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PAINT THINNERS. I. - EFFECT OF DIFFERENT PAINT THINNERS ON THE DURABILITY OF HOUSE PAINTS IN OUTDOOR EXPOSURE TESTS

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PAINT THINNERS. I.--EFFECT OF DIFFERENT PAINT THINNERS ON THE DURABILITY OF HOUSE PAINTS IN OUTDOOR EXPOSURE TESTS[1]

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Description of Paper

Results of experiments on the effect of paint thinners on the durability of coatings of house paints are reported. The kind of thinner proved to be a minor factor in durability. Nevertheless coatings were definitely more durable when the paint had been thinned with a deliberately oxidized turpentine that left a considerable residue on evaporation than when the paint was thinned with ordinary turpentine or with petroleum or coal tar distillates. The results point to the possibility that turpentine may find its most valuable use in paint after it has been converted into a nonvolatile product whose incorporation in paint coatings makes them more durable.

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The experiments described in this paper were first proposed in a conversation between the writer and F. P. Veitch of the Bureau of Chemistry and Soils, in June, 1926. I. F. Odell, Pine Institute of America Fellow at the Mellon Institute of Industrial Research, was planning similar tests at about the same time and it was decided to join forces in a single undertaking. H. K. Salzberg has since taken Odell's place for the Pine Institute. Besides the outdoor exposure tests at five testing stations reported here a corresponding series of exposures was made in an accelerated testing device at the Mellon Institute, together with additional exposure tests and laboratory experiments on other characteristics of paint thinners. The experiments at Mellon Institute, which still continue, will be reported subsequently by Salzberg. This paper is therefore the first of a series on the general subject of paint thinners.

Introduction

One reason usually given by painters for preferring turpentine to other thinners for house paint is the belief that turpentine makes coatings more durable, especially on those softwoods in which the bands of summerwood are wide (23, 21). Chemists are not as well agreed on the subject (19, p.44), although most of them think that turpentine has an advantage in the thinning of priming-coat paint for resinous softwoods such as southern yellow pine. Painters and chemists alike base their opinions about the relative value of thinners chiefly on theoretical considerations.

The following theories have been advanced:

1. The solvent theory maintains that turpentine obtains deeper penetration of paint in resinous wood because it is a better solvent than petroleum distillates for the resin supposed to interfere with penetration (23, 21, 19, p.44). If the theory is sound, coal tar distillates should be still better paint thinners than turpentine and for that reason benzol or solvent naphtha is sometimes recommended (10). The theory, however, rests on certain misconceptions. The cavities in the summerwood of softwoods, over which paint fails soonest, are not "filled with resin." On the contrary, paint liquids penetrate the summerwood of both resinous and nonresinous softwoods more readily than the springwood, on which paint lasts longer (3, 13). Hence poor adhesion of paint to summerwood is not due to insufficient penetration of paint liquids (4). Further, the

solvent action of turpentine on fresh paint has been said to promote adhesion between coats (16) but under normal conditions of exposure paint never fails by separation between coats. The solvent theory, therefore, may be dismissed as inherently illogical.

2. The catalyst theory attributes to turpentine some of the properties of metallic driers. Turpentine does oxidize readily and is able to transfer some of its combined oxygen to any linseed oil with which it may be subsequently mixed (19 p.32, 11, 22). Yet freshly distilled turpentine has no observable drying action on linseed oil. In its ordinary use as a paint thinner turpentine does not replace any of the metallic drier. It is therefore difficult to see why the alleged drying action of the turpentine should affect the durability of the paint.

3. The dispersion theory holds that turpentine-thinned paints utilize their metallic driers to better advantage and dry more promptly and uniformly because metallic soaps remain more finely dispersed in linseed oil in the presence of turpentine than in the presence of mineral spirits (25). Since the amount of drier necessary in paint is not affected by the choice of thinner the verity of this theory is doubtful; the effect of turpentine on the dispersion of paint pigments may well prove more important. Turpentine apparently causes the white pigments to flocculate more than petroleum or coal tar distillates do (20), and the choice of thinner may therefore affect the structure of the aggregates of pigments in the paint coating. It is not yet known what sort of pigment structure in coatings makes for durability.

4. The residue theory assumes that the nonvolatile residue left behind when turpentine evaporates from thin films adds to the durability of paint coatings (19 p.32, 11, 26). Objection to the theory has been made (19 p.32) because the amount of residue left by freshly distilled turpentine is very small, so that only old, oxidized turpentine should prove materially better than mineral spirits. There is evidence, however, that paint driers catalyze the oxidation of turpentine and consequently that turpentine leaves more residue in paint coatings than is commonly supposed (26). To verify the theory fully it must be shown that the residue is a desirable ingredient in paint coatings.

