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Publisher's version / Version de l'éditeur:

<https://doi.org/10.4224/40002801>

Research Paper (National Research Council Canada. Division of Building Research); no. DBR-RP-13, 1955

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THE BLISTERING OF PAINT IN THE PRESENCE OF WATER



BY

J. M. KUZMAK AND P. J. SEREDA

A REPRINT FROM THE CANADIAN JOURNAL OF TECHNOLOGY JANUARY 1955

RESEARCH PAPER No. 13

OF THE

DIVISION OF BUILDING RESEARCH

OTTAWA

NRC No. 34

PRICE 35 CENTS
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THE BLISTERING OF PAINT IN THE PRESENCE OF WATER¹

By J. M. KUZMAK AND P. J. SEREDA

ABSTRACT

Experiments on the blistering of paint on wood in the presence of water were carried out. It was found that the paints which blistered when subjected to a temperature gradient blistered also when placed in water kept at a constant temperature. Experiments using fluid pressures were carried out also. With each paint, whether or not it blistered when subjected to a temperature gradient, the presence of water at the wood-paint interface was found to have reduced the fluid pressure necessary to produce blisters.

INTRODUCTION

Although it has been known for some time that the blistering of paint on wood is in some way associated with the presence of moisture, neither the mechanism by which the moisture is transferred through the wood nor the mechanism by which the blisters are formed is known. Adhesion measurements show that it takes a pressure of 200 to 500 p.s.i. to pull a dry paint film away from the substrate. To account for pressures of this magnitude during blistering, Dunn (3) has suggested that osmosis and osmotic pressure may be involved. Hopkins and Smart (4) state that, in addition to moisture, a temperature gradient is necessary. One of their experiments consisted of fastening a wooden panel, painted with ordinary linseed oil house paint, to the open side of a container which was then filled with water so that the unpainted back of the panel was in continuous contact with water under a slight head. There was no sign of blistering during a period of 13 days. A temperature gradient applied across a similar panel in a somewhat similar apparatus readily produced blisters. Hopkins and Smart state, "No matter how wet the back of the siding, blistering does not occur unless there is a temperature differential." On the basis of this observation, Babbitt (1) suggests a mechanism which will lead to a transfer of moisture similar to osmosis and which will give rise to pressures of the same magnitude. An equation is presented by means of which the pressures can be calculated. The theory is interesting not only because it accounts for the large pressures thought necessary to produce blistering but also because it may represent an advance in the understanding of the mechanism of moisture transfer.

The present paper describes an investigation of the observation by Hopkins and Smart that blistering does not occur unless there is a temperature difference. Also, related experiments on fluid pressures necessary to produce blisters are described.

MATERIALS AND APPARATUS

Materials

The following paints which represent a wide range of susceptibility to blistering were used:

¹Manuscript received September 2, 1954.
Contribution from the Division of Building Research, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3453.

No. 1—Composition: Titanium dioxide 16.7%, zinc oxide 34.2%, basic carbonate white lead 34.2%, and magnesium silicate 14.9% by weight of total pigment, in linseed oil;

No. 2—A commercial, red, floor enamel;

No. 3—Composition: Zinc oxide 86% and magnesium silicate 14% by weight of total pigment, in linseed oil;

No. 4—A commercial, black, vinyl resin paint.

White pine was used as the substrate material. In order to ensure that the pressure (described in the following section) at the wood-paint interface was equal to the applied pressure, it was necessary to select a wood which was very permeable. The wood selected permitted both air and nitrogen as well as water to pass freely through unpainted samples at a pressure of 1 p.s.i. (see Fig. 4). All the samples were taken from the same flat-sawn board.

Only distilled water was used.

Apparatus

Three main pieces of equipment were used.

