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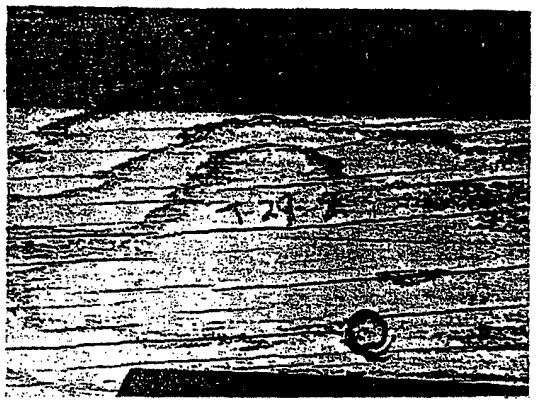

Disintegration of paint by checking and crumbling, after it has served its useful life. Note how the "crumbs" fall from the bands of summerwood long before they come from the springwood underneath. This form of disintegration is characteristic of low-swelling paints.

Disintegration of paint by cracking, curling, and flaking, after it has served its useful life. Note how the "flakes" fall from the bands of summerwood before the springwood begins to be laid bare. This form of disintegration is characteristic of high-swelling paints.

## UNDERSTANDING THE MECHANISMS OF

# Deterioration of House Paint[1]

F. L. Browne
Forest Products Laboratory[2], Forest Service U. S. Department of Agriculture

**Water, especially in conjunction with ultraviolet light, accelerates chemical deterioration. The products of the decomposition cause normal and abnormal failure. Shrinking and swelling caused by water also stress and disrupt paint films.**

ALTHOUGH MARKED IMPROVEMENTS have been made in the appearance and some aspects of the wear of house paints, they remain prone to deterioration by undesirable crumbling or flaking from bands of summerwood, especially on such widely available softwoods as Douglas-fir and southern yellow pine; and, under some conditions of service, to unexpectedly early failures by blistering or other abnormalities. For some time the Forest Products Laboratory has therefore been conducting research on the mechanisms of paint deterioration by more fundamental methods than the predominantly empirical procedures that have been customary in the past.

### Chemical Changes During Drying and Deterioration

The chemical processes by which paint coatings deteriorate are continuations of much the same oxidative processes by which the coatings are formed in the first place. When paint is exposed to air in a thin film, oxygen reacts at the unsaturated carbon atoms of the drying oil to form hydroperoxides.

The *Author*: F. L. Browne holds a PhD in colloid chemistry from the University of Wisconsin. He joined the FPL in 1918, and since has been a frequent contributor to the *Journal*.

The hydroperoxides initiate chain reactions of two kinds (20, 24, 26, 30, 35)[3]. One kind leads to cross-linked polymers or gels that make the hardened paint film. The other kind proceeds in the opposite direction to split molecules of drying oil and subsequently of the polymerized gel into a succession of smaller oxygenated fragments.

The ultimate products of the disruptive oxidation, which begin to appear even during the initial drying of coatings, are gases or vapors that escape from the film, such as water, carbon dioxide, carbon monoxide, formaldehyde, and formic acid (20, 21, 24, 25, 26). Intermediate products are larger fragments that are less volatile or nonvolatile. They include propionic, caproic, nonylic, and azelaic acids, still higher saturated and unsaturated acids (22, 39), hydroxyacids (33, 38), aldehydes (2), ketones (20, 22, 24, 26), and glycerol (39), although the ester linkage to the glycerol is stable enough to persist through aging and weathering (22). The nonvolatile fragments remain in the film until it comes in contact with water, when those that are soluble in water may be extracted. The insoluble oxidation products and the oxygenated groups formed in the polymerized gel are highly polar and hydrophilic, and therefore increase the capacity of the film for absorbing water (22, 24, 49).

Pigments materially alter the course of both polymeric and disruptive oxidation and therefore the drying and deterioration of coatings. The consumption of oxygen and the evolution of volatile products are increased by some pigments and decreased by others (41). Such effects are exerted by pigments that are as inert chemically as titanium dioxide, silica, and barium sulfate as well as by chemically active pigments. Basic pigments, such as zinc oxide and white lead, in addition react with acid decomposition products to

[1] Presented at the Short Course in Paint Technology at the Univ. of Florida, Gainesville, Feb. 1959.
[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
[3] Numbers in parentheses refer to Literature Cited at the end of this report.

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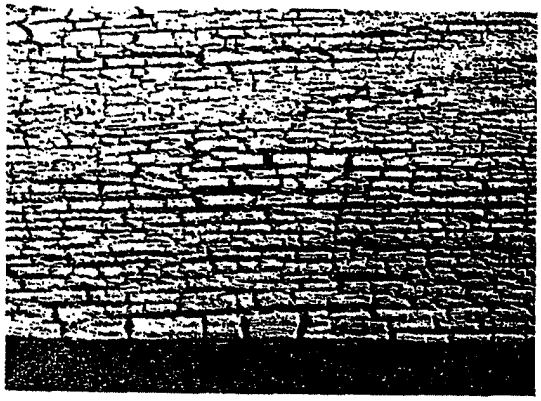
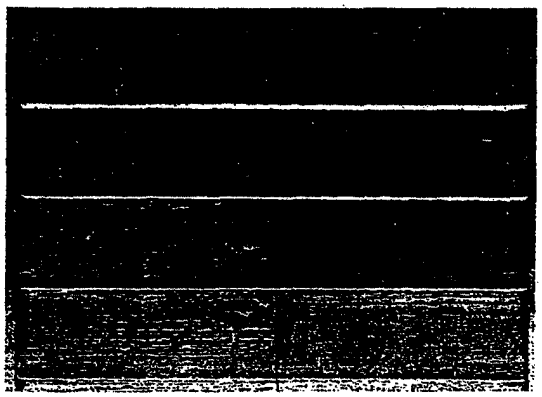


Abnormal disintegration of paint by alligatoring. In this case a pigment house paint was applied over a clear varnish used as a wood sealer in place of a paint primer.



The boards on the left were painted with three coats of a high-swelling, titanium-lead-zinc paint, which blistered badly under conditions of cold-weather condensation. Boards on the right were primed with low-swelling aluminum house paint and finished with two coats of the same titanium-lead-zinc paint.

form soaps that may be more or less soluble in water than the corresponding free acids (33, 38, 39).

The nonvolatile decomposition products that remain in the film significantly affect the properties of coatings (32, 45, 49). Liquids or soft solids of low molecular weight act as plasticizers to impart flexibility and distensibility and perhaps to ketp the degree of cross linking of the polymeric gel from becoming excessive. Loss of the plasticizing products by leaching with water impairs flexibility and distensibility and promotes embrittlement. On the other hand, hard, crystalline solids, such as are formed by some of the zinc soaps, act like pigments to make the film harder and less flexible. Water-soluble or strongly hydrophilic decomposition products make the film absorb more water. Although the absorbed water acts helpfully to plasticize the film, it also has the harmful effect of causing swelling.

In the first stages of drying, there is a gain in weight despite loss of volatile products, because the weight of oxygen retained in the film exceeds the weight of volatile products lost (18). The oxygen retained soon reaches a maximum. Linseed oil, for example, contains 11.5 percent of oxygen to begin with, but may gain more than 13 percent to reach a maximum of 25 percent. But loss of volatile products continues during aging or weathering, so that the weight of the film declines from its maximum. The volume of the film, on the other hand, begins to shrink from a very early stage in the drying (19), partly from loss of volatile products and partly from increase in density of the oxidized film. Thus the density of linseed oil increases from 0.93 to more than 1.1 within 2 days.

Young coatings that are highly plasticized by oxidation products and by incomplete cross linking of the polymeric gel can adjust their internal stresses. Old coatings that are more completely cross linked and have lost plasticizers necessarily develop great internal stresses (1, 35, 36, 46), because two of their three dimensions must continue to conform to the requirements of their substrate. This leaves only the thickness free to take up the changes in volume. Further changes in volume imposed by periodic absorption of water and redrying during weathering eventually build up enough internal stress to disrupt the coating.

