DUNCAN

Soaps of tung oil

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Approved.
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AN INVESTIGATION OF THE DRYING PROPERTIES OF THE LEAD, MANGANESE, AND COBALT SOAPS OF TUNG OIL

by

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T A B L E   O F   C O N T E N T S

HISTORICAL

Tung oil (or Chinese wood oil) is now recognized as one of the best of drying oils, and holds a place both important and unique in the varnish industry of today. It was probably first investigated by the French Chemist, Cloëz[1] about 1875, who "expressed" the oil from the seed of the "elaeococca vernica", imported from China.

Cloëz found that when this oil is heated to 200°C, it solidifies to a transparent jelly having totally different properties from the oil itself. On exposure to the air the oil dries in a few hours to a white, frosty-appearing film, and on saponification with an alcoholic solution of potassium hydroxide gives a crystalline soap. He also found that this soap is easily decomposed by phosphoric acid, yielding a white, solid, fatty acid, m. 48°C., resinifying rapidly on exposure to air. To this compound, which he called "elaeomargaric acid", Cloëz assigned[2] the formula $C_{17}H_{30}O_2$. He also determined the physical and chemical constants of the oil, besides preparing and analyzing [3] the lead, silver, and barium soaps, to which there will be later reference.

Moreover, he discovered that when exposed to the light, tung oil is changed to a crystalline mass, a phenomenon also shown by solutions of the elaeomargaric acid in organic solvents, and due to the rays in the violet end of the spectrum. From this crystalline mass, formed by photo-chemical change, Cloëz isolated an acid, m. 71°C., isomeric with elaeomargaric acid,

and which he termed "elaeostearic acid."

In 1902, Marquenne,[4] after repeating a part of Cloëz's work, assigned the formula $C_{18}H_{30}O_2$ to the so-called "elaeomargaric acid", and proposed the name "α-elaeostearic acid", which has since been retained.

Both Cloëz and Marquenne based their formulas of this principal acid derived from tung oil on the elementary analysis of the acid itself, but owing to the rapid oxidation of this compound, their formulas were open to criticism. However, in 1903 Kamataka[5] prepared a very stable tetra-bromo-derivative of the acid, and found by analysis that it corresponded to the formula $C_{18}H_{32}O_2Br_4$, indicating that α- elaeostearic acid has the formula $C_{18}H_{32}O_2$. He further found that the principal oxidation product of this acid is sativic acid, which is also the principal oxidation product of linoleic acid; and ~~is~~ also that the tetra-bromo derivatives of α- elaeostearic and linoleic acids have the same melting points. Kamataka thus showed that α-elaeostearic acid belongs to the linoleic acid family; and his empirical formula of this acid, together with the theory of its stereo-isomerism with linoleic acid, is generally accepted.

Majima[6] concluded that ~~this~~ α-elaeostearic acid has the structural formula:- $CH_3 \cdot (CH_2)_3 \cdot CH : CH \cdot (CH_2)_2 \cdot CH : CH \cdot (CH_2)_7 \cdot COOH$, having the double bonds between the fifth and sixth and between the ninth and tenth carbon atoms, since by the action of ozone he obtained azelaic and normal valeric acids.

S C O P E   O F   I N V E S T I G A T I O N

Lead, manganese, and cobalt linoleates are well known "driers" of linseed oil, and the drying properties of oils boiled with litharge and manganese dioxide are thot due, at least in

part, to the formation of linoleates in the oil. Because of the isomerism existing between linoleic acid, and α- elaeostearic acid, and also because of the rapid drying properties of the tung oil, the following investigation was undertaken:

1. The preparation and purification of the α-elaeostearates of lead, manganese, and cobalt.
2. A study of the "drying" properties of these soaps dissolved in linseed oil as compared with standard driers, e.g., litharge and manganese dioxide.

EXPERIMENTAL

Constants of the Oil.

The following physical and chemical constants were determined for this sample of tung oil, (which was obtained thru the courtesy of the Standard Varnish Works) are listed below in the first column. The constants of tung oil as given by Lewkowitsch[7] are given in the second column.

