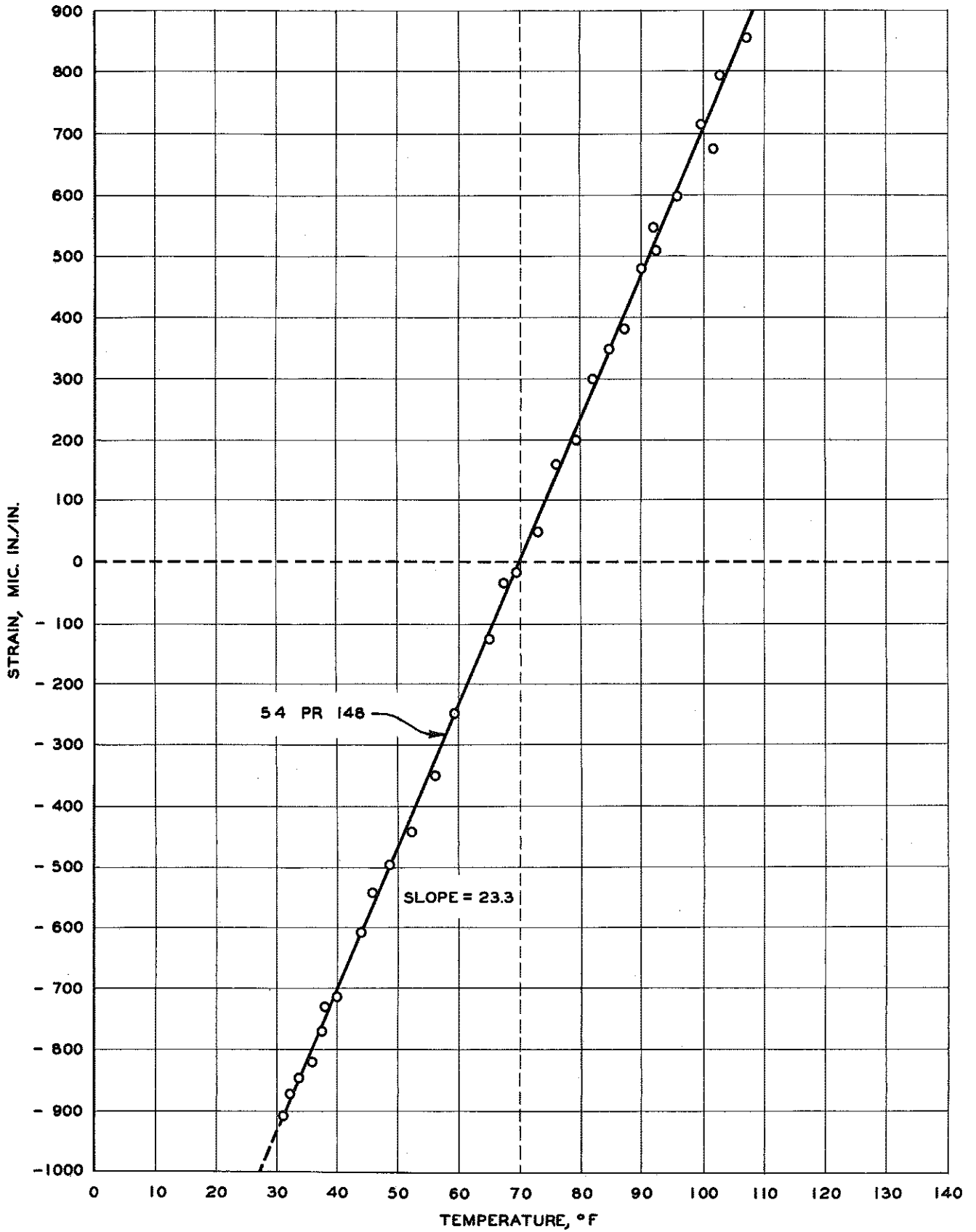
Assembled Test Samples

Figure 6

Equipment Used

(Left to right) Temperature Recorder, Freezer, Paint