Light speeds both the polymeric and the disruptive oxidation in the drying and deterioration of coatings (20, 21, 25, 26). Light is more effective the shorter its wave length (24, 35, 42). The ultraviolet components of sunlight with wave lengths from 280 to 400 millimicrons are more effective than visible light with wave lengths from 400 to 800 millimicrons. Wave lengths shorter than 280 millimicrons, although still more effective, are of little practical importance because they are absorbed in the atmosphere before sunlight reaches the earth's surface. Window glass absorbs much of the ultraviolet from sunlight.

On the other hand, the longer waves of light penetrate to the full depth of paint films of ordinary thickness, whereas the shorter ultraviolet light penetrates only part way (25). Pigments of high opacity to ultraviolet light, such as zinc oxide (40), further restrict the action of short waves to a very thin superficial layer. The shorter waves stimulate particularly the production of volatile compounds of carbon, and result in deterioration by chalking and erosion, whereas longer waves promote less drastic cleavage with volatilization of more hydrogen (as water) than carbon, increased cross linking, and further shrinking and embrittlement of the coating (25, 26, 37).

Less attention has been paid to the action of water in deterioration, although its importance has been recognized (26, 35, 42, 50). It has even been claimed that water causes much the same deterioration as light, but at a slower rate (43, 45). Certainly paints exposed outdoors are repeatedly brought in contact with water (28), which, from the knowledge already reviewed, can be expected to affect materially the composition and properties of the coating and contribute to faster deterioration outdoors than indoors.

## Experimental Procedure

Previous publications reported the behavior of paint coatings and free films (detached from their substrate), both before and after weathering, when brought in contact with water (4 to 14). The absorption of water, changes in density, volumetric swelling, changes in dimensions, recovery on redrying, extraction of water-soluble ingredients, and losses by volatilization and leaching during weathering were measured. The coatings were weathered by exposure either outdoors or in a Weatherometer so that deterioration was accomplished by the combined action of sunlight and water, together with oxygen. Changes during the first 10 days after the liquid paints were applied, that is while the paints dried and hardened, were not measured.

The experiments described here afford information about changes in

weight, volume, and density of some linseed oil paints during the drying period and about the effects on these properties of subsequent exposure under various conditions for 15 days and their behavior toward water. In particular, the purpose was to learn more about the relative action of water and light in paint deterioration.

All of the 8 paints used were made at 30 percent pigment volume in a vehicle of raw linseed oil containing lead-manganese naphthenate drier. The composition was always 0.261 gallon of pigment, 0.609 gallon of linseed oil, and 0.130 gallon of mineral spirits and liquid drier to the gallon of paint. The paints differed only in pigment composition. In paint *L* the pigment was entirely basic carbonate white lead, in paint *Z* lead-free zinc oxide, in paint *T* rutile titanium dioxide, in paint *A* antimony oxide, in paint *X* magnesium silicate. The other 3 paints contained mixtures of 3 or 4 of these pigments from the same lots. In paint *TLX* the pigment consisted of 14 percent titanium dioxide, 40 percent white lead, and 46 percent magnesium silicate by volume. In paint *TZX* the pigment contained 19 percent titanium dioxide, 20 percent zinc oxide, and 61 percent magnesium silicate. In paint *TLZX*, the pigment contained 14 percent titanium dioxide, 20 percent white lead, 20 percent zinc oxide, and 46 percent magnesium silicate.

The paints were spread on clean tinplate by means of a suction plate and doctor blade, at a thickness of coating calculated to yield 4 mils after the volatile thinner evaporated. The weight of paint was determined by weighing each tinplate before and immediately after application. The initial weight, volume, and density of the coatings after evaporation of the volatile thinner were calculated from the composition of the paint, the bulking values of the ingredients, and the weight of paint applied. The coated tinplates were allowed to stand 10 days in light filtered through a glass window facing north. Temperature and humidity were not controlled, but the temperature did not depart much from 80°F. and the relative humidity was always less than 40 percent. Specimens of each paint were weighed daily for the first 10 days and then at suitable intervals up to 83 days to follow the changes in weight.

On the 10th day, a set of specimens, one for each paint, was selected and the coatings stripped from the tinplates by floating them on mercury until the tin was amalgamated and the paint film set free. The free films were submitted at once to test for their behavior toward water by the methods described in previous publications (9).

Table 1.--Changes in weight, volume, and density of paint coatings while drying and aging indoors in dry air[1].

| Paint[2] | Density | | | Age at maximum weight | Changes in weight | | | | Loss in volume after | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1st day | 10th day | 25th day | | Maximum gain | Decline from maximum after 10 days | Decline from maximum after 25 days | Decline from maximum after 83 days | 10 days | 25 days |
| | | | | Days | Cg/cm³ | Cg/cm³ | Cg/cm³ | Cg/cm³ | Mm³/cm³ | Mm³/cm³ |
| L (white lead) | 2.70 | 2.90 | 2.94 | 6 | 6.75 | 0.50 | 1.13 | 3.18 | 47.7 | 63.0 |
| Z (zinc oxide) | 2.32 | 2.47 | 2.52 | 8 | 9.18 | .46 | .63 | 1.79 | 24.4 | 45.6 |
| T (titanium dioxide) | 1.91 | 2.04 | 2.10 | 2 | 10.75 | 1.29 | 2.56 | 4.95 | 17.1 | 51.2 |
| A (antimony oxide) | 2.38 | 2.53 | 2.54 | 2 | 12.25 | 1.76 | 3.02 | 5.00 | 14.9 | 24.6 |
| X (magnesium silicate) | 1.51 | 1.68 | 1.69 | 6 | 7.90 | .55 | 1.70 | 4.46 | 59.1 | 68.5 |
| TLX (titanium-lead-silicate) | 2.04 | 2.23 | 2.24 | 6 | 7.63 | .38 | .80 | 2.68 | 51.3 | 54.0 |
| TZX (titanium-zinc-silicate) | 1.74 | 1.92 | 1.92 | 8 | 9.72 | .33 | .68 | 2.56 | 46.6 | 48.2 |
| TLZX (titanium-lead-zinc-silicate) | 1.97 | 2.15 | 2.14 | 8 | 8.50 | .17 | .20 | 1.89 | 44.8 | 39.4 |

[1] Coatings on tinplate were approximately 4 mils thick when 10 days old. Changes calculated for 1 cubic centimeter of liquid paint free from volatile thinner.
[2] Linseed oil paint at 30 percent pigment volume.

Also on the 10th day, 6 other sets of specimens were taken, each set to be submitted for 15 days to one of the following conditions of exposure:

1. *Indoor light, dry air:* This was a continuation of the conditions already described for the initial 10-day drying period.

2. *Darkness, dry air:* The specimens were kept in a totally dark room in which temperature and relative humidity were the same as in condition 1.

3. *Darkness, damp air:* The specimens were kept in a totally dark room held constantly at 80° F. and 97 percent relative humidity.

4. *Repeated water:* From 7 to 10 a.m. and again from 2 to 5 p.m. daily the specimens were submerged in rapidly running tap water at about 50° F. Between immersions, the specimens were allowed to drain and dry under condition 1.

5. *Sunlight without water:* The specimens were irradiated constantly with artificial sunlight from a flaming carbon arc enclosed in a Corex D glass globe.

6. *Sunlight with water:* The specimens were irradiated constantly with the artificial sunlight and sprayed generously with distilled water for approximately 2 minutes in each period of 20 minutes.

Tests under conditions 5 and 6 were conducted simultaneously in a Weatherometer with the specimens to be kept dry arranged in the upper tier of the rotating drum and protected by suitable baffles from the water sprayed on the specimens of the lower tier at each rotation of the drum.