	Duncan	Lewkowitsch
Specific Gravity	0.9381 at 19°C.	0.9330-0.9418 at 15.5°C.
Refractive Index	1.5225 at 12.6°C.	1.5030 at 19°C.
Saponification Number	190	156.6 - 211
Iodine Number (Hubl)	156.5	149.7 - 165.7
Acid Number	7.325	

In addition, the oil gelatinized on heating to 190°C., and when exposed to the sunlight in a sealed glas tube for a few days formed a crystalline mass. Both of these tests are characteristic of tung oil, and serve to distinguish it from the other drying oils.

PREPARATION AND PURIFICATION OF SOAPS.

Potassium Soap

Tung oil was saponified by heating for thirty minutes with a bare exess of an approixmately twenty percent alcoholic solution of potassium hydroxide, the reaction being carried on in a darkened flask in an atmosphere of hydrogen. On cooling, the soap crystallized out, was filtered off and washed several times with 95 per cent alcohol, then dissolved in hot alcohol, filtered hot, and again allowed to crystallize. It separated in the form of radiating clusters of white needles. After five recrystallizations, the potassium α-elaeostearate was filtered off and dried. It was considered practically free from potassium oleate, which is very soluble in alcohol.

Drying this soap was difficult as it resinified rapidly in light and air, but after trying several methods, it was found practicable to dry it at 100°C. in a darkened Drexel bottle in an atmosphere of hydrogen.

The potassium α-elaeostearate was found to be slightly soluble in cold alcohol, very soluble in hot alcohol, and easily soluble in water with the formation of a strong lather. On exposure to air it darked and resinified. On hydrolysis with HCl it gave a solid white crystalline, fatty acid with a melting point of 44°C, which was practically identical with that found by Kamataka, and by DeNegri and Sburlati for the α- elaeostearic acid isolated by them.

ANALYSIS OF POTASSIUM SOAP.

The percentage of potassium in the potassium α-elaeostearate was determined both by decomposing the soap with dilute hydrochloric acid, filtering off the fatty acid, and precipitating the potassium as the chloroplatinate in the usual way, and by decomposing the soap with dilute sulfuric acid, filtering and weighing the potassium as the normal sulfate. The determinations I, II, and III listed below were made on a soap that had been kept for about four months in a dissicator with a vacuum of 1-2 cms., while IV and V were made on another sample of freshly prepared potassium soap dried in vacuuo.

	Wt. Sample	Wt. K_2SO_4	percent K
I	1.4070 grams	0.3454 grams	11.01
II	1.4070 grams	0.4306 grams	10.86
		Wt. K_2PtCl_6	
III	1.0000 grams	0.6690 grams	10.73
IV	1.0000 grams	0.6686 grams	10.72
V	1.0000 grams	0.6660 grams	10.86

Cloez[3] found 12.12 % potassium in his corresponding soap, which is slightly less than the theorectical percentage for the compound $C_{18}H_{31}O_2K$, which is 12.29 %.

Lack of time prevented us from determining why the percent of potassium in the potassium α-elaeostearate isolated by us varied so considerably from the theoretical percentage, and from the percentage found by Cloëz, who closely checked the theoretical. The soap may possibly have contained an alcohol of crystallization, for the theoretical percent of potassium in $C_{18}H_{31}O_2K.\frac{1}{2}C_2H_5OH$ is 10.74 which almost exactly coincides with the percent of potassium in our soap. The presence of alcohol in the soap was not determined experimentally.

HEAVY METAL SOAPS

The heavy metal soaps were all made in the same general way by dissolving the purified potassium soap in a large volume of water (600-700 cc.) filtering, and precipitating the lead, manganese, and cobalt soaps by the adition of dilute solution of lead acetate, manganous chloride, and cobaltous chloride respectively. The lead soap came down as a very fine grained white precipitate, the manganese soap a curdy white precipitate, and the cobaltous soap was curdy, light pink at first, but rapidly deepening to a purple.

Various methods of washing the precipitated soaps were tried, such as washing with water and subsequently with alcohol and ether. It was found however, that washing with water alone until the soaps were free from inorganic matter and salts was the most satisfactory method, the alcohol and ether in the case of the cobalt soap having a very marked solvent action. In all cases the washing was carried out as rapidly as possible to insure minimum oxidation.

The dessication of the heavy metal soaps was even more difficult than in the case of the potassium soap, as they decomposed at a temperature as low as 50°-60°C. They were finally dried in vacuuo (1-2 cm.s pressure) over fused calcium chloride.

