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EFFECT OF CERTAIN PIGMENTS ON LINSEED OIL

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By E. W. Boughton

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PURPOSE OF THE INVESTIGATION

Since white lead, as supplied to painters and paint dealers, is almost always ground to a paste with raw linseed oil, it seemed desirable to determine whether or not the constants of the oil in the paste are materially changed during storage. Furthermore it seemed desirable to obtain some numerical data regarding the extent to which certain pigments combine with linseed oil during the drying process, and also to make some experiments with drying paint films to determine the relative effects of different pigments on the rate of oxidation of the oil.

EFFECT OF STORAGE OF WHITE LEAD—LINSEED OIL PASTE

In a previous paper [1] the author showed that when mixtures of linseed oil and various pigments (including white lead) in the proportions of paint ready for use were kept in closed containers for two years only slight changes in the constants of the oil resulted. These results showed that if, in the analysis of such mixtures from closed paint cans, oils were obtained which showed abnormal constants, they should not be considered as pure linseed oils. Hannay [2] stated that there is absolutely no combina-

[1] Circ. 111, Bureau of Chem., Dept. of Agriculture; 1913. This paper contains a review of the literature on the action of pigments on linseed oil in closed containers.

[2] Chemical News, 67, p. 268; 1893.

29311°—16

tion of oil and white lead in a paste during storage in closed containers; that the oil can be completely extracted from the paste; and that the extracted oil contains no lead. Harland [3] disagreed with Hannay and stated that the extracted oil always contains small amounts of lead. Davis and Klein [4] confirmed Harland's statement, and also showed that in the extraction of the oil from the paste very small amounts of oil remain with the pigment. They attribute this to the formation of insoluble lead salts of stearic acid or of oxidized unsaturated acids. In a later paper [5] Klein stated that the formation of the small amount of "organometallic" salt is due to the action of the free fatty acids in the oil on the white lead, and that no saponification of the glycerides occurs. Thompson [6] stated that, while a small amount of lead is dissolved by the oil in a white-lead paste, there is no evidence to show that there is any considerable chemical reaction between the pigment and the oil.

In August, 1913, G. W. Thompson, of the National Lead Co., prepared for the author a quantity of white lead—linseed oil paste. Several friction-top cans, holding 1 pound each, were filled with the paste, and these, together with samples of the oil and dry pigment used, were sent to the author. The results of analyses of oil, pigment, and paste are shown in Table 1.

TABLE 1

Analyses of White Lead, Linseed Oil, and Paste

White lead:[a]			Linseed oil:		
Specific gravity		6.78	Specific gravity at 15.6/15.6° C		0.936
Moisture	per cent	.21	Refrac. index at 25° C		1.481
$PbCO_3$	do	71.00	Acid number		1.9
$Pb(OH)_2$	do	28.29	Saponification number		190
$PbSO_4$	do	.23	Iodine number (Hanus)		188
$PbSO_3$	do	.05	Ash	per cent	.20
SiO_2	do	.004	Paste:		
$Al_2O_3+Fe_2O_3$	do	.02	Pigment	per cent	91.9
Bi_2O_3	do	.01	Oil (by difference)	do	8.1
CaO	do	.03			
MgO	do	.02			
Alkalies as Na_2O	do	.06			
Acetates as $C_2H_4O_2$	do	.14			
Total		100.064			

[a] Analysis by F. W. Smither.

The oil was divided into several 100 cc samples and kept in stoppered bottles. With each examination of the oil from the

[3] Chemical News, **67**, p. 301; 1893.

[4] J. Soc. Chem. Ind., **26**, p. 848; 1907.

[5] A paper read before the Paint and Varnish Society of England, December, 1913; published as Lab. Bull, National Lead Co., February, 1914.