Few exposure tests of the effect of paint thinners on the durability of coatings have been reported. Undoubtedly many have been made but remain unpublished either because paint manufacturers conducted them for their own information or because of the common reluctance to publish results that are considered negative. Exposure tests at North Dakota Agricultural College (14, 17, 18) made on white pine, a wood with narrow bands of summerwood, failed to reveal any differences in durability that could be attributed to the kind of thinner. Tests by the American Paint and Varnish Manufacturers' Association (12) indicated equal durability on white pine for paints thinned with gum spirits or with any of five wood turpentines. A former study at the Forest Products Laboratory on southern cypress, eastern hemlock, and southern yellow pine (5) likewise showed no differences between thinners of widely different nature. None of these tests permitted close comparisons, however, because they were not made on matched boards. Differences in density and ring width between boards may have much more effect on the behavior of coatings over them than the kind of thinner in the paint. Another series of exposures made on matched boards (5) indicated that paint when thinned with turpentine is slightly more durable on southern cypress than when thinned with benzol.

Outline of the Tests

The tests reported here were made on longleaf pine (*Pinus palustris*), which is a variety of southern yellow pine that often has wide bands of summerwood, high density, and high resin content. The boards used averaged somewhat higher in density than the general value for the species (15); according to current theories any differences in durability of coatings caused by the nature of the paint thinner should be most marked on wood of this kind. The boards for the test panels were matched; that is, long boards were each cut into 10 short pieces and these pieces were then built into sets of 10 panels, each of which was coated with a paint thinned with one of the 10 thinners tested.

Tests were made with two paints, one a straight white-lead paste paint and the other a lead-zinc inert prepared paint. The 10 thinners included four turpentines, four mineral spirits, one painters' naphtha, and one coal tar naphtha. All painting was three-coat work.

Exposures were made out-of-doors at Madison, Wis., Pittsburgh, Pa., Washington, D. C., Gainesville, Fla., and Fresno, Calif. The panels were exposed in a position inclined at 45° to the vertical, facing south. The exposures began in the fall of 1927 and were completed at all stations except Pittsburgh by June, 1930. Inspections, using methods that have been published elsewhere (6), were made by the writer at least once a year.

Details of the Tests

The four turpentines were steam-distilled and destructively distilled wood turpentine, and ordinary gum-spirits, and gum-spirits turpentine purposely oxidized in the laboratory. To prepare the oxidized turpentine a part of the shipment of gum-spirits turpentine was warmed by placing the 5-gallon container in a bath of hot water and bubbling air into the turpentine through a glass tube reaching to the bottom of the container.

All of the thinners were examined at the Bureau of Chemistry and Soils, U. S. Department of Agriculture. The results appear in Table 1. The gum-spirits and steam-distilled wood turpentines conform to specification 7b of the Federal Specifications Board (7) and specification D13-26 of the American Society for Testing Materials (1). The destructively distilled wood turpentine conforms to specification D236-27 of the A. S. T. M. (2). The oxidized turpentine falls outside the limits of the specifications for gum-spirits turpentine.

The amounts of residue left when weighed samples of the four turpentines evaporated from tared Petri dishes under arbitrarily chosen conditions were determined at the Forest Products Laboratory as follows:

Turpentine	Per cent
Oxidized gum-spirits	5.9
Steam-distilled wood	2.1
Destructively distilled wood	1.5
Ordinary gum-spirits	1.3

When a sample of the gum-spirits turpentine was redistilled, the fresh distillate left 0.1 per cent residue on evaporation. The figures are relative and are approximate only, because the amount of residue varies with the conditions under which

Table 1.--Results of examination of thinners at the Bureau of Chemistry and Soils, U.S. Department of Agriculture

A.--TURPENTINES

	Steam-distilled wood	Destructively distilled wood	Ordinary gum-spirits	Oxidized gum-spirits
Specific gravity 15.5/15.5° C...	0.8610	0.8610	0.8668	0.8818
Initial boiling point at 760 mm.	154° C.	150° C.	154° C.	156° C.
Distilled below 170° at 760 mm..	93%	74%	98%	78%
Distilled below 180° at 760 mm..	....	96%	....	....

B.--PETROLEUM PRODUCTS

	Mineral spirits from crude oil from --				V.M. & P. naphtha
	California	Pennsylvania	Mid-Continent	Mexico	
Copper strip test for sulphur...	negative	negative	negative	positive	negative
Initial boiling point at 760 mm.	138° C.	145° C.	158° C.	149° C.	54° C.
5 per cent over at............	164°	159°	175°	164°	70°
97 per cent over at...........	209°	204°	236°	218°	190°

C.--COAL TAR PRODUCT

	160° Solvent naphtha
Initial boiling point at 760 mm..........	126° C.
5 per cent over at.....................	134°
97 per cent over at....................	170°

the evaporation takes place. On evaporation from paint coatings in the presence of linseed oil, paint driers, and pigments the residues probably are greater (26).