All three soaps changed rapidly on exposure to air, the manganese soap darkening very quickly. But the cobalt soap proved to be the most interesting, for besides its color changes, it showed other curious phenomena. When dissolved

in ether, and the ether allowed to evaporate, a dark red varnish remained, and on long standing, unless at a very low pressure, the dry soap changed to a dark red, ill-smelling resin. Also on being precipitated from its alcoholic solution with water, or even on being allowed to stand in contact with the solution from which it was first precipitated, the cobalt soap separated into what appeared to be two soaps, one purple and the other white.

ANALYSIS OF THE HEAVY METAL SOAPS.

The lead in the lead soap was determined by decomposing the soap with dilute hydrochloric acid, filtering hot, adding an excess of sodium acetate, and then precipitating the lead as the chromate.

	Wt. Sample	Wt. $PbCrO_4$	% Pb
I	0.8288 grams	0.3633 grams	28.00
II	0.8288 grams	0.3662 grams	28.01

Cloëz's results on this soap show 27.74 % of lead, while the theoretical for $(C_{18}H_{31}O_2)_2$ Pb is 27.05 % of Pb.

The manganese in the manganese spap was determined by decomposing with dilute hydrochloric acid, adding sodium phosphate and ammonia, then igniting to the pyrophosphate.

	Wt. Sample	Wt. $Mn_2P_2O_7$	% Mn
I	1.0000 grams	0.2572 grams	9.96
II	1.0000 grams	0.2572 grams	9.96

The theoretical for $(C_{18}H_{31}O_2)_2$ Mn is 8.97 % of Mn.

The percent of cobalt in the cobalt soap was determined by strongly igniting the soap in air or in oxygen, and then reducing to metallic cobalt in an atmosphere of hydrogen.

	Wt. Sample	Wt. Co.(Metal)	% Co.
I	0.7152 grams	0.0640 grams	9.06
II	0,7412 grams	0.0670 grams	9.04

The theoretical for $(C_{18}H_{31}O_2)_2$ Co would be 9.56 % of Co.

The barium and silver soaps prepared by Cloëz did not show the theoretical percent of metal. The results of this analysis together with the theoretical for $(C_{18}H_{31}O_2)_2$ Ba and $C_{18}H_{31}O_2$ Ag, are given in the following table.

SOAP	THEORETICAL	FOUND
Barium	19.76 %	20.24 %
Silver	27.88 %	28.81 %

The failure to obtain pure, normal α-elaeostearates of lead, cobalt and manganese was not entirely unexpected, altho a satisfactory explanation for this non-success has not

~~has not~~ been found. It will be noted that Cloëz's [3] lead, silver, and barium salts of the same acid did not check the theoretical metal content. Whether the soaps formed are in reality mixtures, or complexes of fairly constant composition or whether the results are due to changes caused by rapid oxidation are questions requiring further investigation, and are beyond the scope of this paper.

D R Y I N G   T E S T S

Behavior of Oils on Drying.

Several years ago Kissling[8] and Lippert [9] showed that as an oil film dries to a hard elastic surface, i.e., as its unsaturated components absorb oxygen, it increases in weight to a maximum, followed by a subsequent gradual decrease. However, an oil film is ordinarily assumed to have "dried" when the maximum weight is reached. Sabin[10] has drawn curves representing this drying process, and has shown that the decrease in weight continues for several months until most of the gain weight has been lost. Moreover he has shown that the drying process is accompanied by a considerable shrinkage in volume, And recently Gardner [11] has proven that immediately on exposure to the air, a drying oil film begins to give off considerable quantities of CO_2, traces of Co, and some other organic substances.

Very little is definitely known of the chemistry involved in the drying of oil films, and for the sake of unity, all discussion of the theories will be omitted from this paper. It is generally accepted however, that the drying is due to an absorption of oxygen and a liberation of volatile compounds, and it is believed that the weight at any one time is perhaps, as Sabin says, a result of partially balanced gains and losses. As previously indicated the solutions of certain metallic oxides and metallic soaps in hot linseed oil give rise to so-called "boiled oils" whose thin films "dry" far more rapidly

than a film of the same oil heated for the same length of time at the same temperature. However, the theories and speculations regarding this phenomenon are generally vague and not well formulated, and will not be included in this paper. (12 & 13)

PREPARATION OF BOILED OILS.