At the end of the 15-day exposure periods, when the specimens were 25 days old, the exposures were discontinued, the specimens were allowed to dry, were weighed, and the films stripped from the tinplate for test for behavior toward water.

## Aging Indoors in Dry Air

Within 24 hours after application, all paints were gaining in weight. Evidently most of the volatile thinner had evaporated, a minimum in weight had been passed, and absorption of oxygen was greater than the combined losses of volatile decomposition products and any residue of volatile thinner still left. With further passage of time, all paints reached a maximum weight and then declined when losses of volatile products began to exceed further absorption of oxygen.

The changes in weight, volume, and density of the 8 paints during drying and aging indoors in dry air are summarized in Table 1. It is to be remembered that, in Table 1, the changes are computed from the starting point of the weight, volume, and density of the unoxidized paint free from volatile thinner, and that all paints contained the same volumetric proportion of linseed oil at the outset.

All paints reached maximum weight within the 10-day drying period, but they differed strikingly in the magnitude of the maximum and in the time required to reach it. Paints *A* and *T* in 2 days reached maxima of 12.25 and 10.75 centigrams per cubic centimeter; *L*, *X*, and *TLX* took 6 days to reach maxima of 6.75 to 7.90, and paints *Z*, *TZX*, and *TLZX* required 8 days to reach 8.50 to 9.18. After they passed the maximum, paints *A* and *T* declined in weight more rapidly than the other paints, and the 3 paints that contained zinc oxide declined less rapidly than the others. Although all of the paints still exhibited a net gain in weight even after 240 days, all experienced a substantial loss in volume with consequent increase in density within the first 10 days. There usually was further loss in volume and increase

Table 2.--Behavior of 10-day-old paint films during soaking and after redrying.[1]

| Paint[2] | Change during soaking | | | | | Soluble material extracted | Change after redrying | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Density | Water absorbed | Volume | Area | Thickness | | Density | Volume | Area | Thickness |
| | | Cg/cm³ | Percent | Percent | Percent | Cg/cm² | | Percent | Percent | Percent |
| L (white lead) | -0.07 | 5.6 | +5.9 | +1.0 | +2.4 | 3.4 | +0.04 | -2.6 | -0.2 | -2.4 |
| Z (zinc oxide) | -.69 | 91.0 | +90.5 | +33.4 | +41.0 | 3.3 | +.02 | -2.3 | +8.9 | -10.4 |
| T (titanium dioxide) | -.15 | 22.3 | +22.6 | +10.0 | + 8.8 | 2.9 | +.04 | -2.9 | +1.0 | -3.9 |
| A (antimony oxide) | -.03 | 1.8 | +2.2 | +.5 | +.5 | 1.3 | +.01 | -1.2 | -.5 | -.7 |
| X (magnesium silicate) | -.20 | 42.8 | +43.7 | +15.0 | +22.2 | 3.1 | +.02 | -3.1 | +1.9 | -4.8 |
| TLX (titanium-lead-silicate) | -.15 | 14.5 | +14.9 | +4.5 | +7.7 | 3.5 | +.02 | -2.5 | -.1 | -2.3 |
| TZX (titanium-zinc-silicate) | -.38 | 71.9 | +72.0 | +33.5 | +27.1 | 3.1 | +.008 | -2.0 | +9.5 | -10.7 |
| TLZX (titanium-lead-zinc-silicate) | -.39 | 50.6 | +50.7 | +17.3 | +27.0 | 2.6 | +.005 | -1.4 | +4.1 | -5.5 |

[1] Soaked in distilled water for 3 days and then allowed to dry out for 3 days in a desiccator. Coatings, approximately 4 mils thick, stripped from their substrate before starting the soaking test. Percent change calculated on the basis of the volume of the dried film before soaking in water.

[2] Linseed oil at 30 percent pigment volume.

in density during the next 15 days except for paint *TLZX*, which apparently recovered a small part of its initial loss in volume with a slight decrease in density.

Table 1 shows clearly that none of the pigments used can be considered "chemically inert." All exert profound effects on the course of oxidation of the drying oil. In particular they affect the extent of disruptive oxidation, which produces volatile products that escape from the coating and presumably also somewhat larger fragments that remain behind but are extractable by solvents (36). Pigments likewise affect the shrinkage in volume during drying and aging. Still further effects of pigments on the behavior of paint films toward water are therefore to be expected.

When 10-day-old coatings were stripped from their substrates and the free films soaked in distilled water for 3 days and then allowed to dry again for 3 days in a desiccator, they behaved as reported in Table 2. The changes are computed on the basis of the volume of the 10-day-old films rather than that of the volume of nonvolatile in the liquid paint as in Table 1. All films absorbed water and swelled in volume but in widely differing amounts. Paint *A* absorbed only 1.8 centigrams per cubic centimeter, whereas paint *Z* absorbed 91.0 centigrams. Volumetric swelling was nearly but not necessarily exactly equal to the volume of water absorbed. Film density decreased in proportion as the absorption increased.

When redried, all films were lighter in weight than they were immediately before soaking by the weight of soluble matter extracted by the water. Most of the soluble material can be recovered by evaporating the soaking water to dryness (8). From the data of Table 1 it can be shown that loss of volatile material during the 3 days in the desiccator in no case was as much as 0.2 centigram per cubic centimeter. The redried films shrank below their volume before soaking by amounts that were comparable to the solubility losses. The density of the redried films was greater than it was before soaking.

The free films swelled in volume when soaked in water by increasing both in area and in thickness. The paints differed widely in the distribution of their volumetric swelling between swelling in area and swelling in thickness. Thus paint *Z* increased 33.4 percent in area and 41.0 percent in thickness, whereas paint *TZX* increased 33.5 percent in area but only 27.1 percent in thickness. Shrinkage on redrying was always accomplished more by contraction in thickness than in area; in fact, the redried films of 5 of the paints remained larger in area although much thinner than they were before soaking. The paints containing zinc oxide, which are harder and less flexible than the others, contracted least in area when redried.

## Deterioration under Different Conditions of Exposure

Changes in weight, volume, and density of the paint coatings under the 6 different conditions of exposure already described are reported in Table 3. Table 3 gives also the behavior of free paint films after exposure when submitted to the soaking water test.

During 15-day exposure in dry air with or without indoor light (conditions 1 and 2), the changes in weight, volume, and density were small, as was to be expected in the relatively brief exposure period. Much longer exposure and closer control of the exposure conditions would be needed for satisfactory quantitative measurements to reveal any effect of indoor light on the rates of deterioration. Nevertheless, measurable deterioration clearly occurred both in indoor light and in darkness, as is indicated by loss in weight usually accompanied by loss in volume and gain in density. Paint *TLZX*, however, increased slightly in volume and decreased slightly in density despite its loss in weight, and paint *TZX* likewise decreased in density. Table 1 shows that these 2 paints declined from their maximum weight less rapidly than the other paints up to the 25th day, but thereafter they lost weight about as fast as the others. The behavior of the free films toward water after the 15-day exposure in dry air with and without indoor illumination did not differ greatly from the behavior of the 10-day-old films reported in Table 2.

Exposure to damp air in darkness for 15 days, condition 3, markedly altered the behavior of the free films toward water by increasing the absorption of water and swelling. Thus paint *L*, which swelled 5.9 percent in water after exposure to dry air in darkness, swelled 11.5 percent after exposure in damp air. Paint *Z* swelled 91.5 percent and 121.5 percent in water after exposure to dry and to damp air, respectively. The effect of damp air on weight, volume, and density does not appear to be consistent. Its effect may be complicated by chemical reactions of moisture with decomposition products formed in the presence of some pigments but not in the presence of others. Thus paint *Z*, which in previous tests (6) was found to absorb 20 centigrams of moisture per cubic centimeter in 7 days in 97 percent relative humidity, showed (Table 3) an anomalous gain after redrying of 1.4 centigrams per cubic centimeter whereas paint *L*, which in the previous tests absorbed only 2.9 centigrams of moisture per cubic centimeter, exhibited greater loss in weight and volume in damp than in dry air. Similar differences between paints *Z* and *L* have been reported by others (40). On the whole, the data of Table 3 support the conclusion that dampness is more potent than indoor light in altering the properties of paint coatings, at least in the early stages of deterioration.