[6] Drugs, Oils, and Paints, **30**, p. 375; 1915.

paste a simultaneous examination of one of these samples was made. These examinations were made at varying intervals during a period of two and one-half years, the oil in the paste being extracted with ether, recovered, and freed from the last traces of solvent by heating in carbon dioxide at 105–110° C. The results of the analyses, as given in Table 2, show that no material changes in the constants of the oil had occurred during 25 months. It will be noted that the percentage of ash obtained from the oil extracted from the paste was less, in every analysis but the last, than that from the oil alone, although the former contained lead. This diminution of yield of ash by mixing an oil with a pigment is a common occurrence and may be explained by the removal of calcium phosphate from the oil. The experiment is being continued.

TABLE 2

Analyses of Raw Linseed Oil and Oil from Paste

	Time after grinding									
	Five days		Five months		Ten months		Twenty months		Twenty-five months [a]	
	Oil alone (original oil)	Oil from paste	Oil alone	Oil from paste	Oil alone	Oil from paste	Oil alone	Oil from paste	Oil alone	Oil from paste
Specific gravity at 15.6/15.6° C.	0.936	0.937	0.936	0.937	0.936	0.937	0.936	0.937	0.936	0.937
Acid number	1.9	1.6	2.1	1.3	2.0	1.4	2.3	1.5	2.1	1.7
Saponification number	190	190	191	189	192	192	189	189	189	190
Iodine number (Hanus)	188	187	189	189	189	190	191	190	188	188
Ash (per cent)	0.20	0.19	0.20	0.16	0.19	0.14	0.20	0.19	0.18	0.19
Iodine number of fatty acids (Hanus)	.....	.....	195	196	197	196	196	196	194	194
Refr. index of fatty acids at 25° C.	1.471	1.471	1.471	1.471	1.471	1.471	1.471	1.471	1.471	1.471

[a] Subsequent to the preparation of this paper analyses were made after the samples had been kept for 31 months. The figures obtained were all within experimental error of those given in the columns under the heading "25 months," with the exception that the acid number of the "oil alone" was 3.0.

EFFECT OF STORAGE OF MIXTURES OF LINSEED OIL AND VARIOUS PIGMENTS IN PARTIALLY FILLED CONTAINERS

At the completion of the experiments by the author [7] on the action of pigments on linseed oil (see p. 1) the jars containing the remainder of the paints were closed and allowed to stand for 1 year in a closet having a glass door where the light was dim

[7] Loc. cit.

and diffused. The jars were of glass, having a square bottom 2 by 2 inches and rectangular sides 2 by 6 inches, and were approximately one-third filled. The oil was then extracted by ether, recovered, and examined. The results of the examinations, as given in Table 3, show that considerable change had taken place in the oil, except in the zinc yellow, chrome yellow, and artificial graphite paints. White lead and white zinc were the only pigments that caused a large increase in the yield of ash from the oil.

TABLE 3

Constants of Oils Recovered from Pigment—Oil Mixtures After Storage for one year in Partially Filled Containers

Pigment	Per cent pigment	Per cent oil	Constants of oils			Nature of oils
			Specific gravity at 15.6°/15.6° C	Iodine number (Hanus)	Per cent ash	
White lead [a]	72	28	0.976	145	1.02	Orange red; viscous; skin on surface.
China clay (kaolin)	50	50	.976	138	.18	Bleached; viscous; skin on surface.
Indian red	50	50	.973	144	.13	Orange red; viscous; skin on surface.
Flake graphite	40	60	.964	151	.14	More viscous than original oil.
Magnetic oxide black [b]	46	54	.949	167	.13	Do.
Zinc yellow [c]	45	55	.934	177	.15	Same as original oil.
Chrome yellow [d]	66	34	.934	175	.18	Bleached.
Artificial graphite	42	58	.935	181	.11	Same as original oil.
White zinc [e]	39	61	.969	162	.99	Bleached; viscous; skin on surface.
Chromium oxide green	51	49	.970	153	.06	Orange red; viscous.
Original oil			.934	180	.13	

[a] Basic carbonate of lead.
[b] Mainly $FeCO_3$, Fe_3O_4, and Fe_2O_3.
[c] Zinc potassium chromate, containing excess of ZnO.
[d] Lead chromate, containing small excess of PbO.
[e] Zinc oxide.

