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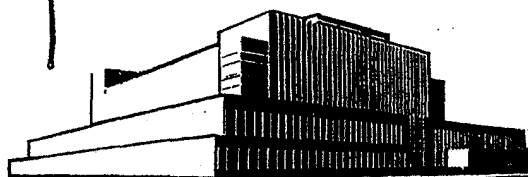
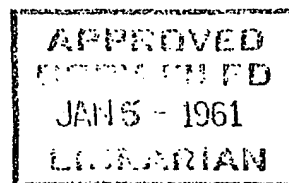
DETERIORATION OF PAINT COATINGS DURING
PROLONGED EXPOSURE INDOORS

By

F. L. BROWNE, Chemist



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UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE

In Cooperation with the University of Wisconsin

DETERIORATION OF PAINT COATINGS DURING

PROLONGED EXPOSURE INDOORS

By

F. L. BROWNE, Chemist

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U.S. Department of Agriculture

A previous publication (3)² reported the changes in weight, volume, density, and other properties of coatings of linseed oil house paints while drying in the laboratory for 10 days after spreading and during a succeeding period of 15 days of exposure to each of the following conditions: (1) laboratory air and light from glazed windows facing north, (2) laboratory air in darkness, (3) darkness in a room at 97 percent relative humidity, (4) twice daily immersion for 3 hours in running water, (5) artificial sunlight in a weatherometer without spraying with water, and (6) artificial sunlight in a weatherometer and spraying with water three times each hour. After the initial loss of volatile thinner during the first few hours after application, all of the coatings gained in weight, reached a maximum in weight within 2 to 8 days, and then lost weight steadily throughout the rest of the 25-day period. The density of the coatings increased and the volume shrank continuously, even during the first few days while the weight was increasing. Changes occurred in the other properties such as water absorption, swelling, and solubility. During the final 15-day exposure to different conditions, artificial sunlight caused the most rapid changes in coatings, leaching with water stood next, high humidity next, and laboratory air, either in darkness or

² Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

¹ Underlined numbers in parentheses refer to Literature Cited at the end of this report.

in north light through windows, caused the slowest changes. Nevertheless, all coatings were still losing weight and changing in properties at the end of the 25-day period.

It was of interest to see whether a much longer period of exposure to the mild conditions of laboratory air and indoor light would bring the coatings to a stable state with no further change in weight. Accordingly, samples of the coatings that had been exposed only to laboratory air and indoor light were retained and are still being weighed at suitable intervals more than 2 years after they were spread. Moreover, in the course of tests for other purposes, coatings of additional paints, including emulsion paints, were prepared and weighed at suitable intervals.

The work reported here consisted of extensions and supplements to tests made for other purposes. As a result, it was not planned in advance as carefully as could now be desired. Despite some shortcomings in technique, however, the data are too significant to be left unreported, especially since the work could not be repeated by improved methods in less than 2 years.

Experimental Procedure

The linseed oil paints tested were ground from their ingredients at the Forest Products Laboratory. The emulsion paints, emulsion-type primers, and oil-type primers were commercial products among which all but brand C bore statements of composition on the label. The content of nonvolatile material and the weight per gallon of all commercial paints were determined experimentally and agreed with computations from the label formulas.

Paints were spread by doctor blade and suction plate on clean, tared tinplate, 4 by 6 inches in size. The weight of wet paint applied was determined

by reweighing the tinplate as quickly as possible (within 1 minute) after the wet paint was spread. Since all of the paints contained volatile thinners (usually mineral spirits or water), there was a slight loss in weight while the paints were being spread and the specimens weighed. Such error did not exceed a few milligrams in a total weight of nonvolatile that ranged from 1 to 3 grams. The weight of nonvolatile applied, which was calculated from the measured weight of wet paint applied and the known fraction of nonvolatile in the wet paint, was therefore underestimated by an amount that can be neglected safely.

The coated tinplate specimens were weighed frequently, usually daily, for the first 10 days after applying paint. After that, the intervals between weighings were lengthened more or less progressively as the coatings became older and the weight changed less rapidly.

The change in weight of coating at any time was calculated as follows:

$$\frac{1,000 (W_t - W_0)}{V_0} = \Delta W_t$$

in which W_t is the weight in grams of the specimen at time t , W_0 is the calculated weight in grams of tinplate plus paint nonvolatile originally applied, V_0 is the volume in cubic centimeters of paint nonvolatile originally applied, and ΔW_t is the change in weight at time t in milligrams per cubic centimeter of nonvolatile originally applied.

Typical Graphs of the Changes in Weight With Time

In figure 1, the changes in weight for each of five single-pigment linseed oil paints are plotted against the logarithm of time in days for a period of

more than 2 years. The paints were made with antimony oxide (A), rutile titanium dioxide (T), lead-free acicular zinc oxide (Z), magnesium silicate (X), and basic carbonate white lead (L), respectively, in the following proportions:

	<u>Gallon</u>
Pigment	0.261
Linseed oil	.609
Mineral spirits	<u>.130</u>
	1.000

The linseed oil always contained the same amount of lead-manganese naphthenate drier.

Approximately 24 hours after spreading the paints, there was a net gain in weight of nonvolatile coating ranging from 65 milligrams per cubic centimeter for paint L to 110 milligrams per cubic centimeter for paint A. Only a small fraction of the weight increase could be mineral spirits still retained in the coating. It would be overgenerous to assume that, after 24 hours, the coating retained 5 percent of the 105 milligrams of mineral spirits originally present, which would be only 5.25 milligrams. Even this small error is offset by the error of similar magnitude due to loss of mineral spirits while spreading and weighing the wet paint.