(a) The temperature gradient apparatus is shown in Fig. 1. A circular, porous, ceramic plate, *A*, was sealed into a retaining metal ring, *B*, which supported the plate inside a large evaporating dish, *C*. The evaporating dish

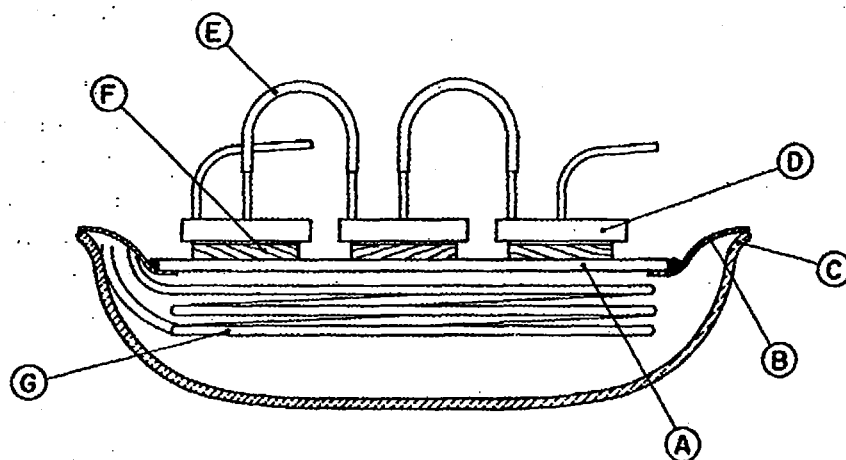


FIG. 1. Temperature gradient apparatus.

was filled with water so that there was contact between the bottom of the ceramic disk and the water. The water was heated to any given temperature by means of a copper heating coil, *G*. The temperature of the hollow cooling plates, *D*, made of brass and joined together by rubber tubing, *E*, was controlled by circulating water from a constant temperature bath. The apparatus could handle seven samples, *F*, at one time.

(b) The apparatus used to produce blisters, using nitrogen, is shown in Fig. 2. The unit consisted of a brass cylinder, *A*, machined to provide a compression seal against the sample, *B*, and thus serve as a pressure chamber. The samples were cut to fit closely into a rubber ring, *C*. The tightening of a

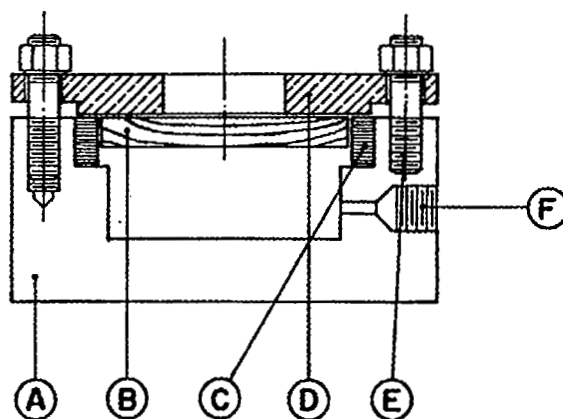


FIG. 2. Apparatus to produce blisters, using nitrogen.

brass ring, *D*, with three screws, *E*, provided an adequate edge seal to nitrogen. The brass unit was connected, at the point *F*, to a nitrogen cylinder and a pressure gauge by copper tubing and standard brass fittings.

(*c*) The apparatus to determine the pressure of water required to produce blisters is shown in Fig. 3. The sample, *A*, was sealed to a brass plate, *B*, which had a 1-in. hole at the center. An adequate seal between the sample and the plate was produced by a rubber gasket, *C*, when a brass retaining ring, *D*, was tightened against the sample by means of three screws, *E*. A seal between the brass plate and a cylindrical lucite chamber, *F*, was provided by another rubber gasket, *G*, when six screws, *H*, were tightened. The copper tube, *J*, was connected to the source of pressure.

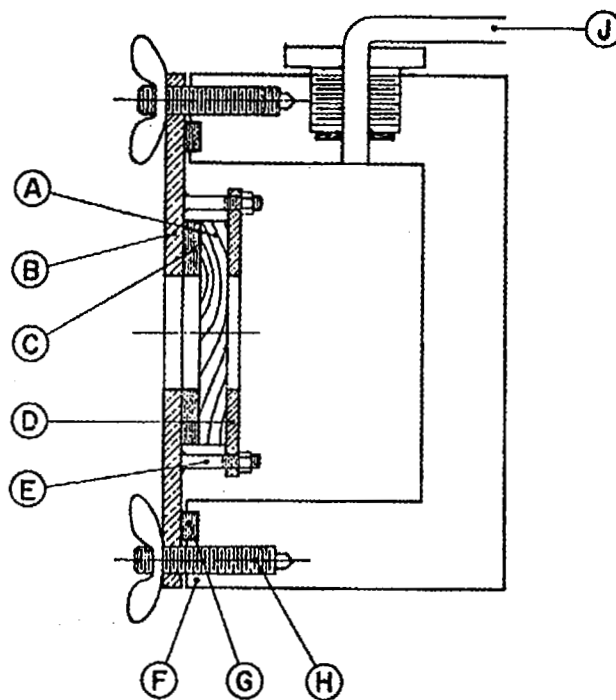


FIG. 3. Apparatus to produce blisters, using water.