EXAMINATION OF OIL EXTRACTED FROM PARTIALLY OXIDIZED FILMS OF PIGMENT—LINSEED OIL MIXTURES

Several investigators, among the recent ones being Olsen and Ratner,[8] Ingle,[9] Gardner,[10] Klein,[11] and Friend,[12] have found that the following changes occur during the drying of linseed oil: oxidation, polymerization, a rise in acid number, and the formation

[8] Proc. Eighth Intern. Cong. Applied Chem., Section Ve; 1912.
[9] J. Soc. Chem. Ind., 32, p. 639; 1913.
[10] J. Ind. Eng. Chem., 6, p. 9; 1914.
[11] J. Ind. Eng. Chem., 7, p. 99; 1915.
[12] Drugs, Oils, and Paints, 30, p. 50; 1914.

of volatile organic compounds (such as acids and aldehydes) of carbon dioxide and of water. Gardner claimed to have detected carbon monoxide in the vapors from drying paint, but Klein stated that the carbon monoxide detected by Gardner was formed when the latter led the vapors from the paint through fuming sulphuric acid. King,[13] however, detected carbon monoxide in the vapors from drying paint with an apparatus wherein fuming sulphuric acid was not used.

Gardner [14] stated as follows: "On account of its alkaline nature this pigment [white lead] acts on the saponifiable oil in which it is ground, forming lead soaps, which accelerate the chalking of white-lead paint." He also states that white zinc saponifies linseed oil. Gardner mixed 5 portions of raw linseed oil with various pigments and allowed the mixtures to stand in beakers for one month. The oil was then extracted and the ash thereof determined. Some of his results were as follows:

	Per cent ash.
Original oil	0.003
Oil from zinc-oxide mixture	.105
Oil from basic carbonate of lead mixture	.116
Oil from basic sulphate of lead mixture	.033
Oil from red-lead mixture	.211

He states that these results show that the pigments had a "direct saponifying action on the oil." This last statement is open to question, since he obtained yields of ash small enough to have been caused by the action of the free fatty acids on the pigments. Since the mixtures stood in open beakers, the amount of free fatty acids in the oils must have increased during the experiment. If pigments like white lead and white zinc have a "direct saponifying action" on linseed oil, oils extracted from mixtures of these pigments and linseed oil after storage in closed containers should yield large amounts of ash, whereas actually only small amounts are obtained.

Klein [15] stated as follows: "The ultimate composition of a white lead-linseed oil skin has not been investigated with any accuracy and I am unable to state whether, in the process of drying, saponification takes place to any considerable extent with consequent formation of lead linoleate, an interaction indicated by certain writers."

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[13] J. Ind. Eng. Chem., 7, p. 502; 1915.

[14] Paint Technology and Tests; 1911.

[15] A paper read before the Paint and Varnish Society of England, December, 1913; published as Lab. Bull. of the National Lead Co., February, 1914.

Since no solvent has yet been found which will completely dissolve linoxyn, we have no means of ascertaining the amount of metal which is in combination with the oil in a dried paint film. The following experiments were made to ascertain the amount of metal which is in combination with the oil in that portion of a partially dried film which is still soluble in such solvents as ether and benzene (C_6H_6). White zinc and white lead were the pigments used for the tests, and since these had reacted with linseed oil to an appreciable extent in partially filled containers, it was expected that similar results would be obtained with drying films. In the experiments with raw linseed oil the mixtures were spread on glass in layers thicker than would be made in painting work. When boiled oil was used the mixtures were brushed out to thin films on glass. For control experiments mixtures of barytes and oil were used. After certain intervals the films were removed from the glass and treated with ether (experiment 1, Table 5) or with a mixture of 60 volumes of benzene and 40 volumes of 95 per cent methyl alcohol (experiment 2, Table 5).