The four mineral spirits were products derived respectively from Pennsylvania, Mid-Continent, California, and Mexican crude oil. With the exception of the one from Mexican crude oil, they met specification 16 of the Federal Specifications Board (8). The mineral spirits from Mexican crude oil contained enough sulphur to give a positive copper strip test but it did not cause noticeable discoloration of the paints, both of which contained white lead.

The varnish makers' and painters' naphtha was a product from Mid-Continent crude oil. It had a much lower range in boiling point and a higher rate of evaporation than the mineral spirits.

The coal tar product was 160° solvent naphtha.

The Paints

The two paints represented common practice with paste paint and with prepared paint, respectively.

The paste paint was commercial basic carbonate white lead containing 92 per cent pigment and 8 per cent raw linseed oil by weight. It was reduced for application as follows:

	First coat	Second coat	Third coat at stations except Gainesville	Third coat at Gainesville
Paste white lead, lb.	100	100	100	100
Raw linseed oil, gal.	1.5	1.5	3.5	2.0
Thinner, gal.	2.0	1.5	.125	1.0
Paint drier, gal.	.125	.125	.125	.25

The priming-coat reduction departs markedly from the customary recommendation of 4 gallons of linseed oil and 2 gallons of thinner. The increased proportion of thinner is thoroughly conventional, however, since the wood to be painted was longleaf pine, but the high content of pigment is unusual. In the writer's opinion it had much to do with the conspicuously better service given in these tests by the paste paint. The second and third coat reductions conform to customary practice. The special third-coat reduction at Gainesville was designed to reduce discoloration of white-lead paint by lichen and sooty mold. In that respect it was at best only partly successful.

The prepared paint was ground at the Forest Products Laboratory. The pigment paste was reduced for third-coat application as is done in manufacturing prepared paint except that the thinner was withheld so that the chosen thinner could be incorporated later. To make third-coat paint the required amount of the desired kind of thinner was added. To make second-coat paint there was added 1 pint of thinner per gallon of third-coat paint. To make priming-coat paint 3 pints of thinner were added per gallon of third-coat paint. A prepared paint does not permit reduction to the heavily pigmented priming and second-coat paints possible with paste paint. In that respect the prepared paint was at a distinct disadvantage in these experiments as compared with the paste paint.

The composition of the prepared paint, after addition of the amount of thinner necessary for the third coat, was;

Pigment, 66 per cent by weight,
composed of;

Basic carbonate white lead	45 per cent by weight
Zinc oxide, lead free	40 " " " "
Silica	8 " " " "
Barytes	7 " " " "

Vehicle, 34 per cent by weight,
composed of:

Raw linseed oil	90 per cent by weight
Liquid paint drier	5 " " " "
Thinner	5 " " " "

This composition lies within the limits of specification 10b of the Federal Specifications Board, in effect at the time these tests were started (9), and conforms closely to the great majority of paints that the government was receiving under that specification. In its characteristic behavior it differs from that of straight white-lead paint as much as any paint could that fell within the limits of the specification. The specification has since been changed in a way that excludes paint of this composition.

The constants of the raw linseed oil used for grinding the prepared paint and for making the reductions with both paints were not determined. Its acid number may have been higher than that desirable in paint containing zinc oxide. If so the prepared paint was put at a further disadvantage as compared with the paste paint.

The Test Panels

The longleaf-pine lumber was in the form of boards 1 by 6 inches by 16 feet, surfaced on four sides, of a select grade, and air dry.

Most of the boards were flat grained. Many came from small trees or from the centers of logs so that the annual rings curved sharply and thus some boards presented partly flat-grain and partly edge-grain surfaces. A few had pith through a portion of their length, making the surfaces near one end mostly edge grain while near the other end they were predominantly flat grain.

The boards were sorted into groups of three, each of which provided the lumber for one set of 10 panels corresponding to the 10 thinners. For each exposure station except Pittsburgh there were two sets of panels, one set for paste paint and the other for prepared paint. The three boards for a set of panels were each cut into 10 pieces 18 inches long. The 30 cuttings were assembled into 10 panels each of which had one piece from each board. The pieces were distributed among the 10 panels so that successive cuttings from the boards were coated with paints thinned as follows:

Destructively distilled wood turpentine
Steam-distilled wood turpentine
Gum-spirits turpentine
Oxidized gum-spirits turpentine
Mineral spirits, Mid-Continent oil
Naphtha from Mid-Continent crude oil
Mineral spirits, Pennsylvania oil
Solvent naphtha from coal tar
Mineral spirits, California oil
Mineral spirits, Mexican oil

Alternating the turpentines with the other thinners, instead of grouping them together at one end of the boards would have improved this lay-out greatly.