The paints reached maxima in weight at 123 milligrams per cubic centimeter after 2 days for the antimony oxide paint, 109 milligrams per cubic centimeter after 2 days for the titanium dioxide paint, 92 milligrams per cubic centimeter after 8 days for zinc oxide paint, 79 milligrams per cubic centimeter after 6 days for magnesium silicate paint, and 67 milligrams per cubic centimeter after 6 days for white lead paint. Clearly the pigments exerted marked specific effects on the mechanism of drying of the linseed oil in the paints. Such chemically inert pigments as magnesium silicate, titanium dioxide, and antimony oxide seem to be as effective as the reactive pigments white lead and zinc oxide.

After passing the maximum, all of the coatings followed a generally downward course, subject to some minor wavering, for as long as the experiments have continued. After 300 to 400 days, the coatings of paints L and X weighed less than the weight of the nonvolatile applied initially, before oxidation and drying. Paints A and T were following a roughly parallel course. Paint Z, however, lost weight less rapidly than the other paints.

All of the curves in figure 1 exhibited a distinct dip near the 10th day. Such dip seems to be characteristic of linseed oil paints because it appeared in all tests made subsequently. Apparently there is a brief period following the first attainment of maximum weight during which gain in weight from absorption of oxygen again exceeds the loss of volatile decomposition products. Some of the other fluctuations in the course of the curves were due to variations in moisture content of the coatings with changes in relative humidity of the laboratory air as discussed farther on.

Variability of Results

Paint Txl₂₀, p/nv 0.30, was included in six series of tests, and paint Txl₄₀, p/nv 0.30, in two series started at different times between August 1958 and July 1959. Since the plotted results present a confusion of overlapping curves, certain characteristics of the individual curves are given in table 1, namely the gain or loss in weight (above or below the weight of nonvolatile initially applied) after 1 day, at the maximum gain, at 30 days, at 300 days, and at the last day of observation, and the average rate of change in weight during the intervals between maximum gain and 30 days, 30 to 300 days, and 300 days to the last day of observation.

Although the variability in results with a given paint tested at different times was substantial, it was not great enough to obscure the larger differences in results obtained with different paints, especially when comparisons were made among paints tested contemporaneously. The variations undoubtedly arise chiefly from the uncontrolled variations in temperature and relative humidity in the laboratory in which the work was done. It is well known that the mechanism of drying of oil paints is sensitive to temperature, relative humidity, and illumination. Aging after drying seems to be largely a continuation of the drying mechanism and presumably is sensitive to the same ambient conditions.

Effect of Relative Humidity of the Atmosphere

Previous tests (1), made with coatings and films when 10 days old, indicated that the weight of moisture absorbed from air at relative humidity below 65 percent was less than the loss of volatile decomposition products during the time required to make the measurements. When the present tests were started, therefore, it was thought that the variations in humidity and temperature in the laboratory could be neglected safely. Such proved to be nearly true for the first 30 days of aging, but was not the case later on when, as table 1 shows, the rate of loss of volatile products fell to a fraction of the rate during the first 30 days. It was soon noticed that beyond age 30 days, the plotted curves presented a saw-tooth appearance with ups and downs related to the prevailing relative humidity. This was most noticeable, of course, during the summer months, especially so during the unusually damp summer and fall of 1960.

When the oil-type and emulsion-type paints of series 4 were 382 days old, the coatings were equilibrated in a desiccator over calcium chloride, weighed, then equilibrated and weighed successively in the 30, 65, 80, and 90 percent

relative humidity rooms, and finally equilibrated and weighed again in the desiccator. The results are presented in the stepped bar charts of figure 2. For each paint, the weight of the coating when first equilibrated in the desiccator is taken as the base for calculating the subsequent changes in weight. In each bar, the lengths of the steps in order from top to bottom represent the weight change attained in 30, 65, 80, and 90 percent relative humidity and when returned to the desiccator, respectively. The weight gain from moisture absorbed in 90 percent relative humidity ranged from 10 milligrams per cubic centimeter for oil-type primer of brand C to 55.2 milligrams per cubic centimeter for emulsion-type primer of brand E. When equilibrated in the desiccator for the second time, none of the paints returned exactly to its weight in the desiccator 9 days earlier; oil paint TxZ_{20} and emulsion paint brand D retained less than 1 milligram per cubic centimeter of the weight gained in 90 percent relative humidity, whereas the other paints fell 0.8 to 5.5 milligrams per cubic centimeter below their weight in the desiccator the first time. For most paints, perhaps the exposure to high humidity, which softens and swells the coating, may facilitate the escape of accumulated volatile products.

Of the two linseed oil paints, TxZ_{20} proved more hygroscopic than TxL_{40} , in agreement with past experience. Oil-type primer brand A, which was TxL_{11} , p/nv 0.42, made with bodied linseed and tung oils, in hygroscopicity fell between paints TxZ_{20} and TxL_{40} . Primer brand B, which was Tx , p/nv 0.24, made with linseed alkyd resin, and primer brand D/1, which was TxL_{19} , p/nv 0.36, made with tung-linseed resin, were less hygroscopic than paint TxL_{40} . Primer brand C was outstandingly low in hygroscopicity. Three of the emulsion-type paints, the two primers and brand B finish paint, were more hygroscopic than linseed oil

paint TxZ_{20} , at least in 90 percent relative humidity. All emulsion-type paints except brand C were more hygroscopic in 90 percent relative humidity than linseed oil paint Td_{40} .