The treated, or "boiled" oils prepared for the drying tests (which form the bulk of the present investigation) were made as follows: Commercial raw linseed oil was mixed with such amounts of the soaps as to contain 1 % of lead or an equivalent amount of dobalt or manganese, i.e., in each case the ratio

$$\frac{\text{atomic weight of metal}}{\text{weight of metal in amount of soap taken.}}$$

was constant. The formulas for these boiled oils are shown in the following table.

SOAP	Wt. of Soap	(Linseed) Wt. of Oil	(wt. of Metal calc. from wt.of soap)
Mn α-elaeostearate	0.2957 gr.	10 gr.	(o.0265 gr.)
Pb "	0.3695 gr.	10 gr.	(0.1000 gr.)
Co "	0.2990 gr.	10 gr.	(0.0287 gr.)

Besides these, two boiled oils were made up using litharge and manganese dioxide for use as standards in the drying tests. Such amounts of the oxides were taken as would contain the same amounts of metal as the corresponding soap mentioned above. The formulas for these "boiled" boils are

given in the following table:

OXIDE	Wt. of Oxide	(Linseed) Wt. of Oil	(wt. of metal in oxide calc. from wt. of oxide)
PbO	0.1072 gr.	10 grams.	(0.1000 grams)
MnO_2	0.0420 gr.	10 grams	(0.0265 grams)

Two sets of tubes were prepared containing the five oil mixtures described above, together with a sixth tube containing raw linseed oil alone (for control). The open tubes were heated for six hours in a Freas electric oven, set I being heated to 350°-375°F. and set II from 225°-250°F. The oil mixtures were well shaken, both before, and at intervals during the heating.

After cooling and settling, the oil boiled with litharge, in set (I) was very thick and dark, while the boil boiled without a drier, and that treated with MnO_2 had darkened very little. The color of the boiled oils made with the three soaps lay midway between these extremes. The respective colors of the oil mixtures of Set II were not changed to the same extent, altho darkening had taken place in about the same order.

METHODS OF TESTING.

The respective rates of drying of the boiled oils containing the soaps were studied by the following methods:

1. By a comparison of the time required for a film of the boiled oil being tested to become "tacky" with the time required for a film of boiled oil made with a standard drier under identical conditions to become "tacky".

2. By a comparison of the time required for a thin film of the boiled oil being tested to reach its maximum weight with the time required for a thin film of a boiled oil made with a standard drier under identical conditions to reach its maximum weight (according to the method suggested by Lippert[9]).

APPLICATION OF METHODS

When the oils were treated according to method No. 1, the films of those oils treated with litharge and the three soaps became tacky in a few hours, and tho the manganeese soap seemed slightly in the lead, a satisfactory differention could not be made.

Method No. 2 was then tried in the following manner :- Smooth films of the boiled oils were spread upon carefully weighed glass plates of uniform size and about 25 gms. weight. (The exact area of 5.2 cms.x 8.25 cms .had been previously marked off with a glass cutter, leaving a margin of about 1 cm. around the film.) The plates were weighed quickly,placed in a ventilated,dust-free glass box exposed to diffused daylight, and weighed at rather frequent intervals. The time of drying in hours, the temperature in degrees Centrigade,the weights of oil films in grams, etc.,are given below, duplicate drying tests being made in each case. For the sake of brevity, simply the name of the active drying agent in the boiled oil, and the number of the set of drying tests are given at the head of each tabulation.

LEAD-OXIDE FILM Set 1.

Hrs. of Drying	Temp. of Room	Wt. of Oil Film A	Wt. Film A Standardized	Wt. of Oil Film B	Wt. Film B Standardized
0	23.5	0.1343	0.1000	0.1407	0.1000
8	17	0.1370	0.1021	0.1439	0.1023
12	17	0.1406	0.1047	0.1480	0.1052
16	16	0.1450	0.1080	0.1525	0.1084
19.5	15.5	0.1486	0.1107	0.1563	0.1111
23	14	0.1506	0.1121	0.1585	0.1127
34	19	0.1522	0.1133	0.1602	0.1139
37	21.5	0.1522	0.1138	0.1606	0.1142
41.5	20	0.1526	0.1136	0.1604	0.1140
47	16	0.1522	0.1133	0.1600	0.1137
59.5	21	0.1520	0.1132	0.1598	0.1135
66	20	0.1520	0.1132	0.1600	0.1137
71	19	0.1518	0.1130	0.1599	0.1136
82.5	21	0.1516	0.1129	0.1597	0.1134
94.5	20	0.1520	0.1132	0.1600	0.1137
107.5	25	0.1518	0.1130	0.1600	0.1137
121.5	23	0.1505	0.1121	0.1582	0.1124
132	22	0.1503	0.1119	0.1582	0.1124
143.5	23	0.1503	0.1119	0.1582	0.1124
156	24	0.1502	0.1118	0.1580	0.1123
168	23	0.1500	0.1117	0.1578	0.1122
180	21	0.1498	0.1115	0.1576	0.1120
193	23	0.1490	0.1109	0.1570	0.1116
217	22	0.1489	0.1108	0.1568	0.1115