Repeated immersion of the paint coatings in water, condition 4, produced greater losses in weight and in volume, usually with greater increase in density, than any of the other conditions of exposure without sunlight. These greater losses were due in part, but perhaps only in part, to extraction of soluble materials by the water, because the free films nearly always exhibited a diminished content of water-soluble substances when they were tested after the exposure period. In the test of the free films for behavior toward water after exposure, the films exposed to repeated immersion in water always swelled much more than

those exposed to dry air with or without indoor light, but they swelled somewhat less than those exposed to damp air. This effect was probably caused by the water-soluble products extracted during the repeated immersion treatments.

Exposure to artificial sunlight without water in the Weatherometer (condition 5), produced much greater loss in weight, loss in volume, and increase in density than did any of the exposure conditions without sunlight. But water acting in conjunction with sunlight (condition 6), caused still further changes that were often as great as those produced by sunlight alone. Thus for paint *T* sunlight alone increased the weight loss from 1.1 centigram per cubic centimeter in dry air and darkness to 7.2 centigrams, whereas water with sunlight increased the weight loss to 21.9 centigrams. In practice, water may be even more important than the data indicate, because the test conditions were such that each exposure to water was very brief, 2 minutes of spray, possibly 5 or 6 minutes to drain and dry, followed by 12 or 13 minutes of dryness and warmth. Water could scarcely penetrate the coatings very deeply. In natural weathering the periods of wetness, although less frequent, usually last long enough to permit thorough penetration of the coatings (28).

The 3 paints that contained zinc oxide (*Z*, *TZX*, and *TLZX*) suffered smaller losses of weight and of volume during exposure to sunshine, either with or without water, than any of the other paints. On the other hand, the losses were greater for the magnesium silicate paint *X* than for any of the others. Zinc oxide is highly absorptive of ultraviolet light, whereas magnesium silicate is more transparent than any of the other pigments to both ultraviolet and visible light (40).

After exposure to sunlight, free films of paints *L* and *A* absorbed more water in the soaking test than they did before exposure (Table 2) or after exposure to dry air in darkness. These are paints of exceptionally low absorption; in fact, they absorb less water than films of unpigmented linseed oil (9, 11). After exposure to sunlight alone, the swelling in water was nearly as much percentagewise as the absorption of water but after exposure to water and sunlight together the swelling lagged behind the absorption. This is attributed to development of porosity within the paint coating when water extracts soluble matter after the coating has become rigid enough to resist collapse.

Table 3.--Effect of conditions of exposure on the changes in paint coatings and on the behavior of their free films during soaking and after redrying[1].

| Exposure conditions[2] | Change during exposure[3] | | | Change during soaking[4] | | | | Change on drying[5] | |
|---|---|---|---|---|---|---|---|---|---|
| | Density | Weight | Volume | Density | Water absorbed | Volume | Soluble material extracted | Density | Volume |
| | | g/cm³ | Percent | | g/cm³ | Percent | g/cm³ | | Percent |
| **PAINT L (white lead)** | | | | | | | | | |
| Indoor light, dry air | +0.038 | -0.7 | -1.6 | -0.076 | +6.5 | +6.6 | 2.6 | +0.050 | -2.6 |
| Darkness, dry air | +.033 | -.7 | -1.5 | -.067 | +5.8 | +5.9 | 2.9 | +.042 | -2.4 |
| Darkness, damp air | +.040 | -.9 | -1.8 | -.182 | +11.5 | +11.5 | 1.9 | +.024 | -1.4 |
| Repeated water | +.061 | -2.7 | -3.0 | -.109 | +7.4 | +7.2 | 1.4 | +.024 | -1.4 |
| Sunlight without water | +.260 | -10.6 | -11.6 | -.168 | +10.7 | +9.5 | 4.1 | +.012 | -1.7 |
| Sunlight with water | +.356 | -17.3 | -16.3 | -.116 | +6.8 | +2.0 | 2.8 | -.090 | +2.0 |
| **PAINT Z (zinc oxide)** | | | | | | | | | |
| Indoor light, dry air | +0.057 | -0.2 | -2.2 | -0.752 | +98.5 | +98.0 | 1.8 | +0.015 | -1.8 |
| Darkness, dry air | +.053 | -.3 | -2.1 | -.720 | +92.0 | +91.5 | 2.9 | +.014 | -1.7 |
| Darkness, damp air | +.061 | +1.4 | -1.2 | -.822 | +122.0 | +121.5 | 3.0 | +.025 | -2.2 |
| Repeated water | +.067 | -1.4 | -3.2 | -.782 | +105.0 | +104.0 | 1.3 | +.010 | -1.3 |
| Sunlight without water | +.194 | -6.0 | -9.2 | -.416 | +35.2 | +34.4 | 1.5 | +.008 | -.9 |
| Sunlight with water | +.259 | -11.2 | -13.5 | -.392 | +31.2 | +30.4 | .9 | +.009 | -.7 |
| **PAINT T (titanium dioxide)** | | | | | | | | | |
| Indoor light, dry air | +0.054 | -1.3 | -3.5 | -0.261 | +34.2 | +34.5 | 4.2 | +0.044 | -4.2 |
| Darkness, dry air | +.045 | -1.1 | -2.5 | -.263 | +35.4 | +35.5 | 4.7 | +.045 | -4.3 |
| Darkness, damp air | +.057 | +.1 | -2.6 | -.365 | +52.7 | +52.7 | 4.5 | +.041 | -8.6 |
| Repeated water | +.078 | -3.8 | -5.5 | -.303 | +39.2 | +39.2 | 3.1 | +.027 | -3.1 |
| Sunlight without water | +.134 | -7.2 | -9.5 | -.062 | +9.6 | +9.8 | 5.4 | +.054 | -4.8 |
| Sunlight with water | +.332 | -21.9 | -23.0 | -.091 | +8.3 | +8.6 | 1.3 | +.023 | -1.5 |
| **PAINT A (antimony oxide)** | | | | | | | | | |
| Indoor light, dry air | +0.010 | -1.3 | -1.0 | -0.001 | +1.3 | +1.6 | 2.2 | +0.027 | -1.9 |
| Darkness, dry air | +.001 | -1.3 | -.5 | -.001 | +1.3 | +1.3 | 2.1 | +.019 | -1.6 |
| Darkness, damp air | -.014 | -.6 | +.5 | 0 | +2.0 | +2.1 | 2.4 | +.028 | -2.0 |
| Repeated water | +.024 | -2.9 | -2.1 | -.010 | +1.3 | +1.5 | 1.5 | +.017 | -1.3 |
| Sunlight without water | +.197 | -8.1 | -10.3 | +.024 | +3.3 | +3.1 | 6.0 | +.079 | -5.0 |
| Sunlight with water | +.457 | -22.1 | -22.7 | -.010 | +2.2 | +1.9 | 2.5 | +.026 | -1.7 |
| **PAINT X (magnesium silicate)** | | | | | | | | | |
| Indoor light, dry air | +0.005 | -1.2 | -1.0 | -0.167 | +34.0 | +34.1 | 5.2 | +0.019 | -4.2 |
| Darkness, dry air | +.008 | -.6 | -.7 | -.193 | +40.5 | +40.7 | 5.4 | +.021 | -4.4 |
| Darkness, damp air | -.019 | -1.2 | +.3 | -.358 | +99.0 | +99.3 | 5.8 | -.051 | -.4 |
| Repeated water | +.009 | -4.4 | -3.0 | -.250 | +57.8 | +57.8 | 3.7 | +.010 | -2.8 |
| Sunlight without water | +.166 | -14.7 | -17.0 | -.206 | +38.4 | +38.3 | 14.0 | +.066 | -10.8 |
| Sunlight with water | +.299 | -27.4 | -29.2 | -.047 | + 4.9 | + 5.2 | 1.7 | +.006 | -1.1 |
| **PAINT TLX (titanium dioxide, white lead, magnesium silicate)** | | | | | | | | | |
| Indoor light, dry air | +0.005 | -.4 | -.3 | -0.115 | +12.0 | +12.3 | 3.3 | +0.030 | -2.8 |
| Darkness, dry air | 0 | -.1 | -.1 | -.110 | +11.4 | +12.0 | 3.4 | +.035 | -3.0 |
| Darkness, damp air | -.017 | -.5 | +.6 | -.158 | +15.8 | +16.1 | 1.5 | +.016 | -1.4 |
| Repeated water | +.020 | -3.0 | -2.1 | -.139 | +13.4 | +13.6 | 1.8 | +.018 | -1.5 |
| Sunlight without water | +.179 | -9.4 | -11.5 | -.126 | +11.3 | +11.2 | 2.9 | +.031 | -2.5 |
| Sunlight with water | +.241 | -16.1 | -16.3 | -.103 | +8.1 | +8.3 | 2.4 | +.014 | -1.5 |
| **PAINT TZX (titanium dioxide, zinc oxide, magnesium silicate)** | | | | | | | | | |
| Indoor light, dry air | -0.004 | -0.4 | -0.2 | -0.371 | +68.0 | +68.2 | 3.8 | +0.019 | -2.9 |
| Darkness, dry air | -.007 | -.2 | 0 | -.360 | +65.7 | +66.0 | 3.5 | +.023 | -3.0 |
| Darkness, damp air | -.019 | -.2 | +.7 | -.438 | +94.6 | +94.9 | 2.9 | +.019 | -2.5 |
| Repeated water | -.011 | -1.0 | -.3 | -.377 | +70.5 | +70.8 | 2.9 | +.011 | -2.0 |
| Sunlight without water | +.071 | -5.0 | -5.4 | -.244 | +33.7 | +33.3 | 2.0 | +.014 | -1.2 |
| Sunlight with water | +.091 | -5.4 | -5.1 | -.298 | +42.2 | +42.3 | 1.2 | +.007 | -.9 |
| **PAINT TLZX (titanium dioxide, white lead, zinc oxide, magnesium silicate)** | | | | | | | | | |
| Indoor light, dry air | -0.009 | -0.4 | +.4 | -0.299 | +36.3 | +36.6 | 3.2 | +0.018 | -2.3 |
| Darkness, dry air | -.008 | -.2 | +.4 | -.335 | +42.3 | +42.7 | 3.3 | +.022 | -2.5 |
| Darkness, damp air | -.014 | -.3 | +.5 | -.472 | +72.2 | +72.5 | 3.0 | +.024 | -2.5 |
| Repeated water | -.010 | -1.3 | 0 | -.358 | +46.2 | +46.6 | 2.8 | +.018 | -2.1 |
| Sunlight without water | +.087 | -4.4 | -6.0 | -.250 | +26.5 | +25.5 | 2.2 | -.007 | -.7 |
| Sunlight with water | +.119 | -7.4 | -8.5 | -.289 | +29.4 | +29.2 | 1.5 | -.006 | -.4 |