The difference between 30 and 65 percent relative humidity in the laboratory when the coatings were weighed could make a difference of 8 to 10 milligrams per cubic centimeter in the moisture content of the coatings and readily accounts for the saw-tooth course of the later portions of the curves of change in coating weight with time. When the tests of series 3 were weighed on the 13th day (May 20, 1959), the relative humidity in the laboratory was about 60 percent, and the coatings were found heavier than they had been on the 10th day when the humidity was lower. The coatings were then placed in a desiccator for 8 hours and weighed again. Paint TxZ_{20} lost 6.9 milligrams per cubic centimeter. Ten other coatings in the series, which consisted of paint TxZ_{20} with various additives, lost from 4.1 to 8.6 milligrams per cubic centimeter. Similarly, the paints of series 1 were found heavier on the 780th day (October 1960) than they had been on the 535th day (February 1960). Equilibration in the desiccator produced the following losses in milligrams per cubic centimeter: paint TxZ_{20} , 8.0; $Td_{20}Z_{20}$, 6.2; Td_{40} , 5.9; L, 6.0; A, 7.0; and T, 9.4.

Linseed Oil Paints of Series 1

Series 1 consisted of five single-pigment paints and three mixed-pigment paints, all made with the same raw linseed oil vehicle at pigment volume 0.30. For the single-pigment paints, the complete data for change with time in the gain or loss in coating weight are plotted in figure 1. Table 2 records significant points on the curves for all eight paints together with the average rate of change in weight during three intervals of time.

One day after applying the paints, the coatings were heavier than the weight of nonvolatile applied by 6.5 milligrams per cubic centimeter for paint L to 113 milligrams per cubic centimeter for paint A. Assuming that all of the mineral spirits in the paint had evaporated, the gain in weight represents the difference between the weight of oxygen absorbed from the air and the weight of volatile decomposition products given off. Loss of volatile products was substantial from the earliest part of the drying process.

Rhodes and Van Wirt (4) measured the oxygen absorbed and the volatile products given off by coatings of linseed oil containing lead linoleate drier and from coatings of linseed oil paints made with various pigments when the coatings were exposed to pure oxygen for various lengths of time. Some of their results, recalculated for comparison with table 2, are given in table 3. Their pigmented coatings were much lower in pigment volume and dried much slower than the paints of table 2, and the methods of test differed greatly. Nevertheless, Rhodes and Van Wirt, in agreement with the findings of this report, observed a rise in net gain in weight to a maximum followed by decline in net gain and the net gains at 10 and 17 days were remarkably close to the net gains for the most nearly comparable paints at maximum and 30 days, respectively, in table 2. In particular, however, the results of Rhodes and Van Wirt show that volatile products are given off in a substantial amount even during the first day after paints are applied. Both the absorption of oxygen and the loss of volatiles increase continuously from the beginning; only their differences, the net gain in weight, passes through a maximum. Although the net gain in weight of white lead paint after the maximum has been passed is always less than the corresponding net gain for zinc oxide paint, both the oxygen absorbed and the volatile products given off are substantially greater in white lead paint than in zinc oxide paint.

As reported in table 2, pigmentation with antimony oxide and titanium dioxide led to relatively high net gain in weight after 1 day and at maximum weight, which was attained after only 2 days. It is unlikely that these pigments hastened the early absorption of oxygen. Presumably, therefore, they retarded the loss of volatile products. In the stages beyond 30 days, when changes in weight were due chiefly to loss of volatile products, the antimony oxide and titanium dioxide paints lost weight more rapidly than any of the paints that contained zinc oxide.

The characteristic points for the mixed-pigment paints fell throughout between those of the two or three single-pigment paints made with the components of the mixture. When zinc oxide was a component, however, the mixed-pigment paint fell closer to pure zinc oxide paint than to the titanium dioxide or the white lead paint. Previous studies of the swelling of paint films in water likewise showed that zinc oxide tends to dominate over other pigments in mixed-pigment paints (2).

The three paints that contained zinc oxide exhibited distinctly slower rates of loss in weight beyond the 30-day mark than any of the other paints. It is possible that the rate of loss of volatile products from the zinc-containing paints is greater than the weighings indicate by reason of an offsetting gain in weight from slow absorption of carbon dioxide from the air and conversion of zinc oxide to zinc carbonate. It was found previously (2) that stocks of zinc oxide pigment, when stored in an unheated and occasionally damp shed, become seriously carbonated.

Linseed Oil Paints of Series 6

The linseed oil paints of series 6, reported in table 4, reveal the effect of variations in pigment values, which is the volumetric ratio of total pigment

in the total nonvolatile ingredients of a paint. Among the titanium zinc paints and among the titanium lead paints, the rate of loss in weight usually decreased as the pigment volume increased. Such trend might be expected because of the decrease in the amount of oil in the coating as the pigment volume increases. The paints of very high pigment volume reached their maximum weight sooner than similar paints made at lower pigment volume.

The titanium zinc paint of pigment volume 0.47 and one of those of pigment volume 0.33, during the interval from 300 to 460 days, not only failed to lose weight but actually became slightly heavier. There was no gain in moisture content because the weight after 460 days was checked after equilibration in a desiccator. Such gain in weight offers further evidence that the zinc oxide in paints becomes carbonated by absorption of carbon dioxide from the air.

The last four paints in table 4 contained the relatively new white pigment, barium metaborate, which has been proposed as a substitute for zinc oxide to provide resistance to mildew without making paint sensitive to moisture blistering. Substitution of barium metaborate for zinc oxide consistently hastened the attainment of maximum weight gain and led to more rapid loss in weight during subsequent aging.