LEAD-OXIDE FILM ~~No~~ Set 1.

Hrs.	Temp.	Wt. Film A	Wt. A Standardized	Wt. Film B	Wt. B Standardized
241	23	0.1486	0.1106	0.1564	0.1112
287	20	0.1480	0.1102	0.1556	0.1107
353	20	0.1483	0.1104	0.1560	0.1110
445	19	0.1470	0.1095	0.1548	0.1101

MANGANESE - DIOXIDE FILM ~~No~~ Set 1

Hrs.	Temp.	Wt. Film A	Wt. A. Standard-ized	Wt. Film B	Wt. B Standard-ized
0	23.5	0.1727	0.1000	0.1355	0.1000
8	17	0.1723	0.0997	0.1352	0.0997
12	17	0.1723	0.0997	0.1358	0.1002
16	16	0.1725	0.0999	0.1358	0.1002
19.5	15.5	0.1727	0.1000	0.1360	0.1004
23	14	0.1725	0.0999	0.1358	0.1002
34	19	0.1729	0.1001	0.1363	0.1006
37	21.5	0.1735	0.1005	0.1369	0.1010
41.5	20	0.1739	0.1007	0.1373	0.1013
47	16	0.1743	0.1009	0.1377	0.1016
59.5	21	0.1757	0.1017	0.1392	0.1027
66	20	0.1768	0.1023	0.1404	0.1036
71	19	0.1778	0.1029	0.1414	0.1043
82.5	21	0.1788	0.1035	0.1438	0.1060
94.5	20	0.1825	0.1056	0.1474	0.1087
107.5	25	0.1866	0.1081	0.1512	0.1116
121.5	23	0.1933	0.1119	0.1554	0.1147
132	22	0.1952	0.1130	0.1560	0.1152
143.5	23	0.1960	0.1135	0.1564	0.1155
156.	24	0.1960	0.1135	0.1561	0.1153
168	23	0.1960	0.1135	0.1561	0.1153
180	21	0.1958	0.1134	0.1558	0.1150
193	23	0.1953	0.1131	0.1554	0.1147
217	22	0.1950	0.1129	0.1551	0.1145

MANGANESE-DIOXIDE FILM ~~NO~~ Set .1

Hrs.	Temp.	Wt. Film A	Wt. A Standardized	Wt. Film B	Wt. B. Standardized.
241	23	0.1949	0.1128	0.1547	0.1142
287	20	0.1941	0.1124	0.1537	0.1135
353	20	0.1945	0.1126	0.1541	b0.1138
445	19	0.1929	0.1117	0.1526	0.1127

Mn-SOAP FILM ~~NO.~~ Set 1

Hrs.	Temp.	Wt. Film A	Wt. A Standardized	Wt. Film B	Wt. B Standardized
0	23.5	0.1182	0.1000	0.1324	0.1000
8	17	0.1225	0.1036	0.1370	0.1035
12	17	0.1289	0.1090	0.1436	0.1085
16	16	0.1304	0.1103	0.1450	0.1096
19.5	15.5	0.1308	0.1107	0.1454	0.1099
23	14	0.1308	0.1107	0.1453	0.1098
34	19	0.1312	0.1110	0.1460	0.1103
37	21.5	0.1316	0.1113	0.1462	0.1105
41.5	20	0.1312	0.1110	0.1458	0.1102
47	16	0.1310	0.1108	0.1458	0.1102
59.5	21	0.1312	0.1110	0.1460	0.1103
66	20	0.1311	0.1109	0.1460	0.1103
71	19	0.1311	0.1109	0.1462	0.1105
82.5	21	0.1308	0.1107	0.1460	0.1103
94.5	20	0.1306	0.1105	0.1467	0.1108
107.5	25	0.1306	0.1105	0.1467	0.1108
121.5	23	0.1304	0.1103	0.1454	0.1099
132	22	0.1304	0.1103	0.1454	0.1099
143.5	23	0.1306	0.1105	0.1456	0.1100
156	24	0.1304	0.1103	0.1455	0.1100
168	23	0.1304	0.1103	0.1456	0.1100
180	21	0.1302	0.1101	0.1454	0.1099
193	23	0.1300	0.1100	0.1450	0.1096
217	22	0.1298	0.1098	0.1449	0.1095