Samples, Thermos con-

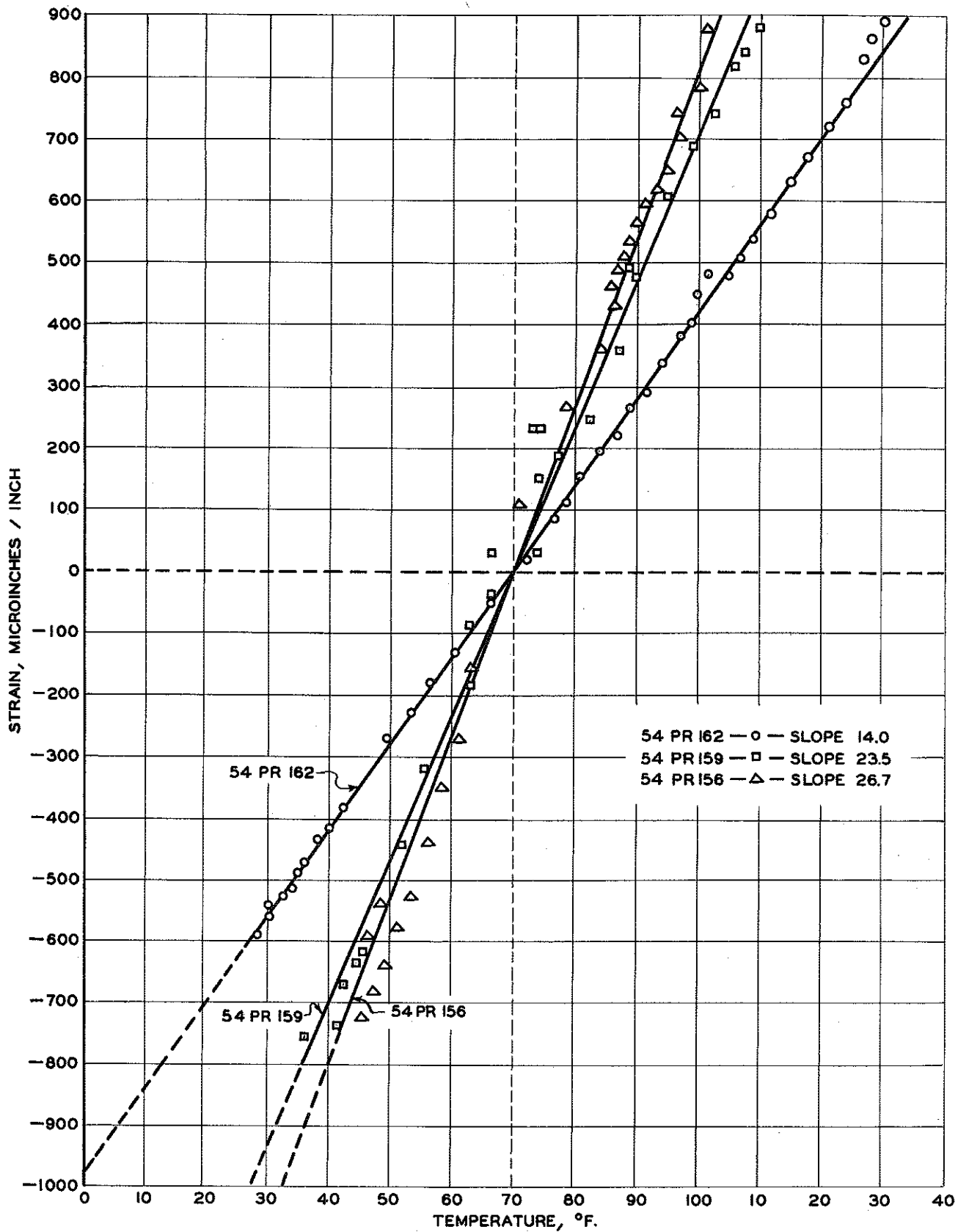taining compensating gage, Strain Analyzer, Oscillograph.