The solutions from the original mixtures of oil and pigment were perfectly clear, but the ether solutions from some of the partially oxidized mixtures in the experiments with raw oil were slightly turbid even after centrifuging and filtering. This slight turbidity may have been due to suspended metallic soaps or to pigment particles and therefore the experiments were repeated, using the benzene-methyl alcohol mixture. With this solvent all the solutions obtained were clear or showed only a faint opalescence in a tube 1 inch in diameter. This was accomplished by repeated centrifuging and filtration through a thick, tightly packed layer of filter-paper pulp. The extracted oils from the oxidized mixtures were red and viscous and had an acrid odor. The extracts were freed from the last traces of solvent by heating in carbon dioxide at 110–115° C. The ash of extracts was determined, ignition being finished in a muffle at a dull red heat. In the white lead experiments a small amount of lead may have been volatilized during ignition, so that the ash of the extracts may have contained slightly less lead than was present in the extracts.[16] The constants of the oils used are shown in Table 4. Complete data regarding the experiments and the results obtained are given in Table 5. The mixture of white zinc and raw linseed oil was allowed to dry

[16] A mixture of 0.5 g of white lead, containing 0.392 g of Pb, and 15 g of linseed oil yielded an ash which contained 0.370 g of Pb. No appreciable loss of Zn was noted in a similar experiment with white zinc.

for eight days (two days longer than the white lead mixture), because at the end of six days it did not appear to be as much oxidized as the white lead mixture.

TABLE 4

Constants of Linseed Oil

	Raw oil	Boiled oil
Specific gravity at 15.6/15.6° C	0.934	0.943
Refrac. index at 25° C	1.482	1.480
Acid number	2.7	7.1
Saponification number	190	193
Iodine number (Hanus)	189	181
Ash (per cent)	0.14	[a] 0.52
Unsaponifiable matter (per cent)	.....	1.1
Iodine number of fatty acids (Hanus)	195	186

[a] Contains Pb and Mn.

TABLE 5

Changes in Linseed Oil During Drying with Pigments

Composition of mixtures	Exposure of mixture	Experiment 1			Experiment 2: Benzene-methyl alcohol extract—per cent ash
		Iodine number of fatty acids	Ether extract		
			Acid number	Per cent ash	
White lead,[a] 70 per cent, Raw oil, 30 per cent	Original mixture	194	2.3	0.25	0.11
	Two days	132	13.3	.53	.52
	Four days	126	10.7	.66	.84
	Six days	103	17.9	.90	.85
White zinc,[b] 44 per cent, Raw oil, 56 per cent	Original mixture	194	3.2	.14	.15
	Two days	193	2.8	.29	.16
	Four days	180	4.1	.63	.17
	Eight days	101	10.9	1.70	2.17
Barytes, 52 per cent, Raw oil, 48 per cent	Original mixture	195	2.7	.07	.05
	Two days	191	3.0	.07	.04
	Four days	189	3.5	.08	.06
	Six days	139	9.1	.09	.07
White lead,[a] 70 per cent, Boiled oil, 30 per cent	Original mixture	182	8.0	.56	.46
	Six hours	148	10.7	.82	.50
White zinc,[b] 44 per cent, Boiled oil, 56 per cent	Original mixture	180	8.3	.64	.73
	Six hours	141	11.2	.95	1.60
Barytes, 52 per cent, Boiled oil, 48 per cent	Original mixture	182	8.2	.42	.39
	Six hours	145	11.0	.43	.38

[a] Dutch process. [b] French process; obtained from Dr. Gilbert Rigg, of the New Jersey Zinc Co.