Comparison of Emulsion-Type With Oil-Type Paints, Series 4

Emulsion paints of the acrylic-resin type dry presumably without oxidation by coalescence as the water of the emulsion evaporates. Therefore no gain in weight over the weight of nonvolatile ingredients initially present should be expected during the process of drying and aging. Since the acrylic resins are said to be unusually stable to light and moisture, the weight of the dried

paint coating might be expected to remain constant during subsequent exposure to air in the laboratory. Tests of commercial emulsion-type paints, however, did not conform to the expectations.

Table 5 reports results with five brands of emulsion paints, 2 emulsion-type primers, and four oil-type primers of brands corresponding to the emulsion paints. One manufacturer supplied both an oil-type and an emulsion-type primer. Four of the emulsion paints, 1 emulsion primer, and 1 oil primer failed to reveal a period of increase in weight following evaporation of the volatile constituents, possibly because there were insufficient weighings during the first 24 hours after application. Nevertheless, all but one of these products yielded coatings that were decidedly heavier than the nonvolatile portion of the paint applied. All of the coatings, without exception, lost weight continuously during exposure and were still losing weight after 495 days. The weight gains 1 day after application, except for emulsion paint of brand C, ranged from 48.0 to 98.4 milligrams per cubic centimeter compared with 72.0 and 83.0 milligrams per cubic centimeter for the two linseed oil paints tested contemporaneously. Emulsion paint of brand E, which took 2 days to reach a maximum weight gain, was made with an alkyd-resin modified acrylic resin. Some oxidation of the alkyd-resin component is possible. Emulsion primer of brand D/2, which reached a maximum weight gain after 4 days, was made with a linseed-alkyd-resin emulsion rather than an acrylic emulsion.

Emulsion vehicles contain numerous additives such as emulsifying agents, surfactants for pigment dispersion, antifoaming agents, depressants of the freezing point of water, and fungicides. None of the additives listed in the numerous published formulas for acrylic-resin finish coats, however, is a material that oxidizes readily at normal temperatures. Emulsion primers

sometimes contain drying oil for better penetration and bonding to chalky surfaces, but no such additives to emulsion paints for finish coats appear in the literature. The large weight gains above the nonvolatile content of the liquid paint therefore suggest that the acrylic resins absorb oxygen as they dry, although the mechanism of such absorption is not apparent.

The 1-day old coating of emulsion paint brand C was lighter than the nonvolatile components of the liquid paint by 41.9 milligrams per cubic centimeter and subsequently continued to lose weight. Less information about composition was given on the label than on those of any other commercial paint tested. The initial content of nonvolatile ingredients, however, was determined in the customary way by heating a sample at 105° C. for 3 hours. It is unlikely that any ingredient left after 3 hours at 105° C. could evaporate to the extent of 41.9 milligrams per cubic centimeter in 24 hours at room temperature even when exposed in a coating only 2.5 mils thick. Presumably either the acrylic resin or an additive present in the paint in substantial proportion evolved volatile decomposition products during drying to an extent that exceeded the absorption of oxygen, if such absorption took place.

All of the emulsion paints and the emulsion- or oil-type primers for use with them decreased in weight steadily after the first day or the maximum weight within 4 days. All were still losing weight after 495 days. Published formulas for emulsion paints contain such high boiling liquids as ethyl cellosolve, ethylene glycol, and polyglycol added to depress the freezing point. Ethyl cellosolve has a vapor pressure of 12 millimeters of mercury at 20° C., ethylene glycol only 0.12 millimeter of mercury. Such additives would evaporate from coatings very slowly, but it is doubtful that any would remain in coatings less

than 4 mils thick after 495 days. In published formulas for acrylic emulsion paints, the proportions of high boiling liquid additives range from 0 to 100 milligrams per cubic centimeter. Some formulas for polyvinyl acetate emulsion paints recommend as much as 220 milligrams per cubic centimeter. Thus the paints tested might have contained, but did not necessarily contain, high boiling liquids to account for the weight losses observed, provided that the evaporation was slow enough to persist for more than 495 days. Nevertheless, the initial weight gain by all but one of the emulsion paints, together with the long continued subsequent loss in weight, suggests that oxidation and volatilization of decomposition products occur in emulsion paints to nearly as great an extent as they do in oil paints.

Effect of Additives in Paint TiZr_{20} , p/nv 0.30, Series 2, 3, and 5

The paints of series 2, 3, and 5, reported in table 6, which is in two parts, were made primarily in a search for means of reducing the swelling in water of zinc-containing paints such as TiZr_{20} , p/nv 0.30. It was of interest to learn also whether the additives affect the course of the changes in weight of coatings during aging in the laboratory.

Many of the additives exerted little or no effect on the course of the weight changes during aging of the coatings. This group included additives that increased the swelling in water slightly, such as tetraisopropyl titanate, and additives that markedly decreased swelling, such as silazane 31212. Other additives increased the net gain in weight after 1 day and the rate of loss in weight from the maximum to 30 days. This group included additives that increased the swelling in water greatly, such as soya secondary amine, and additives that decreased swelling substantially, such as octylene glycol titanate. Thus no

relation was revealed between the effect on weight changes and the effect on swelling in water. The effect of the additives on weight changes was exerted chiefly during the first 30 days; after that time, the further rate of loss in weight was usually similar to that of the paint without additive.

Conclusions

(1) After a linseed oil paint is spread as a coating exposed to air and its volatile thinner evaporates, its weight increases for a few days, reaches a maximum, and then declines. The increase observed is the difference between the weight of oxygen absorbed and the weight of volatile decomposition products given off. At the maximum, the two processes are in balance; beyond the maximum, evolution of decomposition products exceeds any further absorption of oxygen. Since oxygen absorption and decomposition are each affected independently by environmental conditions of temperature, relative humidity, and irradiation by light, quantitative measurements of a given paint started at different times vary slightly unless the environmental conditions are controlled more closely than is the case in our paint laboratory.