COEFFICIENT OF EXPANSION
1954 PERFORMANCE PAINTS

FIGURE 7

COEFFICIENT OF EXPANSION
1954 PERFORMANCE PAINTS

FIGURE 8

COEFFICIENT OF EXPANSION
1954 PERFORMANCE PAINTS

FIGURE 9

TABLE I

STRAIN–TEMPERATURE DATA FOR PAINTS STUDIED

54 PR 140		54 PR 146		54 PR 148		54 PR 156		54 PR 159		54 PR 162	
Temp. °F	Strain Mic. In. Per In.	Temp. °F	Strain Mic. In. Per In.	Temp. °F	Strain Mic. In. Per In.	Temp. °F	Strain Mic. In. Per In.	Temp. °F	Strain Mic. In. Per In.	Temp. °F	Strain Mic. In. Per In.
44	-750	28	-940	31	-910	45	-720	36	-760	28.5	-590
47	-710	34	-850	32	-875	46.5	-590	41.5	-740	30.5	-560
47	-630	42	-700	34	-850	47.5	-680	43.5	-670	30.5	-540
49	-650	42	-600	36	-820	49	-540	45	-640	33	-530
52	-560	47	-550	37.5	-770	50	-640	46	-620	34	-510
54	-460	48	-460	38	-740	51	-580	52	-450	35	-490
57	-380	52	-350	40	-710	53	-530	56	-320	36	-470
60	-290	54	-230	44	-610	56	-440	63	-190	38.5	-440
64	-170	58	-130	46	-540	58.5	-350	67	30	40.5	-420
68	-50	60	-240	49	-500	51	-270	74	30	42.5	-380
71	-10	63	-200	52	-450	83.5	-160	74	230	50	-270
72.5	110	70	-50	56	-350	64.5	-40	74.5	150	53.5	-230
78	220	70	40	59	-250	71	110	75	230	57	-180
79.5	300	76	100	65	-130	77	190	82	240	60.5	-130
84	400	80	200	67.5	-40	79	260	87	360	66.5	-50
87	470	81	250	69.5	-20	84	360	90	480	72	20
87.5	520	85	300	73	50	86	460	95	610	77	80
89	560	88	400	76	160	87	430	99	690	79	110
91	620	89	440	79	200	87	490	102	740	81	150
91	670	90	450	82	300	88	510	106	820	84	190
95	710	92	460	85	350	89	490	108	840	87	220
98	840	94	530	87	380	89	540	110	880	89	270
99	800	96	550	90	480	90	560			91.5	290
		98	620	92	510	91.5	590			94	340
99	800	96	550	90	480	90	560			91.5	290
		98	620	92	510	91.5	590			94	340
		102	620	92	550	94	620			97	380
		103	700	96	600	95	650			99	400
		103	750	100	720	97	700			100	450
		108	800	102	675	97	740			102	480
		108	850	103	800	100	780			105	480
				107	860	102	880			107	510
										109	540
										112	580
										115	630
										118	670
										121	720
										124	760
										127	830
										128	860
										130	890

Results:

TABLE I I

COEFFICIENTS OF EXPANSION vs DURABILITY RATINGS FOR PAINTS STUDIED

Paint No.	Linear Coefficient of Thermal Expansion (Micro-Inches/inch/^{o}F)	Durability Rating at Days of Exposure *		
		15	195	369
54 PR 162	14.0	10.0	9.3	8.3
54 PR 156	26.7	10.0	5.0	3.5
54 PR 140	30.0	10.0	5.5	3.9
54 PR 146	22.5	10.0	5.4	3.2
54 PR 159	23.5	9.0	3.0	2.4
54 PR 148	23.3	10.0	1.7	0.6
Concrete	5-6			

*A rating of 10 signified 100% paint remaining.

Discussion

Adhesion is a multiple function of many factors. Of these, the coefficient of expansion and drying stress play important roles.

The test for the coefficient of expansion of paint was developed using Carl Konkle's procedure as a starting point. His method is as follows:

Paint films were prepared by placing layers of masking tape on a glass plate so that a 2" x 6" form was constructed. The thickness of the film was determined by the thickness of the tape form; in this case, 10 mils.

After the tape layers were in place, the glass plate was coated with silicone grease and paint was poured into the forms.