The three pieces composing a test panel were placed side by side and held firmly together by cleats nailed on the back. The concealed edges of the pieces remained uncoated. Backs, ends, and edges of the completed panels were protected by two coats of aluminum paint made with long oil spar varnish. About 11 per cent of the pieces were predominantly edge grain. In assembling the pieces no effort to turn them all bark side out was made and consequently about 48 per cent of them, distributed at random, were pith side out. The inferiority of the pith side of flat-grained boards was not appreciated when these tests were started. With some woods this shortcoming in the lay-out would have proved fatal to the object of the test, but boards of southern yellow pine do not develop loose grain easily on the pith side unless subjected to mechanical shock. Only three pieces, all from one board, developed loose grain so that the validity of the conclusions drawn is not seriously impaired by this oversight.

The panels for Pittsburgh were designed differently. Four 12-foot boards were each cut into 10 pieces 12 inches long. The 10 pieces from each board made a set of panels. Two sets, one for each paint, were exposed on the roof of the Mellon Institute. The other two sets were tested in an accelerated testing device the results of which are not included in this report. These panels were painted on backs, ends, and edges with two coats of aluminum paint.

Painting and Exposing the Panels

All painting was done at the Forest Products Laboratory during August and September, 1927, and all exposures were begun by November 14, 1927. In the preparation, all knots were first sealed with 4.5-pound cut orange shellac varnish to which had been added 4 per cent by weight of castor oil. This sealer prevented excellently the early flaking of coatings over knots, although even with its help such coatings finally cracked characteristically. Pitch streaks were not coated with the knot sealer. Painting was done indoors. One week was allowed between coats for drying. The panels were not exposed outdoors to sunlight between coatings. The weight of paint applied to each panel was recorded.

The finished panels were exposed outdoors on test fences, inclined at an angle of 45° from the vertical and facing south. At Pittsburgh the panels were held in racks on the roof of the Mellon Institute.

Inspections

The writer recorded eight inspections at Madison, three each at Washington, Gainesville, and Pittsburgh, and two at Fresno. Independent inspections at Pittsburgh and Gainesville were made by H. K. Salzberg. Exposures were continued until the panels were rated "bad" in integrity of coating, that is, until much of the summerwood was left bare. At some stations much of the springwood coated with prepared paint was also bare at the end of the test. The writer followed his dynamic method of evaluating paint service (6). In addition, since the tests were on matched boards, he made static comparisons of the panels within each set. Because of the 45° angle of exposure, the dense pine lumber, the severity of the climate toward paint at some of the stations, and the high content of zinc oxide in the prepared paint, deterioration of the coatings, especially those of the prepared paint, took place more rapidly than is desirable at stations that could be visited only once a year.

Results and Discussion

On the whole the differences in serviceableness of coatings attributable to the kind of thinner proved to be too small to have much immediate bearing upon painting practice. Differences in the physical characteristics of boards and in the pigment composition of the paints affected the durability of the coatings much more markedly than the choice of thinner. Yet the results with different thinners do contain suggestive information for chemists of the paint and naval stores industries. The trends revealed, although mostly small in magnitude, are distinct and unmistakable. Further research along the lines they indicate may well lead to significant improvement in paints for wood and to more profitable utilization of turpentine. The study also contributes materially to the technic of making paint-exposure tests on wood. The results should therefore be considered primarily from the point of view of paint chemistry rather than that of wood painting practice.

Table 2 summarizes the results of the experiments. The subcolumns in Table 2 headed respectively "Durability, integrity" and "Durability, protection and integrity" are the dynamic records of paint service (6). The subcolumn headed "Order of merit at end" is the static record made when the panels were removed from the test by arranging the panels within each set in the order of increasing amount of wood exposed by paint flaking, the panel showing least bare wood being assigned merit number 1. When two or more panels were so nearly alike that distinction could not be drawn between them they were given the same merit number.

Effect of Thinner on Spreading Rate

The effect of the thinners on the spreading rate of the paints paralleled closely their effect on paint consistency. The consistency and spreading rate of white-lead paint were the same whether it was thinned with turpentine or with mineral spirits. With the lead-and-zinc paint, however, the turpentines made mixtures less fluid than those of the mineral spirits.

	Number of panels	Average amount of paint applied in lb. per 100 sq.ft.	Probable error of the average
White lead paint			
4 turpentines	20	7.37	± 0.07
4 mineral spirits	20	7.44	± 0.08
Lead and zinc paint			
4 turpentines	20	5.02	± 0.06
4 mineral spirits	20	4.76	± 0.04

Observations of the effect of the thinners on the consistency of the paints led to the following conclusions (24):

Table 2.--Effect of different thinners on the durability of paint
Results at Madison, Wis.