(2) The maximum gain in net weight of a linseed oil paint and the subsequent rate of decline from the maximum vary widely according to the nature of the pigments in the paint. Paints of high pigment volume reach maximum weight sooner and then usually decline in weight less rapidly than similar paints of lower pigment volume. Paints made at their critical pigment volume may reach unusually high maximum weight, and may decline rapidly from the maximum during the next 30 days. There is also evidence that zinc oxide in paint may absorb carbon dioxide from the air, which offsets part of the loss of decomposition products of the oil vehicle.

(3) Although the rate of loss of decomposition products becomes slower as time passes, it continues for as long as the observations have lasted, which is more than 2 years for the paints of series 1. Thus decomposition goes on continuously even under the very mild exposure to the environmental conditions of the paint laboratory. At the end of 780 days, white lead paint was lighter than the weight of nonvolatile ingredients applied by 55.5 milligrams per cubic centimeter, which was 10.2 percent of the linseed oil in the paint.

(4) Some additives to linseed oil paint markedly affect the weight changes during the first 30 days. They may either increase or decrease the net gain at maximum weight. There is no relation, however, between the effect of additives on weight changes and their effect on the swelling of paint coatings in water.

(5) Surprisingly, most acrylic-emulsion paints, which do not depend on oxidation for their drying, exhibited a net gain in weight comparable to that of linseed oil paints. The emulsion paints, however, usually attained their maximum weight during the first day after application. No explanation has been found for the net gain in weight other than the assumption that the acrylic resins are subject to oxidation by some mechanism not yet known. Moreover, the emulsion paints, on subsequent aging, lost weight steadily and were still losing weight after 495 days. It remains to be determined whether the loss in weight is due to decomposition of the acrylic resins or to slow evaporation of high boiling liquid additives such as ethylene glycol, polyglycol, and ethyl cellosolve, which are often used as freezing point depressants.

(6) Coatings of all paints tested, whether of oil type or emulsion type, remain significantly hygroscopic even after 2 years or more. Even the moderate changes in relative humidity in the paint laboratory produce corresponding changes in weight of the coatings.

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Table 1.--Variability of results among tests started at different times

Date test started	Gain in weight at time indicated	On day indicated	Rate of change during the interval indicated
1 day : Maximum gain, :	30 days : 300 days :	On day indicated	Maximum : 30 to : Beyond
:	:	:	:
:	:	:	to 30 days : 300 days : 300 days
:	:	:	:
:	:	:	:
:	Milligrams per cubic centimeter	:	Milligrams per cubic centimeter
:	:	:	per day
:	:	:	:
PAINT T22 ₂₀ , P, W 0.30			
August 1958	81.0	97.3 (8)	87.5
April 1959	81.5	88.5 (6)	79.0
May 1959	82.5	88.0 (3)	76.5
June 1959	88.0	90.0 (2)	74.0
July 1959	89.0	94.2 (5)	88.0
July 1959	92.0	86.9 (5)	73.5
			62.0
			59.0
			60.0
			60.0
			75.0
			57.0
			52.0 (783)
			53.0 (533)
			57.5 (524)
			58.8 (495)
			74.2 (489)
			55.4 (420)
			0.44
			0.40
			0.43
			0.57
			0.25
			0.54
			0.09
			0.07
			0.06
			0.08
			0.05
			0.06
			0.02
			0.03
			0.01
			0.006
			0.004
			0.01
			0.02
			0.04
			0.05
			0.06
			0.07
			0.08
			0.09
			0.10
			0.11
			0.12
			0.13
			0.14
			0.15
			0.16
			0.17
			0.18
			0.19
			0.20
			0.21
			0.22
			0.23
			0.24
			0.25
			0.26
			0.27
			0.28
			0.29
			0.30
			0.31
			0.32
			0.33
			0.34
			0.35
			0.36
			0.37
			0.38
			0.39
			0.40
			0.41
			0.42
			0.43
			0.44
			0.45
			0.46
			0.47
			0.48
			0.49
			0.50
			0.51
			0.52
			0.53
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			0.61
			0.62
			0.63
			0.64
			0.65
			0.66
			0.67
			0.68
			0.69
			0.70
			0.71
			0.72
			0.73
			0.74
			0.75
			0.76
			0.77
			0

Table 2.--Tests of linseed oil paints of series 1

Paint ¹	Gain in weight at time indicated						Rate of change interval in	
	1 day	Maximum gain, day indicated	30 days	300 days	780 days	Maximum to 30 days	30	300
	in parentheses							
	Milligrams per cubic centimeter						Milligrams per cu per d	
Z, p/nv 0.30	80	92.0 (8)	83.5	63.0	54.5	0.39	0.0	
Tx ₂₀ , p, nv 0.30	81	97.3 (8)	87.5	62.0	52.0	.45	.0	
TxL ₂₀ ^T ₂₀ , p, nv 0.30	72	85.0 (8)	80.0	56.0	43.3	.23	.0	
A, p/nv 0.30	113	123.0 (2)	88.5	58.0	37.0	1.23	.1	
TxL ₄₀ , p/nv 0.30	67.5	76.2 (8)	66.5	29.0	-16.3	.40	.1	
T, p/nv 0.30	107	109.0 (2)	78.0	42.0	8.0	1.11	.1	
L, p/nv 0.30	65	67.3 (6)	51.0	10.0	-55.5	.68	.1	
X, p/nv 0.30	73	79.0 (6)	59.0	-3.0		.83	.2	

¹Symbols have the following meanings: Z, zinc oxide; Tx, mixture of one part rutile titanium dioxide with 3.2 parts by volume of magnesium silicate; L, basic carbonate white lead; A, antimony oxide; T, titanium dioxide; X, magnesium silicate; subscript number, percent by volume of the pigment in the total pigment; p/nv, volumetric ratio of the total pigment in the nonvolatile ingredients. (In subsequent tables, Tx represents a mixture of either rutile or titanium dioxide with extending pigment of any kind and in unspecified proportions.)