EXPERIMENTS AND RESULTS

The samples were prepared in each case by brushing on three coats of the paint to a board $\frac{1}{4}$ in. thick. The thickness of the paint films when dry varied from approximately 0.003 to 0.005 in., depending on the paint. When the paint had aged for the desired length of time, the board was cut into disks 2 in. in diameter. Each disk was used for only one test.

To determine whether blisters could be produced without a temperature gradient, samples were placed in a covered vessel of water maintained at a constant temperature. Some of the samples were placed with the painted side down, others with the painted side up. The samples were kept immersed $\frac{1}{2}$ in. below the surface of the water by means of a screen which could be fixed at any chosen height. In another experiment, the samples were allowed to float. In all cases, paints No. 1 and No. 3 blistered within 24 hr. The blistering of paint No. 1 is shown in Fig. 5. Paints No. 2 and No. 4 did not blister in seven days at which time the experiment was discontinued.

In the above experiment, as in all the experiments reported in this paper, each test was carried out using five or more samples of any one paint. This was done to serve as a check and to help eliminate any spurious observations which might arise because of any local variations in the properties of the wood.

In studying the effect of temperature, the gradient across the $\frac{1}{4}$ in. sample was 50° F. (53° to 103°), each temperature being held constant within 0.5° F. as determined by copper-constantan thermocouples. The samples were placed on the porous plate of the temperature gradient apparatus with the painted side toward the cold plate. Filter paper was placed between the paint surface and the cold plate in order to allow the blisters to form properly. It was found that, without the filter paper, the blisters were flattened by the weight of the plate. As shown in Table I, paints No. 1 (see Fig. 6) and No. 3 blistered while No. 2 and No. 4 did not.

It is interesting to compare the data obtained when the samples were placed in water held at a constant temperature with those obtained when the

TABLE I
THE BLISTERING OF PAINT DUE TO A TEMPERATURE GRADIENT
AND DUE TO FLUID PRESSURES

Paint	Age	Blistering due to temperature gradient	Pressure of nitrogen required to produce blisters (p.s.i.)	Pressure of water required to produce blisters (p.s.i.)
No. 1	5 months	Marked in 5 hr.	> 500	20
	4-5 days	Marked in 1 hr.	60-80	15
No. 2	5 months	None in 6 days	> 500	125
	4 days	None in 7 days	150-200	25
No. 3	19 days	Marked in 5 hr.	250->450	15
No. 4	1½ months	None in 7 days	180-225	25
	5 days	None in 7 days	110-120	20