[1] Coatings on tinplate dried indoors for 10 days (approximately 4 mils thick when dry), then exposed to the conditions indicated, after which they were stripped from the tinplate and tested for behavior toward water.
[2] From eleventh to twenty-fifth day inclusive.
[3] Based on volume of film on tenth day.
[4] Based on volume of film on twenty-fifth day. Soaking time 3 days.
[5] Based on volume of film on twenth-fifth day. Dried 3 days in desiccator after soaking.

All of the other paints, after exposure to sunlight with or without water, absorbed less water and swelled less than they did before exposure or after exposure to dry air in darkness. The difference was especially striking for those paints that were highest in swelling before exposure, namely, the 3 paints that contained zinc oxide. The zinc-containing paints differed from all the others also in that the absorption of water and swelling after exposure to water and sunlight together were nearly as great or even greater than they were after exposure to sunlight alone. The other paints were less absorptive and swelled less after exposure to water and sunlight than after exposure to sunlight alone.

Paint films after exposure to water and sunlight always yielded less soluble material to the soaking water than corresponding films after exposure to sunlight alone and also less soluble matter than films, with the unexplained exception of paint *A*, before exposure or after exposure to dry air in darkness. On the other hand, films of paints containing no zinc oxide, with the unexplained exception of paint *TLX*, yielded more soluble material to the soaking water than the corresponding films before exposure or after exposure to any of the other conditions. Paint *X* after exposure to sunlight alone yielded the remarkable amount of 14.0 centigrams of soluble material per cubic centimeter. The 3

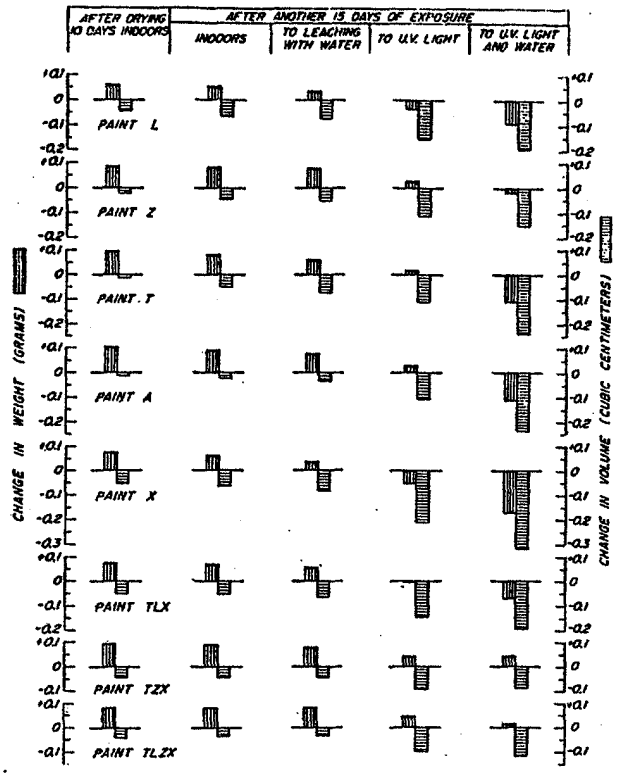



Fig. 1.—Changes in weight and in volume of films under various conditions of exposure. Films contained 1 cubic centimeter of non-volatile when applied.

zinc-containing paints after exposure to sunlight alone gave up less soluble material than their films before exposure or after exposure to dry air in darkness. Apparently sunlight, but not indoor light, acts to increase the formation of soluble decomposition products that remain in the coating unless extracted by water. Zinc oxide, because of its high absorption of ultraviolet light, shields nearly all but the outer surface of the coating from such action. The low opacity of magnesium silicate, on the other hand, offers even less shelding than the other pigments studied.

The changes in weight, volume, and density recorded in Table 3 are those that occurred during the 15-day exposure periods, calculated on the basis of the volume of the dry coatings when 10 days old. Fig. 1 is a graphic presentation of the changes in weight and volume that occurred, first during the 10-day drying period, and then during the entire 25 days for drying and exposure to each test condition, omitting the two exposures in darkness. The changes are calculated on the basis of the volume of unoxidized paint free from volatile thinner applied to begin with. After drying for 10 days, the coatings still retained a net gain in weight, the magnitude of which varied with the kind of pigment in the paint. There was, however, already a loss in volume.