Table 3.--Oxygen absorbed, volatile products lost, and net gain in weight of linseed oil, white lead paint, and zinc oxide paint after various lengths of time, according to data of Rhodes and Van Vort

Item indicated ¹	Time after applying the coating			
	1 day	2 days	10 days	17 days
Linseed oil containing drier but no pigment:				
Oxygen absorbed.....mg. per cc.:	168	233	326	331
Volatile products lost.....mg. per cc.:	65	102	233	242
Net gain in weight.....mg. per cc.:	103	131	93	89
Linseed oil paint L, p/nv 0.08:				
Oxygen absorbed.....mg. per cc.:	136	196	320	337
Volatile products lost.....mg. per cc.:	34	88	243	273
Net gain in weight.....mg. per cc.:	102	111	77	64
Linseed oil paint Z, p/nv 0.10:				
Oxygen absorbed.....mg. per cc.:	75.4	134	218	237
Volatile products lost.....mg. per cc.:	8.4	21	125	152
Net gain in weight.....mg. per cc.:	67.0	113	92	84

¹Symbols have the following meanings: L, basic carbonate white lead; Z, zinc oxide; p/nv, pigment volume or fraction of total pigment by volume in the total nonvolatile matter by volume.

Table 4.--Tests of lined oil paints of series 6

Paint ¹	Gain in weight at time indicated			Rate of change during the interval indicated	
	1 day	30 days	300 days	460 days	Maximum to : 30 to : 300 to 300 days : 460 days
Td ₂₀ p/mv 0.30	82.0	86.9 (5)	73.5	57.0	55.4 : 0.54 : 0.061 : 0.010
Td ₂₂ p/mv 0.33	58.5	75.2 (5)	67.9	55.2	55.5 : .29 : .047 :
Td ₂₂ p/mv 0.33	70.0	76.4 (5)	67.3	56.3	55.8 : .36 : .041 : .003
Td ₁₉ p/mv 0.47	132.0	132.0 (1)	115.2	108.4	109.0 : .58 : .040 :
Td ₁₀ p/mv 0.33	76.1	84.0 (6)	76.4	65.1	64.8 : .32 : .042 : .002
Td ₂₈ p/mv 0.30	70.7	74.0 (5)	57.1	35.1	29.2 : .68 : .081 : .037
Td ₃₂ p/mv 0.35	59.6	66.0 (5)	52.2	36.1	31.3 : .55 : .060 : .030
Td ₂₅ p/mv 0.42	74.8	74.8 (1)	63.8	53.9	53.5 : .38 : .037 : .003
Td ₁₄ p/mv 0.34	78.3	80.6 (2)	60.4	45.3	41.6 : .72 : .056 : .023
Td ₃₂ p/mv 0.33	74.0	77.4 (2)	56.6	36.9	32.3 : .74 : .073 : .029
Td ₃₂ p/mv 0.33	75.1	77.7 (2)	55.3	37.8	32.3 : .80 : .065 : .034
B, p/mv 0.30	71.4	71.8 (2)	52.8	29.3	20.2 : .68 : .087 : .057

Symbols have the following meanings: Tx, mixture of titanium dioxide and extending pigment; L, zinc oxide; L, white lead; B, barium metaborate; subscript number, percent by volume of the pigment to which the subscript is attached in the total pigment; p/mv, pigment volume or fractional volume of total pigment in the total nonvolatile matter.

²Grade with anatase titanium dioxide.

³Grade with half anatase and half rutile titanium dioxide.

⁴Paint supplied by the maker of the barium metaborate pigment.

⁵Paint made at the Forest Products Laboratory according to the same formula as the next preceding paint.

Table 5.---Tests of oil-type and emulsion-type primers and paints of series 4

Paint ¹	Gain in weight in time indicated	Rate of change during the interval indicated
	1 day : Maximum gain, : 30 days : 300 days : 495 days : : day indicated : : in parentheses :	Maximum to : 30 to : 300 to : 495 days : : 30 days : 300 days : 495 days :
	Milligrams per cubic centimeter	Milligrams per cubic centimeter per day
Linseed oil paints:		
Tx ₂₀ , p/nv 0.30	88.0 : 90.0 (2)	58.8 : 0.57 : 0.082 : 0.006
Tx ₄₀ , p/nv 0.30	72.0 : 74.5 (2)	5.5 : .62 : .17 : .055
Oil-type primers:		
Brand A, Tx ₁₁ , p/nv 0.42	116.4 : 117.3 (2)	61.5 : .41 : .101 : .035
Brand B, Tx, p/nv 0.24	82.8 : 92.0 (4)	75.3 : 3.28 : .024 : .010
Brand D ₁ , Tx ₁₉ , p/nv 0.36	98.4 : (2)	64.2 : 2.50 : .047 : .040
Brand C	227.5 : 228.0 (3)	207.5 : .39 : .029 : .010
Emulsion-type primers:		
Brand E, Tx, p/nv 0.20	72.8 : (2)	47.5 : 2.29 : .052 : .015
Brand D ₂ , Tx ₁₀ , p/nv 0.31	88.3 : 92.0 (4)	68.0 : .27 : .059 : .006
Emulsion-type paints:		
Brand A, Tx, p/nv 0.29	63.0 : (2)	14.5 : 2.84 : .083 : .009
Brand B, Tx, p/nv 0.28	75.6 : (2)	30.9 : 2.02 : .050 : .008
Brand E, Tx, p/nv 0.28	48.0 : 48.3 (2)	23.8 : 3.37 : .045 : .011
Brand D, Tx, p/nv 0.50	56.1 : (2)	31.0 : 2.37 : .047 : .009
Brand C	41.9 : (2)	61.0 : 2.45 : .016 : .006

¹Symbols have the meanings reported in footnote 1 to table 4.