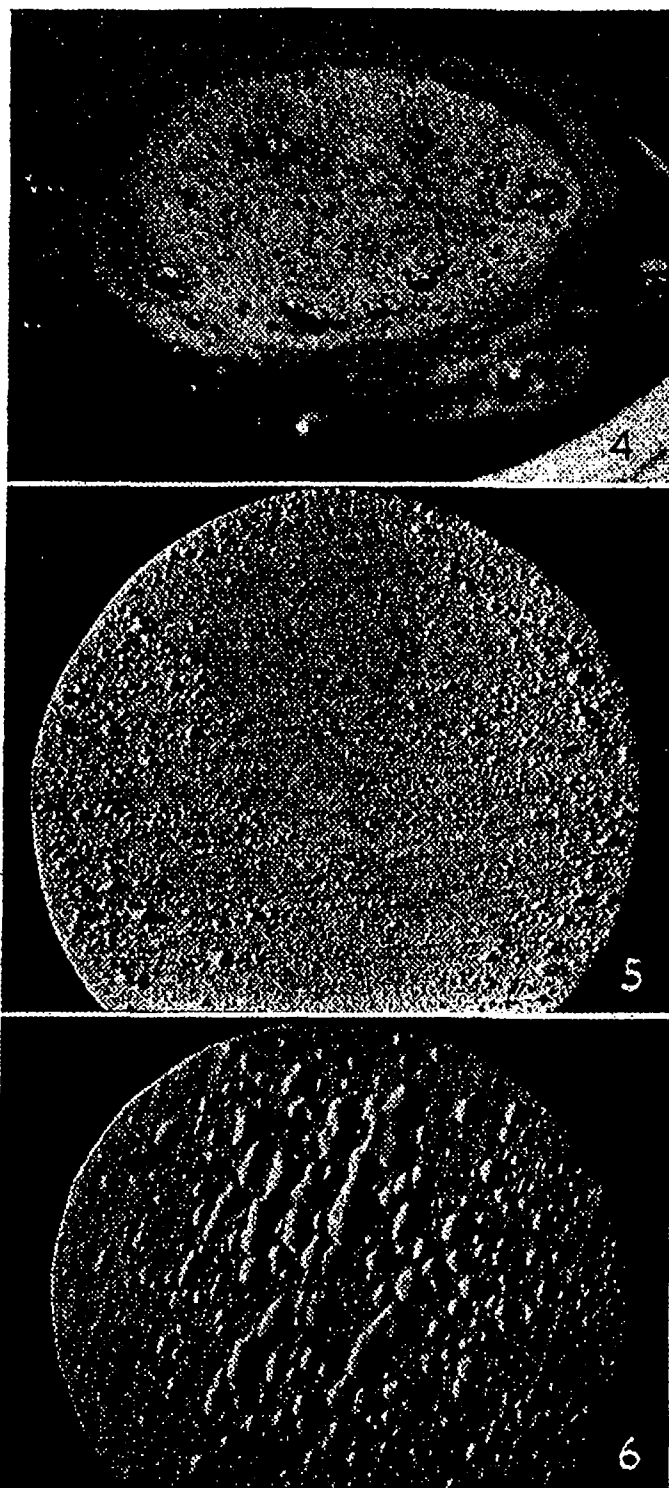


FIG. 4. Air bubbling through water after passing through a wood sample.
FIG. 5. The blistering of paint No. 1 shown by a sample placed in water at a constant temperature.
FIG. 6. The blistering of paint No. 1 shown by a sample subjected to a temperature gradient.

samples were subjected to a temperature gradient. It is seen that paints No. 1 and No. 3 which blistered in the first experiment, blistered in the second also, and that paints No. 2 and No. 4, which did not blister in the first, did not blister in the second. The conclusion, on the basis of the above evidence, would seem to be that the mere presence of water at the wood-paint interface is in some way responsible for the blistering, and that the role of the temperature gradient is probably secondary.

The fact that blistering occurred without a temperature gradient in the experiments reported here appears to contradict the observation of Hopkins and Smart reported earlier. It is possible that, in their experiments with no temperature gradient, the wood was too impervious to allow an appreciable amount of water to reach the wood-paint interface. Preliminary tests with various woods carried out during the present investigation showed that the wood underneath the paint was comparatively dry in those cases where a paint known to blister within a certain time failed to do so within that time.

In order to determine whether and to what extent the presence of water affected the strength of the bond between the wood and the paint, the pressure of nitrogen and the pressure of water required to produce blisters were measured. The pressure of nitrogen was taken as a measure of the strength of the bond before it was affected by water, and the pressure of the water as a measure of the strength after it had been affected by the water.

In the test for blistering using the pressure of nitrogen, the samples were placed in the apparatus shown in Fig. 2. Tightening down the brass ring top forced the rubber against the sample thus forming a good seal. Any small, slow leaks at the seal were not important since they did not affect the applied pressure. The applied pressure was controlled by means of a reducing valve on the nitrogen cylinder. Up to 200 p.s.i., the pressure was read on a low range helicoid gauge; beyond this, the pressure was read on the gauge mounted on the reducing valve. Pressures in excess of 500 p.s.i. could not be used because the wood began to fail at this point. The pressure was increased at the rate of approximately 1 p.s.i. per second. In the case of paints No. 1, No. 2, and No. 3, the rate was found to have no effect on the pressure needed to produce blisters. In the case of paint No. 4, when the rate was decreased by a factor of 10, blistering occurred at a slightly lower pressure. This behavior is very likely associated with plastic flow of the paint film.