Mn-SOAP FILM ~~NO~~ Set .1

Hrs.	Temp.	Wt. Film A	Wt. A Standard-	Wt. Film B	Wt. B. Standard-Ized
241	23	0.1296	0.1096	0.1447	0.1093
287	20	0.1289	0.1090	0.1441	0.1088
353	20	0.1296	0.1096	0.1448	0.1093
445	19	0.1284	0.1086	0.1438	0.1086

Pb-SOAP FILM Set 1

Hrs.	Temp.	Wt. Film A	Wt. A Standardized	Wt. Film B	Wt. B Standardized.
0	23.5	0.1354	0.1000	0.1250	0.1000
8	17	0.1398	0.1033	0.1295	0.1036
12	17	0.1446	0.1068	0.1340	0.1072
16	16	0.1504	0.1111	0.1392	0.1114
19.5	15.5	0.1532	0.1131	0.1415	0.1132
23	14	0.1544	0.1140	0.1422	0.1137
34	19	0.1556	0.1149	0.1436	0.1148
37	21.5	0.1558	0.1151	0.1436	0.1148
41.5	20	0.1552	0.1146	0.1430	0.1143
47	16	0.1546	0.1142	0.1426	0.1140
59.5	21	0.1546	0.1142	0.1426	0.1140
66	20	0.1546	0.1142	0.1426	0.1140
71	19	0.1546	0.1142	0.1424	0.1138
82.5	21	0.1541	0.1138	0.1420	0.1136
94.5	20	0.1546	0.1142	0.1427	0.1141
107.5	25	0.1544	0.1140	0.1424	0.1138
121.5	23	0.1526	0.1126	0.1410	0.1127
132	22	0.1526	0.1126	0.1410	0.1127
143.5	23	0.1526	0.1126	0.1406	0.1125
156	24	0.1524	0.1124	0.1406	0.1125
168	23	0.1520	0.1121	0.1402	0.1122
180	21	0.1518	0.1120	0.1402	0.1122
193	23	0.1512	0.1116	0.1396	0.1117
217	22	0.1510	0.1115	0.1394	0.1115

Pb-SOAP FILM No. L

Hrs.	Temp.	Wt.Film A	Wt.A. Standardized	Wt. Film B	Wt.B. Standardized
241	23	0.1508	0.1114	0.1392	0.1114
287	20	0.1497	0.1105	0.1382	0.1106
353	20	0.1504	0.1110	0.1390	0.1113
445	19	0.1488	0.1099	0.1376	0.1103

CO-SOAP FILM ~~NO.~~ Set 1.

Hrs.	Temp.	Wt. Film A	Wt.A Standard-ized	Wt. B. Film	Wt. B Standard-ized
0	23.5	0.1240	0.1000	0.1092	0.1000
8	17	0.1295	0.1044	0.1137	0.1041
12	17	0.1359	0.1095	0.1196	0.1094
16	16	0.1399	0.1127	0.1238	0.1132
19.5	15.5	0.1407	0.1134	0.1250	0.1143
23	14	0.1408	0.1135	0.1252	0.1145
34	19	0.1416	0.1142	0.1260	0.1154
37	21.5	0.1416	0.1142	0.1260	0.1154
41.5	20	0.1412	0.1140	0.1254	0.1148
47	16	0.1409	0.1138	0.1250	0.1143
59.5	21	0.1410	0.1139	0.1252	0.1145
66	20	0.1408	0.1137	0.1251	0.1144
71	19	0.1406	0.1136	0.1250	0.1143
82.5	21	0.1404	0.1134	0.1246	0.1141
94.5	20	0.1408	0.1137	0.1250	0.1143
107.5	25	0.1402	0.1132	0.1244	0.1139
121.5	23	0. 1384	0.1116	0.1226	0.1123
132	22	0.1382	0.1114	0.1224	0.1121
143.5	24	0.1382	0.1114	0.1224	0.1121
156	24	0.1378	01111	0.1218	0.1116
168	23	0.1376	0.1110	0.1216	0.1114
180	21	0.1376	0.1110	0.1215	0.1113
193	23	0.1370	0.1105	0.1208	0.1106
217	22	0.1368	0.1103	0.1206	0.1105