Weights decreased continuously from the beginning without evidence of a gain to a maximum after the volatile ingredients evaporated.

²Rate computed from the loss between the 1st and the 30th day.

Table 6 (Part 1).--Tests of linseed oil paint 20, p/mv 0.30, with and without various additives

Additive	Gain in weight at time indicated				Rate of change during the interval indicated	
	Amount	1 day	Maximum gain, 30 days	300 days	On day	Maximum 30 to 300 days
Name		day indicated	in parentheses		indicated	to 300 days
						30 days
	Per cent					
Without additive		81.5	88.5 (6)	79.0	59.0	53.0 (533)
Without additive		82.5	88.0 (3)	76.5	60.0	57.5 (524)
Without additive		89.0	94.2 (5)	88.0	75.0	74.2 (489)
Bis (tributyl tin) oxide	10	96.5	96.5 (1)	62.0	34.0	27.5 (533)
Organic tin compound	10	80.7	81.0 (2)	64.5	42.0	36.5 (533)
Tetraisopropyl titanate	10	82.7	85.0 (2)	71.3	51.0	46.0 (533)
Tetra-n-butyl titanate	10	72.7	74.5 (4)	63.0	45.0	40.3 (533)
Tetra 2-ethylhexyl titanate	10	31.3	33.5 (4)	21.0	4.5	0 (533)
Octylene glycol titanate	10	105	105 (1)	81.5	60.5	56.0 (533)
Isopropoxy titanium stearate	10	141	142.5 (4)	123.5	105	99.5 (533)
Vinyl silane X-172	10	64.5	65.0 (1.5)	28.0	12.0	7.5 (533)
Silicone resin C-25	10	85.0	92.0 (3)	78.5	61.0	55.0 (533)
Pinene hydroperoxide	10	75.0	79.0 (0.7)	42.7	27.1	24.2 (489)
Fatty acid compounds						
Coco primary amine	5	56.5	81.2 (4)	68.5	49.5	44.5 (524)
Soya primary amine	5	59.0	88.0 (5)	71.5	53.5	48.0 (524)
Soya secondary amine	5	100.5	112.5 (4)	98.0	81.5	76.5 (524)
Tallow diamine	3	80.0	95.5 (4)	86.0	69.0	63.0 (524)
Tallow diamine dioleate	10	69.5	88.5 (4)	81.5	65.5	59.0 (524)
Soya quaternary ammonium chloride	10	67.0	80.0 (3)	69.5	52.7	48.0 (524)
Soya tertiary amine	3	77.5	90.0 (3)	81.0	65.0	59.0 (524)

Note: The amount of additive present is expressed in percentage of the linseed oil in the paint.

Table 6 (Part 2).--Tests of linseed oil paint Tx_{29} : p/w 0.30, with and without addition of various fillers

Silicazone added	Gain in weight at time indicated	Rate of change during the interval indicated
See	1 day : Maximum gain, : 30 days : 300 days : On day	
Footnote:	: day indicated : indicated	
:	: in parentheses :	
:	:	
Per- :	Milligrams per cubic centimeter	Milligrams per cubic centimeter
cent :	:	per day
Without additive	82.5 : 88.0 (3) : 76.5 : 60.0 : 57.5 (524) : 0.43 : 0.061 : 0.011	
Without additive	89.0 : 94.2 (5) : 88.0 : 75.0 : 74.2 (489) : .25 : .048 : .004	
2311 : 10 :	(1) : 76.0 : 85.0 (4) : 74.0 : 57.0 : 51.0 (524) : .42 : .063 : .027	
2511 : 10 :	(1) : 70.0 : 82.7 (5) : 77.5 : 63.8 : 57.0 (524) : .21 : .051 : .030	
31212 : 10 :	(1) : 74.7 : 90.0 (4) : 87.0 : 74.5 : 69.0 (524) : .12 : .050 : .025	
31212 : 10 :	(1) : 93.8 : 99.2 (4) : 94.3 : 82.3 : 80.5 (489) : .19 : .046 : .010	
31212 : 10 :	(2) : 94.2 : 99.1 (3) : 92.1 : 79.9 : 77.0 (489) : .26 : .045 : .015	
31212 : 5 :	(2) : 91.5 : 97.0 (3) : 86.3 : 72.0 : 70.0 (489) : .40 : .053 : .011	
5010 : 10 :	(1) : 86.4 : 92.0 (4) : 81.3 : 67.0 : 65.2 (489) : .41 : .053 : .010	
5010 : 10 :	(2) : 79.1 : 86.8 (4) : 78.6 : 66.1 : 64.6 (489) : .32 : .050 : .003	
7010 : 10 :	(1) : 81.7 : 84.9 (3) : 68.3 : 52.7 : 49.5 (489) : .61 : .058 : .017	
7010 : 10 :	(2) : 85.2 : 86.0 (2) : 68.0 : 51.5 : 48.7 (489) : .64 : .051 : .015	
7010 : 5 :	(2) : 97.0 : 101.3 (3) : 85.1 : 71.5 : 68.8 (489) : .56 : .054 : .014	
51265 : 10 :	(1) : 89.3 : 96.9 (4) : 90.6 : 78.0 : 75.0 (489) : .24 : .047 : .016	
51265 : 10 :	(2) : 93.0 : 100.7 (4) : 92.2 : 79.7 : 78.1 (489) : .33 : .046 : .009	
71265 : 10 :	(1) : 94.3 : 99.5 (3) : 90.7 : 78.3 : 75.5 (489) : .33 : .046 : .015	
71265 : 10 :	(2) : 92.5 : 98.5 (3) : 90.1 : 77.3 : 74.1 (489) : .31 : .047 : .017	

Isilacane added to paint shortly before the paint was spread as a coating.