To determine the pressure of water required to produce blisters, the samples were placed in the apparatus shown in Fig. 3. When the unit was assembled as already outlined, the chamber was filled with water so that the entire unpainted side of the sample was in contact with water. The air pressure applied to the water was controlled by a reducing valve and measured with a helicoid gauge. Blistering occurred within 10 min. The results of this test along with those described in the preceding paragraph are given in Table I. From this table, it is seen that the pressures required in the two different tests differ by a factor which varies from 4 to 20 or more, depending on the type and age of the paint. Paint No. 1, when pushed by nitrogen and by water, blistered as shown in Figs. 7 and 8 respectively.

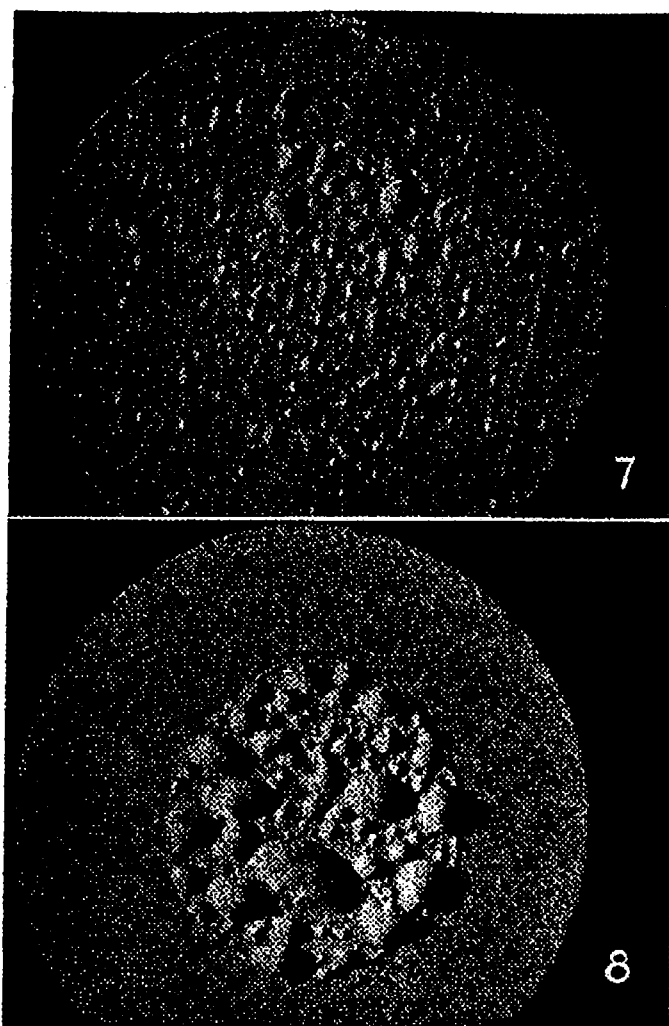


FIG. 7. The blistering of paint No. 1 shown by a sample subjected to a pressure of nitrogen.
FIG. 8. The blistering of paint No. 1 shown by a sample subjected to a pressure of water.

Tests to determine the effect of water kept in contact with the paint surface (painted side of the sample) were carried out. Paints No. 1 and No. 3 were used. The samples were mounted in the apparatus shown in Fig. 3. Water was placed on the painted surface. No water was placed in the reservoir, and an air pressure of 15 p.s.i. was applied to the unpainted side of the sample. The experiment was continued uninterrupted for three days. No blisters developed although the paint surface was affected to the extent that a few small holes developed which allowed some air to pass and bubble through the water. Water was then placed in the reservoir to cover the unpainted side, and a pressure of 15 p.s.i. was applied. Blistering occurred within 30 min. A similar test was carried out but, at the end of three days, instead of water being placed in the reservoir, the air pressure was raised to 100 p.s.i. No blistering was observed. The indication is that water on the surface of the paint did not greatly affect the bond between the paint and the wood.

DISCUSSION OF RESULTS

As already mentioned, the fact that the paints which blistered when subjected to a temperature gradient blistered also when immersed in water at constant temperature leads to the conclusion that the phenomenon is due primarily to the presence of water at the wood-paint interface and not to the existence of a temperature gradient. The results of the experiments in which the pressures required to produce blistering were measured are consistent with the above conclusion. It appears that the main effect of the temperature gradient is to bring water to the wood-paint interface. Many of the samples subjected to the temperature gradient were broken up and visually examined. A very pronounced moisture gradient was observed in all samples exposed for only a few hours. There was a color gradation across from the hot to the cold side, the color deepening toward the cold side, indicating a higher moisture content. In many instances, the water could be squeezed out of the cold side but not out of the other. With time this gradient disappeared as the whole sample approached saturation.