Thinner	With paste paint				With prepared paint			
	Weight of pigment applied	Durability: Integrity	Durability: Protection and integrity	Order of merit at end	Weight of pigment applied	Durability: Integrity	Durability: Protection and integrity	Order of merit at end
	Lbs. per 100 sq.ft.	Months	Months		Lbs. per 100 sq.ft.	Months	Months	
Turpentines,								
gum spirits	6.99	22	21	4	5.23	15	15	3
steam distilled wood	7.05	27	23	2	4.61	14	14	4
destructively distilled wood	7.43	30	30	2	4.48	15	15	4
oxidized gum spirits	7.29	30	24	1	5.05	16	16	1
Mineral spirits,								
from Pennsylvania crude oil	7.17	24	23	3	5.02	16	16	3
from Mid-Continent crude oil	7.48	26	23	3	4.84	16	16	3
from California crude oil	7.15	26	24	3	4.53	15	15	5
from Mexican crude oil	8.08	30	27	1	4.57	15	15	6
Painters' naphtha from Mid-Continent crude oil	7.18	28	26	2	5.15	16	16	2
Solvent naphtha from coal tar	7.07	31	28	2	5.60	16	16	2

Table 2.--Effect of different thinners on the durability of paint

Results at Washington, D. C.

Thinner	With paste paint: Weight of pigment applied	With paste paint: Durability: Integrity	With paste paint: Durability: Protection and integrity	With paste paint: Order of merit at end	With prepared paint: Weight of pigment applied	With prepared paint: Durability: Integrity	With prepared paint: Durability: Protection and integrity	With prepared paint: Order of merit at end
	Lbs. per 100 sq.ft.	Months	Months		Lbs. per 100 sq.ft.	Months	Months	
Turpentines,								
gum spirits	6.88	15	13	3	5.73	13	13	2
steam distilled wood	7.57	18	13	2	5.53	13	13	2
destructively distilled wood	7.18	18	13	2	4.64	13	13	2
oxidized gum spirits	7.54	24	18	1	5.22	13	13	2
Mineral spirits,								
from Pennsylvania crude oil	6.92	15	13	5	5.74	13	13	1
from Mid-Continent crude oil	7.47	15	13	4	4.65	13	13	2
from California crude oil	6.50	18	11	4	4.61	13	13	2
from Mexican crude oil	8.05	18	11	3	4.73	13	13	1
Painters' naphtha from Mid-Continent crude oil	8.14	22	13	3	5.05	13	13	1
Solvent naphtha from coal tar	7.36	18	13	4	5.11	13	13	1

Table 2.--Effect of different thinners on the durability of paint
Results at Gainesville, Fla.

Thinner	With paste paint				With prepared paint			
	Weight of pigment applied	Durability		Order of merit at end	Weight of pigment applied	Durability		Order of merit at end
		Integrity	Protection and integrity			Integrity	Protection and integrity	
	Lbs. per 100 sq.ft.	Months	Months		Lbs. per 100 sq.ft.	Months	Months	
Turpentines,								
gum spirits..................	7.08	15	12	5	4.80	15	15	4
steam distilled wood.........	7.09	15	6	5	4.99	15	15	2
destructively distilled wood	7.49	15	12	5	4.04	15	15	2
oxidized gum spirits.........	8.20	35	18	1	5.17	15	15	1
Mineral spirits,								
from Pennsylvania crude oil.	8.37	23	12	3	4.81	15	15	4
from Mid-Continent crude oil	7.99	18	9	5	4.05	15	15	5
from California crude oil...	6.76	23	12	3	4.65	15	15	3
from Mexican crude oil......	8.08	23	12	2	4.45	15	15	3
Painters' naphtha from Mid-Continent crude oil.....	8.38	23	12	2	5.12	15	15	3
Solvent naphtha from coal tar.	7.89	15	3	4	5.13	15	15	3

Table 2.--Effect of different thinners on the durability of paint
Results at Fresno, Calif.

Thinner	With paste paint				With prepared paint			
	Weight of pigment applied	Durability: Integrity	Durability: Protection and integrity	Order of merit at end	Weight of pigment applied	Durability: Integrity	Durability: Protection and integrity	Order of merit at end
	Lbs. per 100 sq.ft.	Months	Months		Lbs. per 100 sq.ft.	Months	Months	
Turpentines,								
gum spirits	6.61	19	19	3	4.79	11	11	2
steam distilled wood	6.80	19	19	3	5.12	17	17	2
destructively distilled wood	7.50	19	19	2	4.72	6	6	2
oxidized gum spirits	7.78	22	22	1	4.83	17	17	2
Mineral spirits,								
from Pennsylvania crude oil	7.02	19	3	4	5.06	17	17	2
from Mid-Continent crude oil	7.47	19	19	4	4.61	17	17	2
from California crude oil	7.68	19	3	3	4.97	19	19	1
from Mexican crude oil	7.14	19	3	2	4.73	17	17	2
Painters' naphtha from Mid-Continent crude oil	7.00	19	19	3	5.15	19	19	2
Solvent naphtha from coal tar	7.04	19	19	2	4.99	17	17	2

Table 2.--Effect of different thinners on the durability of paint
Results at Pittsburgh, Pa.