²-Sulfurane added 7 days before the paint was spread as a coating.

Note: The amount of additive present is expressed in percentage of the linseed oil in the paint.

Figure 1.--Changes in weight with time of exposure indoors for coatings of linseed oil paints pigmented at 0.30 pigment volume with (A) antimony oxide, (T) rutile titanium dioxide, (Z) zinc oxide, (X) magnesium silicate, and (L) basic carbonate white lead. Changes in weight are in milligrams per cubic centimeter of coating above or below the weight of nonvolatile material in the liquid paint when spread; time is in days plotted on a logarithmic scale.

(M 118 530)

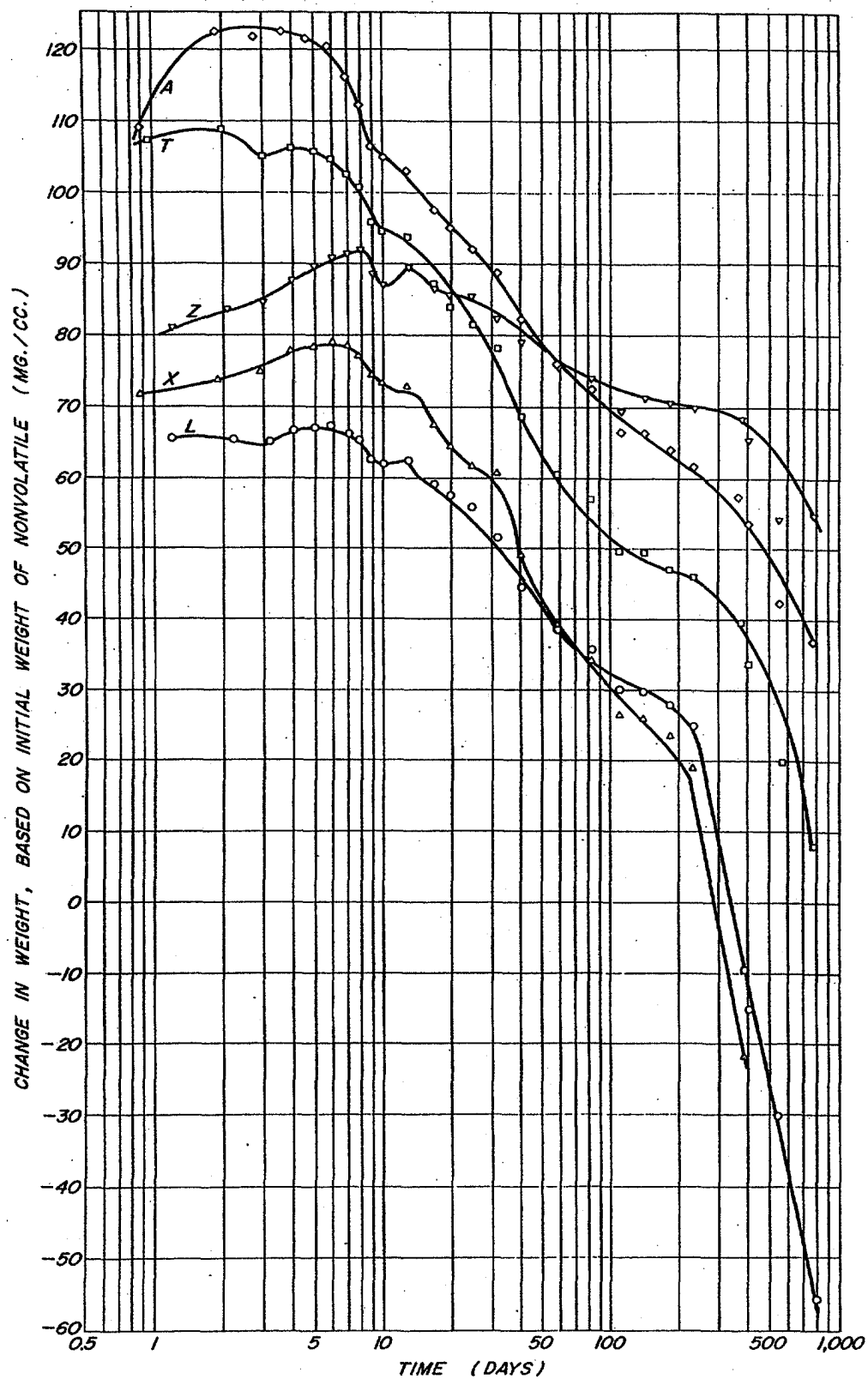


Figure 2.--Changes in weight due to change in moisture content of 382-day-old coatings of various paints brought to equilibrium successively with the atmosphere (1) in a desiccator over calcium chloride (0 moisture content), (2) in 30 percent relative humidity room, (3) in 65 percent relative humidity room, (4) in 80 percent relative humidity room, (5) in 90 percent relative humidity room, and (6) in the desiccator again.

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