Following an initial air cure of one day, the films were placed in an oven operating at 140 degrees F and were alternately heated and cooled for a week. The masking tape was stripped from the glass and the films lifted from the greased plate. The films were then cut in two pieces 2" x 3" x 10 mils. One half of the film was placed on a small glass plate coated with silicone grease. A coat of the original liquid paint was then applied to the film on the glass plate. The thermocouple and the strain gage were placed so that the leads were parallel to the long axis of the film. This arrangement was then coated with another thin layer of the original paint and the other half of the film was pressed over the unit. The liquid paint formed a bond between the two films so that a homogeneous film of about 20 mils thickness was obtained containing the strain gage and the thermocouple in the center. Another glass plate coated with silicone was placed on top of the unit, thus comprising a

sandwich, with a weight of about 2 kg placed on top to assure tight bonding. These samples were then placed in the 140-degree F oven and alternately heated and cooled for another week.

The cured paint specimens were fastened by gluing the bottom glass plate to two narrow wooden strips on a board. These strips provided sufficient circulation on all sides of the paint film to insure even heating and cooling of the films. The silicone grease permits the films to expand and contract between the sandwich of glass. The glass plates allow only horizontal movement, so as to prevent buckling. The top glass plate is held secure in the assembly by means of brads driven into the two wooden strips and bent over the plates to hold them firmly.

The leads are fastened to a barrier strip and extension leads to the SR-4 static strain indicator and a temperature recorder. The presence of the barrier strip prevents any accidental pulling of the leads in the paint film.

These prepared films were placed in a freezing unit which was at room temperature.

The strain readings on the paint were zeroed at 1000 on a 2000 range scale by means of variable resistors. The internal temperature of each film was recorded as the temperature was lowered. The unit was allowed to run for 24 hours to insure completion of the movement of the films. The specimens were then allowed to return to room temperature and stablize, and readings were recorded again. The thermal coefficient was computed by dividing the strain change in inches x 10^{-6}/inch by the temperature change to give a result in inches x 10^{-6}/inch/degree F.

The coefficient for the freezing portion was averaged with the coefficient of the recovery portion to give a mean coefficient for the range of room temperature to the lowest temperature the freezer would produce (approximately - 5 F). The next phase of the test was to heat the paint films in an oven (approximately 140 F). The temperature and strain were recorded at room temperature and at 140 F, and again at room temperature. The coefficient value for the heating cycle was averaged with that for the cooling cycle to obtain the mean value.

Difficulties Encountered

1. Use of a static strain analyzer to determine a dynamic strain change.

2. Uneven distribution of paint in samples as result of arbitrary application of paint used to fasten strips together to form the experimental units.

3. Unfavorable effects of wet paint on strain gages.

4. Insufficient evidence that strain gage adhered properly to sample.

5. Length of time required to run test.

6. Test samples were non-homogeneous.

In Konkle's method of measuring coefficient of expansion, it was necessary for the paint to be in equilibrium in order to obtain readings from a static strain analyzer. In this case, equilibrium is considered to mean that strain readings at given temperatures would be constant. However, by examination of the equation

$$f(P) = a + K_1 \times \triangle T \triangle \propto - \int K_2 \times \sigma S$$

it is seen that the strain readings can never be constant, due to drying stresses being a function of tiem. This fact led the investigators to the use of a dynamic stress analyzer. With the use of this analyzer,

when the temperatures of oven and freezer were changed simultaneously with the temperature of the sample, curved plots were observed. These plots proved to be complementary in nature when ascending and descending in a given temperature range, as shown in Figure 10. This fact seemed to indicate that drying stresses were still playing a major role in causing the difficulty of plotting the coefficient of expansion.