The results of the experiments, as given in Table 5, show that appreciable amounts of lead and zinc have combined with the oil during the drying process. The boiled-oil experiments, of course, more nearly resemble painting practice than those with raw oil, but the iodine number figures show that in the former experiments the films were less oxidized at the end of the exposure than in the latter. The results, as a whole, indicate a greater combination between white zinc and oil than between white lead and oil. In experiment 2 no appreciable increase in ash was obtained after exposure for two and four days of the white zinc-raw linseed oil mixture, but the iodine number of the fatty acids shows that in that time only a very small amount of oxidation had taken place.

As mentioned above, there are no means of ascertaining how much metal is in combination with the oil in a thoroughly dry film. In these experiments the insoluble oxidized oil may have contained a larger percentage of metal combined with oxidized oil than was found in the extracts. If the formation of substances of an acid nature continues for a long time after the film is dry, pigments that are basic in nature, such as white lead and white zinc, probably continue to combine with these acidic compounds. If metallic salts of acids of low molecular weight, such as acetic acid, are formed, decomposition of these salts by the carbon dioxide of the air may occur with the formation of metallic carbonates. Linseed oil films continue to give off volatile matter for a long time, the films losing in weight, and therefore, if the amount of metal in combination with the oxidized oil remains constant, the percentage of combined metal will increase.

Since the composition of thoroughly dry paint films containing such basic pigments as white lead and white zinc is still unknown, assertions that such combination of pigment and oil as occurs is or is not beneficial are not based on established facts. To ascertain with accuracy the amount of metallic soaps in a film and their effect therein would involve a large amount of investigation, requiring better methods of analysis than those now available.

THE ACTION OF LINSEED OIL FATTY ACIDS ON WHITE LEAD AND WHITE ZINC

Thompson [17] stated that white lead is easily ground with linseed oil fatty acids, while white zinc causes a thickening and hardening, presumably owing to the formation of zinc soaps, and that

[17] Drugs, Oils and Paints, 30, p. 375; 1915.

this indicates that the latter pigment has the greater tendency to unite with the fatty acids. According to Thompson, Stas stated that the presence of water aids the combination of white zinc and linseed oil.

To determine whether under certain conditions white zinc combines more readily with linseed oil fatty acids than does white lead, the following experiments were made. One 10 g portion of fatty acids was mixed with 40 g of white lead [18] and another 10 g portion with 33 g of white zinc;[19] thus approximately the same volume of pigment was used in each case. The fatty acids had been previously filtered until clear, but were not heated to remove dissolved water. After one-half hour ether [20] was added to the mixtures and the ash of the ether extracts was determined, the latter having been freed from the last traces of solvent by heating in carbon dioxide at 110–115° C. The ashes obtained were mainly ZnO and PbO, and since the ratio of the combining weights of these two is 1:2.74, the results, as given in Table 6, show that the ether extract from the white zinc mixture contained nearly four times as much fatty anhydride combined as soap as that from the white lead mixture. The mixture of fatty acids and white zinc became quite hot, but no appreciable rise in temperature of the white lead mixture was noted. The experiment confirms Thompson's statement. The ratio of the combining weights of ZnO and PbO should be noted in a consideration of the results given in Table 5.

TABLE 6

Action of Linseed Oil Fatty Acids on White Lead and White Zinc

Pigment	Ash of ether extract (per cent)	
White lead	7.3	(×1=7.3)
White zinc	10.3	(×2.74=28.2)

THE RELATIVE EFFECTS OF CERTAIN PIGMENTS ON THE OXIDATION OF LINSEED OIL IN PAINT FILMS

Although the rate of increase in weight of a drying oil is not an exact measure of the rate of drying, it is roughly proportional to the amount of oxidation that occurs during the increase in weight

[18] Dutch process.

[19] French process.