Thinner	With paste paint: Weight of pigment applied	With paste paint: Durability: Integrity	With paste paint: Durability: Protection and integrity	With paste paint: Order of merit at end	With prepared paint: Weight of pigment applied	With prepared paint: Durability: Integrity	With prepared paint: Durability: Protection and integrity	With prepared paint: Order of merit at end
	Lbs. per 100 sq.ft.	Months	Months		Lbs. per 100 sq.ft.	Months	Months	
Turpentines,								
gum spirits	8.28	41	41	1	5.09	29	29	2
steam distilled wood	7.74	41	41	1	5.75	26	26	3
destructively distilled wood	7.50	41	41	1	5.25	35	35	1
oxidized gum spirits	7.47	41	41	1	5.31	29	29	2
Mineral spirits,								
from Pennsylvania crude oil	7.53	41	41	1	4.96	26	26	3
from Mid-Continent crude oil	7.49	41	41	1	4.91	26	26	4
from California crude oil	7.40	41	41	1	4.74	26	26	5
from Mexican crude oil	7.00	41	41	1	4.52	28	28	2
Painters' naphtha from Mid-Continent crude oil	7.73	41	41	1	4.54	26	26	2
Solvent naphtha from coal tar	7.11	41	41	1	4.62	26	26	5

All panels with paste paint at Pittsburgh were still rated Good in integrity and protection when last inspected, which was 35 months after exposure. The durability was therefore arbitrarily set at 41 months and they were all given the merit rating 1.

Table 2.--Effect of different thinners on the durability of paint
Weighted average for all stations

Thinner	With paste paint				With prepared paint			
	Weight of pigment applied	Durability: Integrity	Durability: Protection and integrity	Order of merit at end	Weight of pigment applied	Durability: Integrity	Durability: Protection and integrity	Order of merit at end
	Lbs. per 100 sq.ft.	Months	Months		Lbs. per 100 sq.ft.	Months	Months	
Turpentines,								
gum spirits	7.09	21.1	19.9	7	5.13	15.6	15.6	6
steam distilled wood	7.23	22.8	18.9	5	5.16	16.3	16.3	5
destructively distilled wood	7.41	23.4	21.7	4	4.58	15.4	15.4	3
oxidized gum spirits	7.68	29.6	23.5	1	5.10	17.2	17.2	1
Mineral spirits,								
from Pennsylvania crude oil	7.40	23.2	16.8	7	5.12	16.7	16.7	5
from Mid-Continent crude oil	7.60	22.5	19.6	8	4.58	16.7	16.7	9
from California crude oil	7.08	24.2	16.6	6	4.82	16.9	16.9	8
from Mexican crude oil	7.73	25.2	17.2	2	4.60	16.8	16.8	7
Painters' naphtha from Mid-Continent crude oil	7.69	25.6	20.7	3	5.03	17.1	17.1	2
Solvent naphtha from coal tar	7.32	23.6	19.4	5	5.12	16.7	16.7	4

In computing the weighted averages the Pittsburgh station was given a weight of two-thirds because the sets of panels were made from two boards instead of three.

"1. Less thinner of any kind is required by white lead than by an equal weight of white lead-zinc oxide mixture.

"2. There appears to be no difference in the thinning effect of the various solvents on white lead when linseed oil is present.

"3. There is a difference between the thinning effect of turpentines on the one hand and other thinners on the other hand upon a mixture of white lead and zinc oxide in the presence of linseed oil. Thinners other than turpentine have greater thinning effect, but the turpentines produce better suspensions, that is, less tendency for the pigment to settle.

"4. Partly oxidized turpentine produces the best suspension of white lead and zinc oxide and appears to give the smoothest and most continuous paint coating. Old gum spirits seems to be the best thinner for white lead and zinc oxide paints for outside use."

Much heavier coatings were applied with the paste paint than with the prepared paint because of the heavily pigmented reductions for priming and second coat paint that paste paint made possible. Although the specific gravity of white lead is only about 13 per cent higher than that of the pigment in the prepared paint, over 50 per cent more white lead than prepared paint pigment was usually applied. In comparing the two paints for durability that fact must be considered.

Effect of Thinner on Appearance of Coating

Although the coatings were judged for appearance at every inspection, the ratings in appearance were omitted from Table 2. The omission is for two reasons: First, there were rarely any differences in appearance within the panels of any one set that might conceivably be attributed to the effect of the thinner and, second, tests made on panels inclined at 45° are subjected to abnormal conditions of dirt collection that throw doubt upon the practical value of observations on appearance. At Pittsburgh both sets of panels became so dirty that they were literally black. In March, 1929, these panels were washed with soap and water, which left the panels painted with prepared paint reasonably clean although those with white-lead paint remained grey. By March of 1930 the white-lead panels were again badly soiled while those with the prepared paint remained fairly clean. There can be no doubt that the excessive accumulation of dirt at Pittsburgh protected the paint coatings from the weather and made them much more durable, if appearance is neglected.