CO*-SOAP FILM ~~No~~ Set.1

Hrs.	Temp.	Wt. Film A	Wt. A Standard-ized	Wt. Film B	Wt. B. Standard-Ized
241	23	0.1366	0.1102	0.1202	0.1101
287	20	0.1358	0.1096	0.1194	0.1094
353	20	0.1365	0.1102	0.1202	0.1101
445	19	0.1356	0.1094	0.1188	0.1189

UNTREATED OIL FILM ~~No.~~ Set 1

Hrs.	Temp.	Wt.Film A	Wt.A. Standard-ized	Wt.Film B	Wt. B. Standard-ized
0	23.5	0.1528	0.1000	0.1221	0.1000
8	17	0.1529	0.1001	0.1219	0.0998
12	17	0.1529	0.1001	0.1221	0.1000
16	16	0.1531	0.1002	0.1223	0.1002
19.5	15.5	0.1530	0.1002	0.1223	0.1002
23	14	0.1529	0.1001	0.1221	0.1000
34	19	0.1535	0.1005	0.1227	0.1105
37	21.5	0.1537	0.1006	0.1229	0.1007
41.5	20	0.1539	0.1007	0.1231	0.1008
47	16	0.1538	0.1007	0.1231	0.1008
59.5	21	0.1547	0.1013	0.1242	0.1025
66	20	0.1555	0.1018	0.1252	0.1025
71	19	0.1561	0.1022	0.1257	0.1030
82.5	21	0.1575	0.1031	0.1273	0.1043
94.5	20	0.1603	0.1050	0.1305	0.1069
107.5	25	0.1638	0.1072	0.1346	0.1103
121.5	23	0.1673	0.1095	0.1381	6.1131
132	22	0.1681	0.1100	0.1387	0.1136
143.5	23	0.1692	0.1107	0.1397	0.1144
156	24	0.1700	0.1112	0.1401	0.1147
168	23	0.1708	0.1117	0.1409	0.1154
180	21	0.1713	0.1120	0.1411	0.1156
193	23	0.1720	0.1125	0.1409	0.1154
217	22	0.1735	0.1136	0.1409	0.1154

UNTREATED OIL FILM ~~NO.~~ Set 1

Hrs.	Temp.	Wt. Film A	Wt. A. Standardized	Wt. Film B	Wt. B Standardized
241	23	0.1745	0.1142	0.1405	0.1151
287	20	0.1741	0.1139	0.1396	0.1143
353	20	0.1748	0.1144	0.1402	0.1148
445	19	0.1731	0.1132	0.1383	0.1133

LEAD-OXIDE ~~No.~~ Set 2

Hrs.	Temp.	Wt. Film A	Wt. A Standardized	Wt. Film B	Wt. B Standardized
0	23	0.0616	0.1000	0.0657	0.1000
~~3~~	24	0.0632	0.1026	0.0674	0.1026
7	24	0.0658	0.1068	0.0704	0.1072
10	24	0.0684	0.1110	0.0732	0.1114
21	23	0.0710	0.1153	0.0757	0.1152
24	24	0.0712	0.1156	0.0758	0.1154
28	21.5	0.0710	0.1153	0.0758	0.1154
31	21	0.0710	0.1153	0.0758	0.1154
34	21	0.0707	0.1148	0.0756	0.1151
45	24.5	0.0704	0.1143	0.0753	0.1148
48	23	0.0702	0.1140	0.0751	0.1145
52.5	23	0.0702	0.1140	0.0749	0.1141
57.5	19	0.0700	0.1137	0.0747	0.1138
67.5	22	0.0698	0.1133	0.0742	0.1129
70.5	22	0.0697	0.1131	0.0744	0.1133
79.5	25	0.0696	0.1129	0.0744	0.1133
89.5	25	0.0696	0.1129	0.0742	0.1129
97.5	25	0.0694	0.1127	0.0740	0.1126
101	27	0.0692	0.1124	0.0740	0.1126
112	27	0.0691	0.1122	0.0739	0.1124
125	18	0.0684	0.1110	0.0730	0.1111
139	20	0.0684	0.1110	0.0731	0.1113
150	21	0.0684	0.1110	0.0732	0.1113
167	21	0.0686	0.1113	0.0732	0.1114
209	18	0.0686	0.1113	0.0730	0.1111
259	22	0.0680	0.1104	0.0726	0.1105