During the succeeding 15 days of exposure, both weight and volume decreased, but to differing extents according to the conditions of exposure and the kind of pigment present. The decreases were least rapid for exposure to dry air indoors, were distinctly faster for repeated immersion in water, still faster for exposure to sunlight, and fastest for exposure to sunlight and water together. Among the 8 paints, the decline in weight and volume when exposed to sunlight was slowest for the 3 paints that contained zinc oxide, but no explanation appears for the greater decline in the paint with 100 percent than in the paints with only 20 percent of zinc oxide. The magnesium silicate paint lost weight and volume faster than any of the other paints.

### Significance of the Experiments

The import of the experiments is that deterioration proceeds in much the same way under all conditions of exposure in which oxygen is present, but that the rate of deterioration can be speeded greatly by such conditions as exposure to sunlight and exposure to water. In darkness or in indoor light, water in the form of either vapor or liquid makes paint films more sensitive to absorption of water and swelling, and in the liquid form it accelerates loss of weight and volume by extracting soluble decomposition products. Indoor light has little stimulating effect on deterioration.

Sunlight, which contains ultraviolet wave lengths, accelerates formation of decomposition products, both volatile products that escape at once and soluble products that remain in the film unless extracted by water. No doubt sunlight also increases polymeric oxidation and cross linking of the gel structure, because it makes coatings more resistant to absorption of water and swelling—except, of course, those coatings that are highly resistant before exposure. When water acts together with sunlgiht, deterioration attains its greatest speed, not only because the soluble decomposition products are extracted but because volatile products form and escape more rapidly. Pigments of high absorption for ultraviolet light, however, retard the action of sunlight, presumably by keeping the ultraviolet light from penetrating much beyond the exposed surface.

Coatings of house paint are called upon to accommodate themselves to substantial changes in volume from two sources, 1) the continual loss in volume from deterioration of the coating, and 2) repeated absorption of water with swelling, redrying with shrinkage, and extraction of soluble components by water. To maintain adhesion to the substrate and remain unbroken, the coatings must make the adjustments entirely by changes in thickness, except as accompanying movement of the substrate may permit some change in area.

The soaking tests reveal that free films, unrestrained by substrates, distribute any change in volume among all three dimensions. Attachment to a substrate, therefore, imposes restraint that necessarily distorts the internal structure. Only a liquid free to flow can submit to such restraint without developing internal stress. As a coating dries and acquires rigidity, internal stresses come into play that increase in magnitude as the rigidity increases. Very young coatings can relax the stresses largely by plastic deformation (23, 32). Older coatings that remain sufficiently distensible can withstand the stresses by elastic deformation. But such adjustments become increasingly difficult as further weathering increases the rigidity of the coating and deprives it of the simpler compounds that act as plasticizers. Eventually the internal stresses exceed the cohesion of the coating or its adhesion to the substrate, whereupon the coating breaks and begins to come loose.

Disruptive stresses in coatings on wood have often been attributed to

movement of the wood surface with change in moisture content (29) Perhaps there are circumstances under which this can occur, but the disintegration of house paints under normal conditions of service cannot be explained in that way (15).

## Applications to Normal House Paint Behavior

Although present knowledge of the mechanisms of paint deterioration is far from complete, an attempt to apply it to the behavior of paints as commonly observed on houses and test fences may suggest directions for promising further research. The Forest Products Laboratory recognizes six stages in the normal wear of house paints: the soiling, flatting, chalking, fissure, disintegration, and advanced break-up stages (27).

**The Soiling Stage:** Newly applied paint gradually becomes dirty. Carbonaceous dirts cling to paint more firmly than do siliceous dirts, glossy paints soil more seriously than otherwise similar flat paints, and the presence of moisture greatly facilitates the attachment of dirt (31, 44). Apparently dirts that are wet by oil more readily than by water stick to the oil vehicle still present in generous amount in the surface of young glossy paint. The actions of water to swell, soften, render the oily surface more tacky, and displace cushions of absorbed air may bring paint and dirt into closer contact. The joining of paint and dirt particles by a film of water, and the subsequent evaporation of the water at the periphery of the junctions, will draw dirt and paint together by the force of surface tension. The water-soluble substances extracted from paint by water may play a part, and conceivably account for the fact that some paints gather less dirt than do other paints that differ only in kind of pigments.

Growth of fungi on paint, commonly called mildew, occurs only when there is moisture, because the microorganisms require water for their metabolism. The organic material extracted from paint by water may provide food for the fungi. Zinc oxide in paint is strongly inhibitive to fungi. Its effect is clearly due to the toxicity of soluble zinc soaps, because zinc has been found in generous amounts in the aqueous extracts from paints containing zinc oxide (4, 8). Soluble salts of lead are also poisonous to fungi, but white lead in paint, although not without prohibitive effect, affords less protection than zinc oxide. The aqueous extracts from paints may contain a little lead (38), but they contain much less lead than zinc (4, 8).

**The Flatting Stage:** House paints gradually lose their initial gloss and become dull or flat. Losses of volatile products and leaching of soluble products, which proceed most rapidly at the exposed surface, destroy the superficial layer of oil vehicle and lay bare the granular bed of pigments (46). In addition, contraction in volume from deterioration of deeper parts of the coating and distortion from repeated swelling and shrinking contribute to the roughening of the surface until its initial ability to reflect light specularly gives way to markedly diffuse reflection. Flatting occurs exceedingly slowly in dry air indoors. It is hastened by contact with water, by the action of sunlight, and particularly by joint action of sunlight and water in the order indicated by the changes in weight and volume recorded in Fig. 1. The part played by water should not be overlooked. House paints and automotive finishes that dull rapidly in the climate of Florida retain their gloss for a much longer time in the equally sunny but very dry climate of southern Arizona (48).

**The Chalking Stage:** Continuation of the processes that cause flatting eventually destroys the binding medium by which those particles of pigment near the surface are held in place. When the loose pigment can be rubbed off, the coating is said to be chalking. Chalking is so easily observed that many have been led to attribute to it the gradual erosion by which paint coatings diminish in thickness (16). But the normal service of house paints, unlike that of automotive finishes, affords little opportunity for mechanical removal of chalk by wiping or abrasion. The shrinkage in thickness of coatings of house paint begins long before chalking is evident, and proceeds primarily by decomposition of the vehicle with release of volatile products and extraction of soluble products by water. Mechanical loss of pigment is secondary.

When chalking sets in, some of the dirt previously acquired is usually sloughed off, a process commonly called self-cleaning. The change from an oil-rich glossy composition to a pigment-rich flat composition makes the surface less able to retain dirt. Dirt dislodged by disappearance of the oil to which it was attached is not readily replaced by fresh dirt. The most successful self-cleaning paints nearly always contain zinc oxide, and therefore yield zinc soaps rather than free organic acids to their aqueous extracts (4, 8). It may well be that the zinc soaps have a detergent action that is lacking in the more acidic extracts.

Paints that contain colored pigments fade when they begin to chalk. This has long been recognized as an optical effect of a porous condition of the superficial chalking layer from which oil vehicle has disappeared. Voids left between particles of pigment make highly reflective optical interfaces that restrict penetration of visible light and reduce the extent of selective absorption by the colored pigment. Other evidence of the development of voids in weathered coatings is found in studies of their swelling in water. Before they are weathered, glossy films swell at least as much, sometimes a little more than, the volume of the water absorbed, whereas films weathered sufficiently by exposure to sunlight and water usually swell less than the volume of water absorbed (5, 7, 8, 14). Weathering develops voids that can hold water without adding to the volume of the coating.

It would be highly desirable for house paints to wear entirely away by erosion without any disruption of the coating or loss of adhesion to the substrate. Repainting would then be required when the coating became too thin to continue to hide the substrate, and could be done without troublesome problems with broken and loosened paint. Although such wear by erosion is now obtained with some paints under favorable conditions, no paint can be relied upon to wear that way under all conditions of practical service.