Still keeping in mind that drying stresses are a function of time, it was decided to maintain the oven and freezer at maximum temperature change before placing the sample inside. This in effect reduced necessary testing time. Results of this change gave a straight line function to the coefficient of expansion for all six paints.
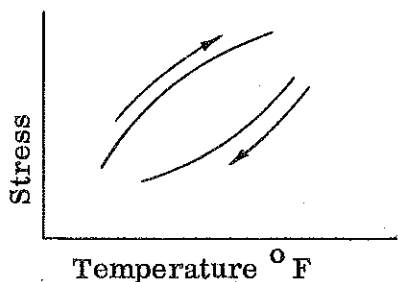

Figure 10

Stress-Temperature Relation of Paints Studied when Time is a Major Factor

The uneven distribution of paint in the sample might cause the strain gage to give very inaccurate readings with the slightest bending caused by uneven heating which may occur. To overcome this difficulty, two strain gages were used by attaching them to opposite sides of the sample in series. This in effect cancelled out any bending strains by a compression strain occurring on one strain gage, and tension strain occurring on the other. When the gages are connected in a series, the sum of the compression and tension reading caused by bending is zero.

When an onion skin strain gage is attached by wet paint, the resistance of the gages will vary due to the solvents in the paint. To overcome this, Duco cement was substituted for the wet paint which is recommended for attaching strain gages.

When there is insufficient evidence of the adhesion between paint and strain gage, there is no assurance that air bubbles are not present on or near the gages, which would give inaccurate readings. By placing the strain gages on the surface of the test sample, visual inspection of the bond can be made.

When employing static strain indicators, it is necessary to reach equilibrium, which requires several days for a sufficient number of readings to be taken. By running the test dynamically, a complete test can be made in an hour and a half.

It should also be noted that by the application of wet paint to paint which has already been cured for a given length of time, a non-homogeneous sample will result. By the use of a single paint sample, wet paint was not required for adhesion.

The results of the field test durability rating were plotted against the coefficient of expansion as shown in Figure 11. The straight line was based on the least squares method. A correlation factor was then derived from the following equations:

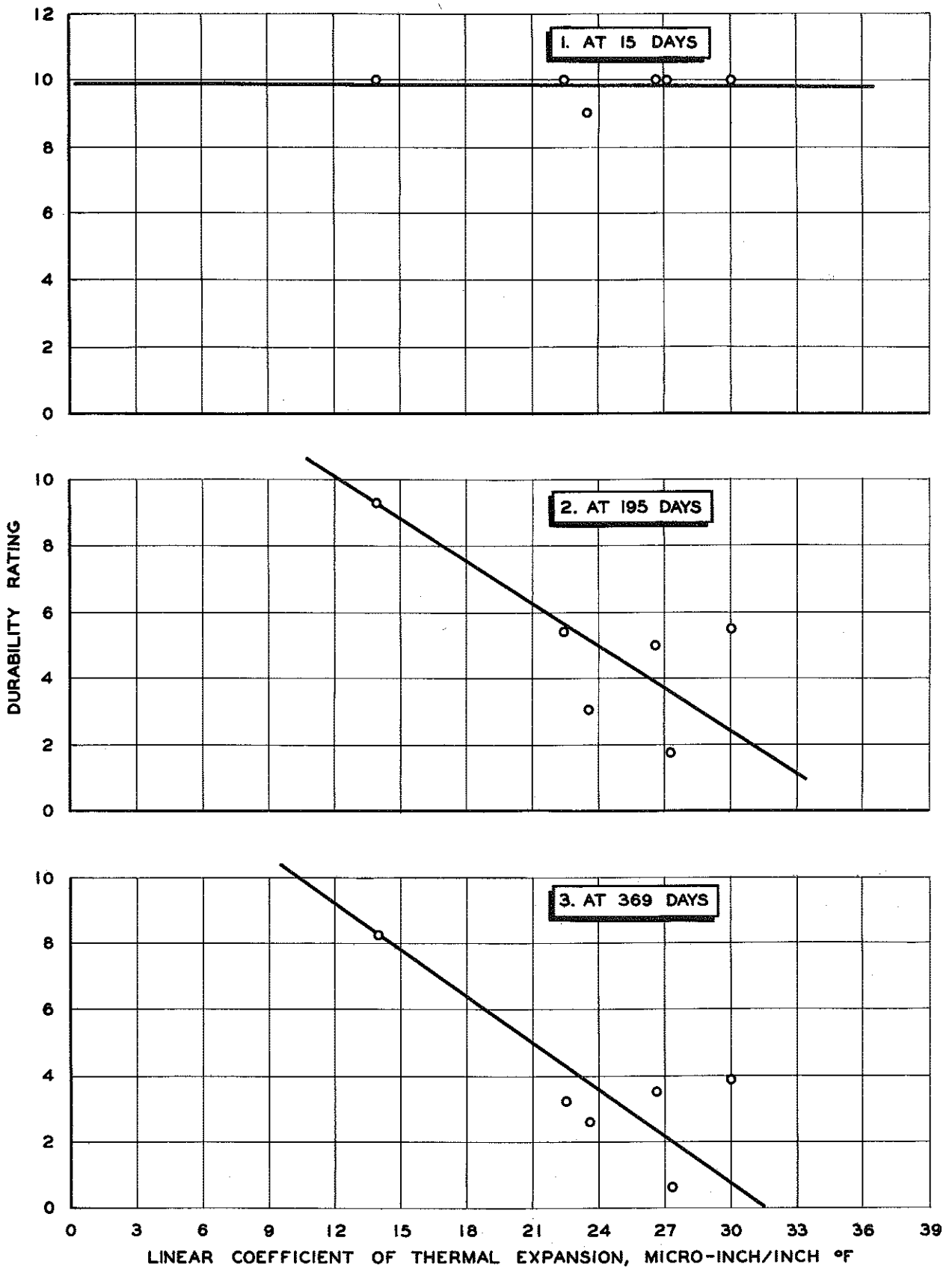$$r = \sqrt{1 - S_y^2 / \sigma_y^2} \qquad = \text{coefficient of correlation}$$