[20] Lead and zinc soaps, prepared by adding solutions of salts of these metals to solutions of the potassium soaps of linseed oil fatty acids, were found to be readily soluble in ether, benzene, and a benzene-methyl alcohol mixture; 10 g dissolved readily in 100 cc of solvent.

to a maximum, and therefore affords a means of ascertaining the effect of pigments on the oxidation of oil in paint films. According to Friend [21] the time required for an oil to "set" is half that required to obtain the maximum weight.

Toch [22] stated that "when white zinc is mixed with linseed oil and the proper amount of drier, it sets and dries more slowly than white lead." Maire [23] stated that "white lead is a good drier of linseed oil and requires but a small admixture of artificial drier to hasten its drying." Sabin [24] stated that "white lead and

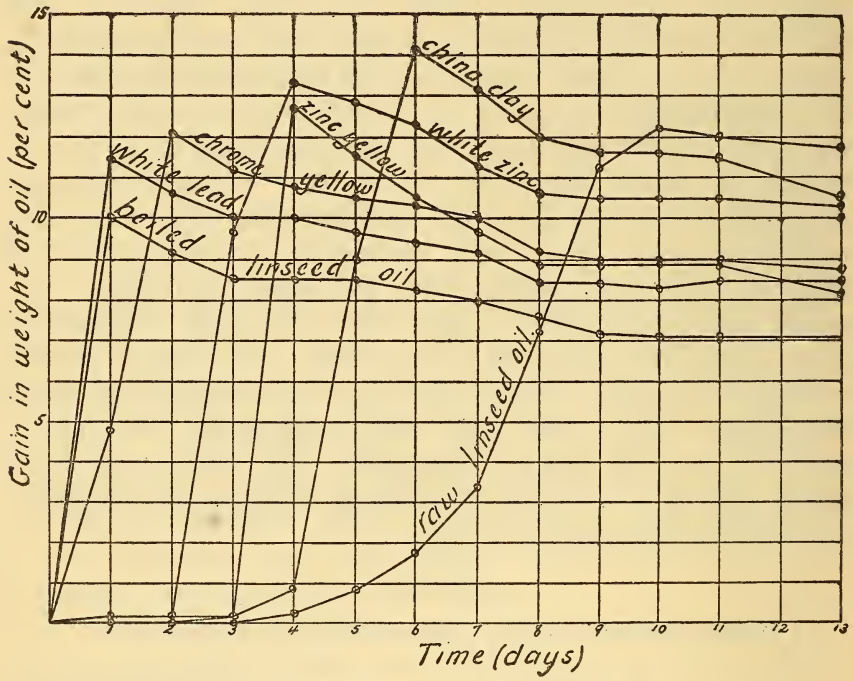

FIG. 1.—*Gain in weight of oil in thin films*

oil do indeed dry more rapidly than oil alone, but so little is this increase that in practice it is not recognized." He made some oxidation experiments with mixtures of various pigments and oil, determining the rate of increase in weight of the oil. His results will be discussed later.

In the present investigation mixtures of raw linseed oil with white lead, white zinc, and china clay were used, and also films of raw and boiled linseed oil. The oils used were those described in Table 4. Further experiments with mixtures of raw linseed

[21] Drugs, Oils, and Paints, 30, p. 50; 1914.
[22] M. Toch, Chemistry and Technology of Mixed Paints; 1907.
[23] Maire, Modern Pigments and Their Vehicles; 1908.
[24] Bottler and Sabin, German and American Varnish Making; 1912.

oil with chrome yellow and zinc yellow were made to ascertain whether or not these pigments would be as "inert" in a drying film as they were in the experiments with paints in partially filled containers. (See Table 3.) The mixtures consisted of approximately one volume of pigment and three volumes of oil, these being the proportions used by Sabin.[25] The composition of each mixture, its specific gravity, and the weight and thickness of film are given in Table 7. The films in experiment 1 were made at approximately the same spreading rate that Sabin used.