Zinc oxide retards the erosion of paint coatings. On vertical test-fence surfaces facing south at Madison, Wis., Forest Products Laboratory research has shown that linseed oil house paints containing zinc oxide lose about 0.4 to 0.5 mil a year in thickness, whereas paints free from zinc oxide lose nearly 0.7 mil a year (17). These observations are explained in the data of Table 3 and Fig. 1, which show that sunlight is less effective in accelerating the production of both volatile and water-soluble decomposition products when zinc oxide is present than when it is absent.

**The Fissure Stage:** Young coatings are able to withstand the internal stresses caused by shrinkage in volume and by swelling in water followed by redrying because they can undergo a high degree of both elastic and plastic deformation (23). On aging, such distensibility diminishes at a rate determined by the progress of deterioration under the conditions of exposure (23). Loss by volatilization and leaching of low-molecular decomposition products which have plasticizing action, and increased cross linking of the vehicle gel embrittle the coating (1, 32, 45). The internal stresses from changes in volume become ever greater

until the cohesion of the coating is exceeded. Fissures then occur in the coating to relieve the stresses.

The fractures occur when the coating is dry. Even very brittle coatings are strongly placticized by absorbed moisture, which restores a considerable degree of distensibility (23). Fissures develop more often in dry summer weather than in winter, and are more severe in dry than in damp climates. The following experiment is illustrative. An exceedingly brittle paint composed of titanium dioxide in sodium silicate was applied to matched edge-grain and flat-grain specimens of Douglas-fir and southern yellow pine. The smooth coatings remained intact and unbroken for a long time when kept at reasonably constant relative humidity and temperature. They also remained unchanged when exposed to damp air for 3 days, during which the wood gained 3 percent in moisture content and swelled accordingly. But within an hour after the specimens were restored to lower relative humidity, the coatings cracked severely in a reticulate pattern entirely unrelated to the grain of the wood and long before the wood had lost much of the moisture it had taken up. The cracking clearly originated in stresses within the coating rather than in movement of the wood under the coating.

Fissures may take the form either of checking or of cracking. In checking, the fissures begin in a superficial layer of the coating but may work their way to the bottom of the coating later on. In cracking, the fissures extend at once throughout the depth of the coating. Checking usually occurs, if at all, at an earlier age than cracking. Checking suggests a condition in which a superficial layer of the coating has become embrittled and shrunken at a time when the deeper portions are still distensible and less contracted. Cracking suggests a coating of high strength in tension that has become embrittled throughout before it yields at all. Coatings of white lead paint, which soon develop checking, retain distensibility for a long time even when exposed to sunshine and water, have only moderate strength in tension, and swell very little in water. Paint coatings containing zinc oxide, which imparts cracking tendencies, become embrittled even in the absence of sunlight, have high strength in tension, and become greatly swollen in water. Paints in which early checking relieves internal stresses either may remain free from cracking or, if they do eventually crack, the cracking may occur in a smaller, less conspicous pattern than in paints in which checking is absent and cracking is long delayed.

Coatings applied by brush or doctor blade possess grain that is absent when the coatings are applied by spray gun, especially if the paint contains acicular pigments. The grain comes from orientation of the acicular particles in the last direction in which the paint flows before it hardens. The grain of the paint is revealed in a preferential orientation of cracks in the direction of the last strokes of the brush (23, 32). It appears also in greater swelling across than with the last brush strokes when the films are stripped and soaked in water (4, 8) and in greater strength in tension along than across the grain when the films are tested mechanically (23). The mistaken belief that the direction of cracking is determined by the grain of the wood underneath arises from the fact that paint is customarily applied with the last strokes in the direction of the wood grain.

Checking, which begins in superficial fissures, usually shows little effect of paint grain, develops with random orientation, and rapidly forms an inconspicuous reticulate pattern of fine meshes. The pattern of cracking is usually much coarser and more conspicuous.

**The Stage of Disintegration:** When checking penetrates to the bottom of the coating, water gains direct access to the wood underneath. Adhesion between coating and wood is greatly weakened by water (34). Moreover, the internal stresses within the coating reach a maximum at the interface between coating and wood, which is the seat of external restraint on the free movement of the coating. There is soon a loosening of the coating along the edges of the checks. The coating then begins to crumble by detachment, one by one, of the tiny polygons outlined by the reticulate fissures.

Paint cracks likewise admit water directly to the wood, and result in loosening along the edges of the cracks. Loose edges of paints that swell greatly in water curl outward markedly, sometimes to the extent of forming scrolls. Free films of such paints curl similarly when soaked in water and even more sharply when redried. The curling may be understood as a response to greater internal stresses in the superficial layer of the coating, where greater exposure has resulted in greater contraction in volume, than in the deeper layers of the coating. Curling tendencies are more marked with high-swelling than with low-swelling paints, but with high-swelling paints the curling can be minimized by formulating the paint as closely as possible to its critical pigment volume.

The loosened areas of coating, now free to change in area as well as in thickness, are often seen to be larger in area than the patch of wood from which they have been detached. This finds explanation in the fact, recorded in Table 2, that high-swelling paints tend to remain distended in area after they have swelled in water and redried. Loose edges of coating eventually break away from the rest of the coating or are broken off by the elements and fall away as flakes.

When disintegration sets in after checking or cracking, the wood begins to affect the course of further deterioration. Loosening occurs much sooner over summerwood than over springwood, particularly so when the bands of summerwood are relatively wide. There is reason to believe that young paint coatings cling to wood by specific adhesion—that is, by a bonding that involves the same polar, oxygenated groups of the vehicle get that are responsible also for cross linking of the gel itself. The progress of weathering may gradually release such wood-paint bonds as the bonds become increasingly engaged in cross linking within the gel, and as plasticizers are lost and the adhesion repeatedly strained by swelling and shrinking of the coating. Specific adhesion may then be lost and the coating left clinging wholly by mechanical adhesion or embedding in the pores of the wood (3). Springwood bands, by reason of their relatively thin-walled wood cells with large cavities, offer much greater play for purely mechanical adhesion than do summerwood bands, which have thick walls and small cavities.

**The Stage of Advanced Break-up:** The progress of crumbling, flaking, or scaling depends largely on the nature of the wood surface under the paint and only partly on the nature of the paint. As a rule, however, paints that tend to swell little in water and wear by checking and crumbling exhibit slower progress of sloughing from the summerwood and less unkempt appearance in the stage of advanced break-up than paints that wear by cracking in a coarse pattern followed by curling and flaking or scaling.

## Applications to Abnormal Paint Behavior

Under some conditions of service, paints depart from their normal pattern of behavior. Among the conditions that lead to abnormal behavior are unsuitable spacing of paint coats or repaintings, unsuitable thickness of coating, incompatibilities between paints, and blistering.

**Unsuitable Spacing of Paint Coats or Repaintings:** Much experience has shown that oil paints applied while the previous paint was still in the soiling or flatting stage often fail to perform normally. The condition frequently

occurs when houses are completed late in the fall or winter, are given a priming coat of paint only, and the rest of the painting is deferred for several months until the weather moderates. Such paint jobs seem to be particularly inclined to early failure, often by intercoat peeling or by moisture blistering. The relatively high content of water-soluble substances and greater swelling capacity of young coatings may well be responsible. In addition it has been found (12) that paint coatings applied at unsuitably low temperatures contain more water-soluble products and swell more in water than similar coatings applied at higher temperatures.

Much the same explanation may apply to early failures of repaint jobs on parts of a house that, by their position, are sheltered from the full impact of sunshine and rain, such as ceilings of porches and overhanging eaves. It is not unusual for new paint to come loose and scale from older paint or for coatings to become blistered on the well-sheltered areas while the same paint is still performing normally on the fully exposed areas. Absence of the leaching effect of full rainfall, together with longer contact with still water in the form of dew, allows soluble decomposition products to accumulate in the protected coatings to a harmful extent.