$$S_y = \sqrt{\frac{\sum (d)^2}{N}} \qquad = \text{standard error estimate}$$

$$d = Y_{(actual)} - Y_{(theoretical)}$$

$$N = \text{number of plots}$$

$$\sigma_y = \sqrt{\frac{\sum (y)^2}{N} - \left(\frac{\sum y}{N}\right)^2}$$

$$\text{Where } Y = Y_{(actual)}$$

DETERMINATION OF THE CORRELATION FACTOR

FIGURE 11

When:

r = 1 the coefficient of correlation indicates a perfect relationship, and when

r = 0 it indicates a wholly imperfect relationship.

In this case, (r = .97 at 15 days, r = .329 at 195 days, and r = .715 at

369 days), indicates that the relationship is more than midway between a wholly imper-

fect relationship and a perfect relationship for the curves at 15 days and 369 days.

It was noted, of those paints tested, the best paint in the field had a linear

coefficient of thermal expansion closest to that of concrete. The other five paints

tested had coefficients which were very near one another and did not correspond to

the durability rating with respect to the difference in the coefficient of expansion of

concrete and paint. Because of the closeness of the coefficients of these five paints

and the fact that only one sample of each paint was tested it is probable that more tests

should be run using more samples. This would give more reliable results and might

increase the coefficient of correlation.

Conclusion

1. From the vector analysis of paint peel, the following two equations were

derived:

(a) $f(P) = a + K_1 \times \Delta T \Delta \propto - \int K_2 \times \propto S = A$

(b) $\lim_{t \to t_0} F(p) = 0$

(Definitions of symbols – page 3)

2. The 1954 performance paints used in this investigation had linear coeffici-

ents of thermal expansion which were constant in the temperature range of 0 to 120

degrees F.

3. The results of this test can be reproduced.

4. When the six paints used in this investigation were plotted against the results of the field test, given in durability ratings from 0 to 10, a correlation factor of $r = .77$ at 15 days, $r = .329$ at 195 days and $r = .715$ at 369 days was shown, indicating that the relationship is more than midway between a wholly imperfect relationship and a perfect relationship for curves at 15 days and 369 days.

5. It was noted, of those paints tested, that the best paint in the field had a linear coefficient of thermal expansion closest to that of concrete. The other five paints tested had coefficients which were very near one another and did not correspond to the percent best with respect to the difference in the coefficient of expansion of concrete and paint. This would indicate that more tests should be run on these paints with respect to the linear coefficient of thermal expansions, or that other paint characteristics such as abrasion resistance, water resistance, etc., are important to durability.

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