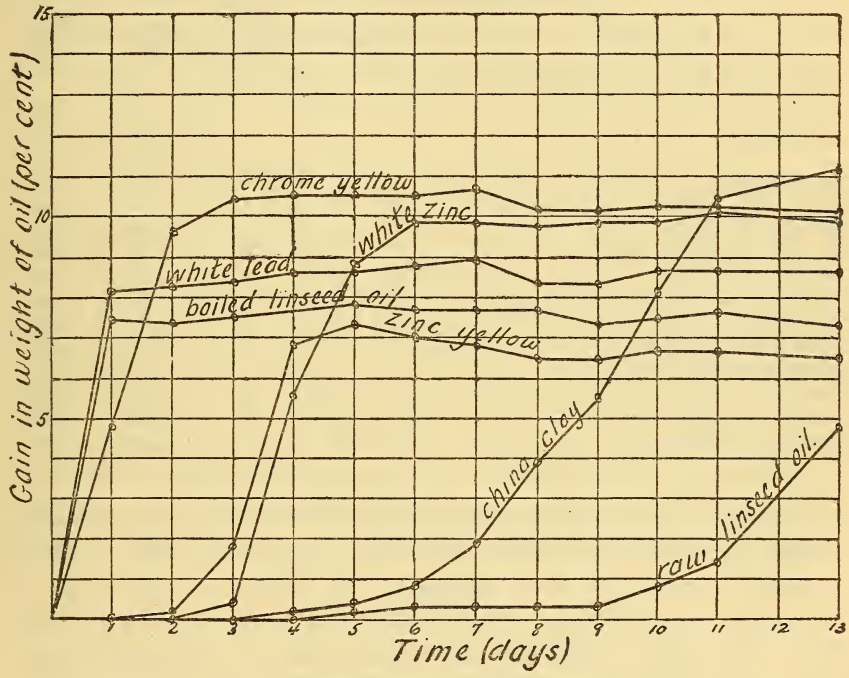

FIG. 2.—*Gain in weight of oil in thick films*

Those in experiment 2 were five times as thick. Owing to the different "oil-taking power" of the different pigments the mixtures varied greatly in viscosity. The films were spread over an area 10 by 10 cm on weighed glass plates and kept in a dust-free cabinet with glass sides and top, there being free access of air. The plates were weighed each day and the gains in weight noted The room temperature during the first seven days was 30–35° C. and during the last six days 25–30° C. The curves representing the increase in weight of the thin films are shown in Fig. 1 and those of the thick films in Fig. 2.

[25] There is an error in the description of Sabin's experiments (German and American Varnish Making, p. 194), the proportions being given as one volume of oil to three volumes of pigment.

The following is a summary of the results with thin films in comparison with Sabin's results. In the present tests white lead greatly accelerated the gain in weight of raw linseed oil, the white-lead curve being very similar to the boiled-oil curve. The white zinc caused no gain in weight during the first two days, but during the third and fourth days had a marked accelerative effect.

TABLE 7

Data on Oils and Mixtures used for Drying Experiments

Composition	Specific gravity	Experiment number	Weight of film	Average thickness of film
			g	mm
Raw linseed oil	0.93	1	0.222	0.023
		2	1.032	.111
Boiled linseed oil	.94	1	.198	.020
		2	.982	.104
White lead, 71 per cent	2.4	1	.886	.037
Raw linseed oil, 29 per cent		2	4.373	.182
White zinc, 66 per cent	2.1	1	.787	.037
Raw linseed oil, 34 per cent		2	3.730	.178
China clay, 48 per cent	1.3	1	.492	.038
Raw linseed oil, 52 per cent		2	2.400	.184
Chrome yellow, 69 per cent	2.2	1	.813	.037
Raw linseed oil, 31 per cent		2	4.100	.186
Zinc yellow, 56 per cent	1.6	1	.574	.036
Raw linseed oil, 44 per cent		2	2.894	.181