**Unsuitable Thickness of Coating:** Practical experience shows that most good house paints serve best when the coating is between 4 and 5 mils thick. Modern paints will hide satisfactorily at half that thickness, but such thin coatings are more quickly penetrated by water, their content of soluble material is greater, sunlight reaches a greater portion of the film, and they have less reserve to waste away than do films of more suitable thickness (7). It is therefore not surprising that they erode unnecessarily rapidly.

On the other hand, unduly thick coatings are prone to bad behavior (16, 17). Cracking often appears earlier, is coarser in pattern and more conspicuous than is normal for the kind of paint, and very often is oriented across rather than with the grain of the paint coating. The coarser cracking leads to unsightly scaling that is unrelated to the summerwood pattern of the wood surface. Such scaling occurs about as early on the woods that hold paint best as it does on the more exacting woods. For each kind of paint there seems to be a critical thickness of coating above which the abnormal behavior sets in. The critical thickness is as little as 6 to 8 mils for the paints that swell greatly in water and form brittle coatings of high strength in tension, whereas it is as great as 15 mils for low-swelling paints that retain plasticity longer and have moderate strength in tension.

Modern practices in paint maintenance tend strongly to build unduly thick coatings after a few repaintings. The paints in predominant use, which erode at the slower rate of 0.4 mil a year when fully exposed to the weather, require 5 years or more to wear sufficiently to accept one good coat of new paint without adding appreciably to the total thickness of coating, yet they are often repainted at intervals as short as 3 years of even less, sometimes with two new coats at a time. A few repaintings suffice to bring the coating thickness above the low critical thickness of such paints. The curious anomaly exists that, in former times, when the paints in predominant use lost 0.7 mil a year and had a higher critical thickness, the customary intervals between paintings were considerably longer and the abnormalities of unduly thick coatings were seldom encountered.

**Incomptabilities Among Paints:** Abnormalities often develop when houses are repainted with a kind of paint that differs too much in some of its properties from the paint used previously. The reason for such incompatibilities were obscure until the swelling effect of water on different paints became known. The junction between coatings of markedly disimilar swelling capacity necessarily becomes the seat of very high stresses when the coating absorbs water and dries out again. Moreover, the adhesion of one coat to the other is impaired by water, just as is the case with the adhesion of paint to wood. Heterogeneous free films that consist of a coat of high-swelling and a coat of low-swelling paint curl into tight scrolls when soaked in water, and after somewhat longer soaking they will often blister and come apart easily. Such heterogeneous coatings on houses may crack, curl, and scale from the wood interface abnormally soon or, in more severe cases, the outer coating may crack and scale from the inner coating. Still another variant is alligatoring, in which the outer coat cracks in a reticulate pattern and then shrinks in area, so that the cracks open into relatively wide gaps and the polygon-shaped islands of topcoat may become wrinkled.

In at least one case, dissimilarity between coats proves advantageous rather than harmful. It is now recognized that, when suitable house-paint primers are used under finish coats that contain zinc oxide, the improved performance obtained comes in part from the fact that the primers are usually made without zinc oxide and at relatively high pigment volume and therefore have low swelling capacity. The low-swelling priming coat buffers the swelling tendencies through the coating by minimizing the strain at the interface between wood and paint without too greatly increasing the strain at the interface between paint layers.

**Blistering:** Paint blistering can occur in several different ways. A necessary condition that they share in common is the development of pressure in a gas or liquid at the interface where the blisters arise.

In temperature blistering, the pressure comes from thermal expansion of air in a porous substrate under the coating. A fairly frequent example occurs when houses are repainted in weather when days are warm and sunny but nights are cool. New paint applied perhaps in the afternoon becomes blistered next morning soon after warm sunshine strikes the surface. Air in the wood expands with warmth and pushes through tiny cracks in the old paint to press against the new coating at a time when its outer skin has hardened but its deeper parts are still soft. Even well-weathered paint may be blistered if the surface is struck by a sudden blast of heated air. Practical use is made of temperature blistering when old paint is removed with a painters' blow torch.

In "glossy-back" blistering, the pressure comes presumably from the gases evolved by deterioration of old paint that has been barred from access of oxygen and ultraviolet light by coatings subsequently applied. Such blisters are characterized by the presence of a transparent, glossy, sometimes sticky material that looks like old varnish on the back of the blisters and on the surface underneath. The glossy material is at least partly soluble in water, and seems to be identical with the material extracted from paint film by water. Events that finally result in glossy-back blisters begin with a yellow or brown discoloration of a layer of the old paint, followed by formation of holes with smooth, glossy walls that look under a microscope like the holes in Swiss cheese. The holes gradually grow larger, join together, and finally form large cavities that become blisters. The glossy material accumulates in a relatively deep portion of the film, perhaps because the thickness of the coating makes its extraction by rain difficult. The deposits may then prevent the ready escape of decomposition gases. There are times, however, when the glossy material exudes from paint coatings and discolors the exposed surfaces or even collects in beads or droplets that can be easily mistaken for wood resin.

The source of pressure in moisture

blistering has not yet been established satisfactorily. It may not be the same in all cases. Pressure may develop in the air in the wood under the coating from thermal expansion or when a wet line in the wood advances toward the coating under a temperature gradient, thereby squeezing the trapped air against the back of the coating. Soluble substances in the paint next to the wood may give rise to osmotic pressure, with the coating acting as a semipermeable membrane. The source of pressure may differ with circumstances, and there may be more than one source in a given case. But unless water in the form of liquid reaches the wood-paint interface, the pressure required to blister well-dried paint coatings is usually very great, often of the order of 500 pounds per square inch (34). Water at the interface is necessary as a rule (47) for moisture blistering, because it weakens the adhesion so much that pressure as low as 15 pounds per square inch (34) may suffice.

Water can reach the interface readily if it enters in sufficient quantity from the unpainted edges or backs of boards. Movement toward the interface between the wood and paint is hastened if the painted face is much colder than the back of the board, but moisture blistering can develop without such temperature gradient (47). On houses, moisture may gain access behind painted woodwork by cold-weather condensation of vapor that originates inside the house. It may also enter from the outside by penetration through joints. The latter is probably the more common cause, but it is often overlooked because cold-weather condensation has been so widely publicized.

Blistering seldom occurs from water that reaches the paint-wood interface through the paint coating alone. Water moves through paint so much less rapidly than it does through wood, and there is usually so much more wood than paint present, that the dry wood keeps the paint at the interface reasonably dry for a longe time. Water does blister paint on non-absorptive substrates such as glass or metal and probably does so on wood if there is time enough for the wood to come to its fiber saturation point. Even free paint films may blister when soaked for several days.

Tests on laboratory blistering boxes, in agreement with long observation of experience on houses, prove that some paints are more sensitive to moisture blistering than others. There is a close parallel between the degree to which paints absorb water and swell and their sensitivity to moisture blistering. The sensitive paints are the high-swelling paints. Resistant paints are low in swelling. When high-swelling paint is used for the finish coat, the sensitivity to blistering is reduced if a low-swelling priming coat is interposed between wood and finish coat.

## Conclusion

Study of the mechanisms of paint deterioration reveals that water must be considered a major destructive agent along with ultraviolet light. Water alone, but even more in conjunction with ultraviolet light, accelerates deterioration chemically by stimulating production of volatile and water-soluble decomposition products that have much to do with the various stages of both normal and abnormal behavior of house paints. Water also attacks physically by swelling coatings and then causing severe internal stresses as the coatings dry and shrink again. The stresses disrupt coatings in one way or another. Water is also involved in the self-cleaning action of paints that has been so greatly emphasized in recent years. In the effort to make modern paints as clean as possible, they have been made increasingly sensitive to the harmful attacks of water. A current trend to the manufacture of paints that are more resistant to water is highly encouraging. But there is still need for more research on the mechanisms by which water attacks paint and means of controlling them, so that more reliable paints can be produced.

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