Assuming that the sample became saturated, it is interesting to calculate, using Babbitt's equation (1), the hydrostatic pressure that should be built up as a result of the temperature gradient. The equation is

$$\pi = \frac{RT}{V} \ln \frac{p}{p_0}$$

where, in this case,

π is the excess pressure,

R is the gas constant,

T is the absolute temperature of the cold face,

V is the molar volume of water,

p is the vapor pressure of water at the temperature of the hot face,

p_0 is the vapor pressure of water at the temperature of the cold face.

Taking the temperature gradient as 12°-39° C. (measured as 53°-103° F.), the following values were substituted into the equation: $R = 82.07 \text{ cm.}^3 \text{ atm./degree}$, $T = 285^\circ \text{ A.}$, $V = 18 \text{ cm.}^3$, $p = 52.4 \text{ mm. Hg}$, $p_0 = 10.5 \text{ mm. Hg}$. The value of π is then calculated as 2090 atm. This tremendous pressure could not have been exerted on the paints because even those which failed to blister as a result of the temperature gradient did blister when pushed by water at a pressure of 25 p.s.i. or less. The exception occurred with paint No. 2 which was five months old and in this case blistering occurred at a pressure of 125 p.s.i.

It should be noted that failure to detect anything like the predicted pressure does not invalidate the theory as far as potential forces are concerned. It may be that, within the wood itself, the confining forces which would be necessary to realize any build-up of pressure are either too small or non-existent under the conditions of the experiment. Though perhaps more improbable, another possible reason may be that in applying Babbitt's equation the temperature difference across only a part of the thickness should be considered.

The experiments in which water was applied to the outer surface of the paint while the wood was kept dry were carried out to investigate whether the water

sorbed by the paint affected the strength of the bond between wood and paint. Browne (2) reports that certain paints absorb an amount of water more than one and one-half times the weight of linseed oil contained in the film, and that the surface area, if the film is free, may increase by as much as 50%. When the paint is attached to wood, this increase in area is prevented to some extent and this gives rise to stresses within the coating which he suggests may have a direct bearing on the phenomenon of blistering.

The data in Browne's paper (2) indicate that, in three days, paints of the type represented by No. 1 and No. 3 in the present experiment absorb more than 75% of the total water they are capable of absorbing. Maximum absorption, according to the data, may require between 15 and 30 days. It is possible, however, that actually much less water was absorbed in the present experiment, where the paint was in contact with water on one side only, than in the case of Browne's work where the films were free and were in contact with water on both sides. The data in the present investigation, although they show that water kept on the surface of the paint for three days did not markedly affect the strength of the bond between the wood and the paint, do not necessarily answer the question concerning the effect of water absorbed by the paint. The amount of water absorbed by the paint films was not determined. It may have been considerably less than 75% of the total possible in the case of a free film. Also, a moisture gradient in the paint film could result in very little water in the paint at the wood-paint interface. The effect of water absorbed by the paint on the strength of the bond between wood and paint requires further investigation.

It is possible that the blistering may be related to the great affinity of wood for water. In the process of swelling, it is believed that water molecules disrupt hydrogen bonds between hydroxyl groups on adjacent cellulose molecules, the water molecules themselves becoming attached to the hydroxyl groups. If the nature and strength of the bond between the wood and the paint are similar in kind and in magnitude to those of the hydrogen bonds mentioned above, then this bond may well be broken by the same mechanism.

Once the bond is broken, it is possible that the actual formation of a blister may be related to the degree of swelling of the paint, the tendency to blister decreasing as the degree of swelling decreases. This view is supported by the fact that paints No. 2 and No. 4, which did not blister when subjected to a temperature gradient, were found to have a low degree of swelling.

CONCLUSIONS

In the case of paint blistering in the presence of moisture, it appears that the primary function of the temperature gradient is to bring the water to the wood-paint interface.

With certain paints, water is able to break or weaken the bond between the paint and the wood with the result that the paint blisters. Even in the case of those paints which did not blister when subjected to a temperature gradient, water was found to have weakened the bond.

ACKNOWLEDGMENTS

The writers appreciated the assistance of Mr. John Harris in selecting and preparing the paints, the assistance of Mr. P. J. Barrette in collecting the data, and the assistance of Mr. H. F. Slade in constructing the apparatus.

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