Effect of Thinner on Paint Checking

At Madison typical checking of white-lead paint set in distinctly later on the panel for which oxidized turpentine was the paint thinner than it did on any other panel in the set. On all the other panels of the set the checking began practically simultaneously. At the other stations inspections were not made frequently enough to detect differences in the onset of paint checking.

Effect of Thinner on Durability

With respect to the effect on the durability of the coating, one thinner stands out distinctly as the best even though the actual amount of the difference was small. This thinner is the oxidized gum-spirits turpentine, which left much more residue on evaporation than the other turpentines. At Washington, Gainesville, and Fresno with the paste paint the advantage in favor of oxidized turpentine was unmistakable. The fact that the prepared paint failed more rapidly than the paste paint made detection of differences caused by thinners more difficult for the prepared paint, but both the dynamic and the static treatments of the inspection data indicate clearly that the oxidized turpentine was the best.

The three types of turpentine that were not deliberately oxidized differed only slightly in their effect on coating durability. These small differences may not be significant, of course, but it is interesting to note that the gum-spirits turpentine, which left the least residue on evaporation, is also the one that seemed to contribute least to the durability of the coatings. The behavior of the turpentines in these experiments therefore bears strong evidence that the residue left permanently in paint coatings for which turpentine is the thinner is the desirable ingredient that tends to make the coatings last longer and that the value of a turpentine in this respect is a matter of the amount of residue it leaves behind.

The coatings of prepared paint thinned with the four mineral spirits were practically identical in behavior. Although differences were observed with the paste paint, they are not considered significant for reasons that are pointed out in the next paragraph.

The three unoxidized turpentines as a group were superior to the four mineral spirits as a group when compared by static treatment of the data. Thus the averages of the merit numbers are:

	Paste paint	Prepared paint
Unoxidized turpentines	5.3	4.7
Mineral spirits	5.8	7.2

When the comparison is made on the basis of the dynamic treatment the average figures for durability are:

	Paste paint		Prepared paint	
	Integrity only	Integrity and protection	Integrity only	Integrity and protection
Unoxidized turpentines.....	22.4	20.2	15.8	15.8
Mineral spirits..	23.8	17.8	16.8	16.8

The shorter average durability in integrity for the paints thinned with turpentine may be traced back to four boards whose physical characteristics varied in passing from the end at which the three pieces for the unoxidized turpentines were cut to the end at which the pieces for other thinners were taken. One of these boards, in the set of panels with mixed paint at Fresno, developed loose grain on the three pieces in the three panels for the turpentines, which were all turned pith side out. Loose grain always causes very early failure of paint containing much zinc oxide. There was no loose grain on any other piece in these experiments. One of the other three variable boards was in each of the sets of panels at Madison and one in the set with paste paint at Gainesville. All three were markedly flat grained at the turpentine end of the set and more nearly edge grained at the other end. On all three of these boards the two mineral-spirits paints for which the pieces were cut closer to the turpentine end compared unfavorably with the two mineral-spirits paints for which the pieces were cut from the opposite end of the boards. The comparisons drawn between the three turpentines, however, can not be attributed to the variations in these boards. Taking these facts and the static ratings into consideration the writer believes that the turpentines proved superior to the mineral spirits in proportion to the amount of residue they left permanently in the coatings, and that the four mineral spirits did not differ significantly from one another.

The results obtained with solvent naphtha are very similar to those with mineral spirits. No superiority for solvent naphtha over mineral spirits is evidenced.

From the standpoint of durability, varnish makers' and painters' naphtha, which is by far the most rapidly volatile of the thinners studied, proved distinctly better than any thinner except oxidized turpentine. The following theory is advanced in explanation of this finding: In coatings of paints containing granular pigments the pigments tend to concentrate at the bottom of the paint film, that is, at the side of the film nearest the supporting surface. Near the exposed surface of the film the concentration of pigment is low (fig. 2 in reference 13). In other words the pigments tend to settle in the fresh paint coating much as they settle in the can of paint when it is not stirred, although the force under which the settling takes place in the fresh paint film probably is not gravity. Rapid evaporation of the paint thinner would therefore tend to decrease the amount of settling in the fresh paint film before the oil hardened enough to prevent further movement.

Comparison of Dynamic and Static Records

In comparing results by the dynamic and by the static treatments of the inspection data it should be remembered that the two treatments are fundamentally different. The dynamic treatment aims to express the age of the coating when it begins to flake generally from the summerwood or to permit the wood to weather. The static treatment merely arranges the panels in the order of the amount of wood area left bare by flaking of the coating at some arbitrarily chosen time. The dynamic treatment is of more practical significance because it tells when the coating requires renewal of repainting. The static treatment is more convenient to the inspector and has been used practically exclusively by previous workers. Within a series of contemporaneous tests the static order of merit is not always the same at succeeding inspections. In the writer's opinion the static treatment is of very doubtful value at best unless the comparisons are confined to matched pieces of wood painted with the same type of paint, as was done in these tests. Even then no closer parallel between results by the two treatments is to be expected than was found.