China clay had no accelerative effect till the fifth day, but greatly increased oxidation during the fifth and sixth days. Sabin obtained during the early stages of the drying a larger gain in weight for raw oil mixed with China clay than for raw oil with white lead, both having an accelerative effect. His curve representing the gain in weight of raw oil with white zinc was very similar to the curve for raw linseed oil alone. In another experiment Sabin obtained during the early stages of the drying a larger gain in weight for raw linseed oil alone than for raw oil with white lead, raw oil with white zinc, or for boiled linseed oil alone. Both white lead and white zinc caused raw linseed oil to gain in weight more rapidly than boiled linseed oil, the white zinc having the greater accelerative effect.

So many factors—temperature, humidity, thickness of film, etc.—influence the drying of linseed oil that variations in the results obtained by different observers is to be expected, but the small catalytic effect of the driers in Sabin's boiled oil is remarkable. If the boiled oil that he used was the commercial article,

containing lead and manganese, it seems to the author that the gain in weight was abnormally slow, the time required to obtain a maximum weight being eight days. It was certainly slower than the commercial boiled oils that have been thus tested in this laboratory. In the present tests with white lead enough pigment combined with the oil to have a marked catalytic effect on the drying, while in Sabin's experiments this did not occur. In the present tests the accelerative effect of white lead was so much greater than that of China clay that it can hardly be explained except by the catalytic effect of combined lead.

Considering the effect of chrome yellow and zinc yellow in the present tests, the results show that both pigments had an accelerative effect on the oxidation of the oil, that of the chrome yellow being the greater.

In the present tests with films of oil alone, raw linseed oil showed a larger maximum gain in weight than boiled oil. This was the case in many previous tests in this laboratory and in Sabin's experiments. It is worthy of note that of all the oils used in the present tests, that which was mixed with China clay showed the largest maximum gain in weight. This pigment is the only one of those used which could not react chemically with the oil to form metallic soaps which could act as catalyzers.

The pigments in the thick film tests showed approximately the same relationships as accelerators of oxidation that they did in the thin film tests. As would be expected, the gains in weight in the former tests were slower and the maximum gains in weight less.

SUMMARY

The constants, including yield of ash, of raw linseed oil mixed with white lead in paste form showed no material change in 25 months.

Storage, in partially filled containers for one year, of raw linseed oil mixed with white lead and with white zinc (in the proportions of paint ready for use) and exposure of films of such mixtures to air for several days resulted in sufficient combination of oil and pigment to cause the extracted oils to yield amounts of ash that were much larger than those obtained from the oils used to prepare the mixtures. Exposure of films of these pigments mixed with boiled linseed oil to air for six hours caused a small but appreciable combination of oil and pigment.

When white lead and white zinc were mixed with linseed oil fatty acids considerable combination of pigment and fatty acids

occurred. The amount of fatty anhydride combined as zinc soap was nearly four times as great as that combined as lead soap, the calculations being based on the amounts of ash yielded by the ether extracts of the pigment-fatty acids mixtures and the ratio of the combining weights of ZnO and PbO.

The results as a whole indicate that white zinc combines with the free fatty acids of linseed oil more readily than does white lead.

Of the three pigments, white lead, white zinc, and China clay, the former showed the greatest accelerative effect on the oxidation of raw linseed oil in films composed of pigment and oil, while China clay had the least accelerative effect.

When a mixture of raw linseed oil and China clay was kept in a partially filled container for one year the constants of the oil were materially changed, while raw linseed oil with chrome yellow and with zinc yellow under the same conditions showed practically no change. In drying films, however, the accelerative effects of the two yellow pigments on the oxidation of the oil were much greater than that of China clay.

It is obviously unjustifiable to draw from the experimental part of this paper any conclusions regarding the relative values of the different pigments as paint materials. Such conclusions can be properly drawn only from the data afforded by exposure tests with painted panels and from general painting experience.

WASHINGTON, January 4, 1916.