A Possible New Use for Turpentine

The results of these experiments suggest that turpentine has not yet found its most valuable use in house paints because it may be capable of conversion into a product whose presence permanently in the paint coating may give greater durability. Merely as a volatile thinner for controlling the consistency of paint, turpentine meeting current (1931) specifications faces keen competition from essentially cheaper liquids to which it is not greatly superior. Since the comparatively small amount of turpentine product left in a paint coating when partly oxidized turpentine evaporates increases the durability observably, it seems likely that larger amounts of the turpentine product may prove markedly beneficial. Research into the possibility of manufacturing from turpentine a product that would be uniquely serviceable in making paint should therefore be profitable to both the naval stores and the paint industries.

Conclusions

1. Exterior exposure tests at five stations made with two types of house paint on longleaf pine, a dense and resinous softwood, show that variations in serviceableness of coatings caused by the nature of the volatile liquid with which the paint is thinned are much less important than such factors as the pigment composition of the paint or the physical character of the wood painted.

2. Turpentine tends to make paint coatings more durable in proportion to the amount of residue it leaves permanently in the coating. When gum-spirits turpentine was oxidized by warming it and passing air through it and then used as the paint thinner the durability was definitely improved.

3. As far as their effect on durability of coatings is concerned, steam-distilled and destructively distilled wood turpentine meeting current (1931) specifications are as acceptable as gum-spirits turpentine for thinning house paint.

4. The type of crude oil from which mineral spirits is refined does not affect the durability of paint coatings for which it is used as thinner.

5. Varnish makers' and painters' naphtha, which evaporates more rapidly than mineral spirits, seems to make paint coatings more durable. It is suggested that the greater speed of evaporation leaves less time for the pigments to settle in the fresh coating and therefore results in more uniform dispersion of the pigments in the hardened coating.

6. Solvent naphtha from coal tar has no advantages over turpentine or petroleum distillates as a paint thinner.

7. Turpentine may find its most valuable use in paint through conversion into a nonvolatile product that will form a desirable permanent ingredient of the coating.

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List of References

1. Am. Soc. Testing Materials, Standards II, 300 (1930).
2. Am. Soc. Testing Materials, Standards II, 302 (1930).
3. Browne, Federation of Paint and Varnish Productions Clubs, Official Digest No. 95, 106 (Apr. 1930); Am. Paint J. 14, 22 (Apr. 7, 1930); Paint, Oil and Chem. Rev. 89, 9 (Mar. 20, 1930).
4. Browne, Ind. Eng. Chem. 23, 290 (1931).
5. Browne, Ind. Eng. Chem. 22, 847 (1930), especially p.850.
6. Browne, Proc. Am. Soc. Testing Materials 30 II, 852 (1930).
7. Federal Specifications Board Specification No. 7b (1926), U. S. Bureau of Standards Cir. No. 86.
8. Federal Specifications Board Specification No. 16 (1923), U. S. Bureau of Standards Cir. No. 98.
9. Federal Specifications Board Specification No. 10b (1927), U. S. Bureau of Standards Cir. No. 89.
10. Gardner, Paint Mfrs. Assoc. U. S., Special Cir. Jan. 1923.
11. Gardner, Paint Mfrs. Assoc. U. S., Tech. Cir. 163, 106 (1923).
12. Gardner, Paint Mfrs Assoc. U. S., Bull. 30 (1910); Bull. 36 (1913).
13. Haslam and Werthan, Ind. Eng. Chem. 23, 226 (1930).
14. Ladd and Ware, North Dakota Agric. College Expt. Station Bull. 92, 173 (1911).
15. Markwardt, U. S. Dept. of Agric. Tech. Bull. 158 (1930).
16. Morgan, J. Roy. Soc. Arts 74, 271 (1926).
17. Pearce, Ladd, and Kelly, North Dakota Agric. College Special Bull. 1 No. 4 (1922).
18. Pearce and Loudon, North Dakota Food Commissioner and Chemist Bull. No. 8 (1925).

19. Pickard, Supplement to Am. Paint J. July 28, 1924.

20. Rhodes and Wells, Ind. Eng. Chem. 21, 1273 (1929).

21. Save the Surface Campaign, Guide Book of Painting and Varnishing p. 23 (1929).

22. Schönbein, J. Prakt. Chem. 52, 135 (1851).

23. Vanderwalker, "Painting and Decorating," official textbook Internatl. Assoc. Master House Painters (1922) pp. 60, 110, 166.

24. Veitch, correspondence in files at Forest Products Laboratory.

25. Wolff, "Die Lösungsmittle der Fette, Oele, Wachse, und Harze," 2d ed. (1927) p. 65.

26. Woodmansey, J. Soc. Chem. Ind. 36, 1253 (1917).