MANGANESE DIOXIDE ~~No.~~ set 2

Hrs.	Temp.	Wt Film A	Wt. A Standardized	Wt. B Film	Wt. B. Standardized
0	23	0.0463	0.1000	0.0485	0.1000
~~3~~	24	0.0465	0.1004	0.0485	0.1000
7	24	0.0464	0.1002	0.0486	0.1002
10	24	0.0464	0.1002	0.0486	0.1002
21	23	0.0464	0.1002	0.0486	0.1002
24	24	0.0466	0.1006	0.0489	0.1008
28	21.5	0.0465	0.1004	0.0490	0.1010
31	21	0.0468	0.1010	0.0491	0.1012
34	21	0.0468	0.1010	0.0491	0.1012
45	24.5	0.0474	0.1024	0.0496	0.1022
48	23	0.0475	0.1026	0.0498	0.1027
52.5	23	0.0480	0.1038	0.0502	0.1035
57.5	19	0.0486	0.1050	0.0509	0.1049
67.5	22	0.0496	0.1073	0.0521	0.1073
70.5	22	0.0504	0.1091	0.0529	0.1090
79.5	25	0.0518	0.1119	0.0543	0.1118
89.5	25	0.0526	0.1137	0.0547	0.1126
97.5	25	0.0528	0.1141	0.0553	0.1138
101	25	0.0530	0.1146	0.0555	0.1143
112	27	0.0534	0.1155	0.0559	0.1151
125	18	0.0526	0.1137	0.0551	0.1135
139	20	0.0529	0.1144	0.0556	0.1145
150	20	0.0533	0.1151	0.0558	0.1149
167	21	0.0532	0.1148	0.0557	0.1147
209	18	0.0530	0.1144	0.0555	0.1143
259	22	0.0526	0.1136	0.0551	0.1135

Mn-SOAP NO. 2

Hrs	Temp.	Wt. Film A	Wt. A Standard-ized	Wt. Film B	Wt. B Standard-ized
0	23	0.0497	0.1000	0.0450	0.1000
3	24	0.0500	0.1006	0.0453	0.1006
7	24	0.0546	0.1098	0.0503	0.1118
10	24	0.0568	0.1142	0.0515	0.1144
21	23	0.0560	0.1126	0.0506	0.1124
24	24	0.0561	0.1128	0.0507	0.1126
28	21.5	0.0560	0.1126	0.0505	0.1122
31	21	0.0558	0.1122	0.0505	0.1122
34	21	0.0557	0.1120	0.0503	0.1118
45	24.5	0.0552	0.1110	0.0500	0.1112
48	23	0.0552	0.1110	0.0500	0.1112
52.5	23	0.0550	0.1106	0.0498	0.1108
57.5	19	0.0550	0.1106	0.0495	0.1102
67.5	22	0.0547	0.1100	0.0495	0.1102
70.5	22	0.0546	0.1098	0.0495	0.1102
79.5	25	0.0548	0.1102	0.0495	0.1102
89.5	25	0.0546	0.1098	0.0493	0.1098
97.5	25	0.0544	0.1094	0.0491	0.1094
101	25	0.0543	0.1092	0.0491	0.1094
112	27	0.0544	0.1094	0.0491	0.1094
125	18	0.0534	0.1074	0.0482	0.1074
139	20	0.0536	0.1078	0.0485	0.1080
150	20	0.0538	0.1082	0.0487	0.1084
167	18	0.0536	0.1082	0.0487	0.1084
201	18	0.0536	0.1078	0.0485	0.1080
259	22	0.0536	0.1078	0.0485	0.1080

Pb-SOAP Set 2

Hrs.	Temp.	Wt. Film A	Wt. A Standard-ized	Wt. Film B	Wt. B. Standard-ized
0	23	0.0288	0.1000	0.0314	0.1000
3	24	0.0298	0.1035	0.0324	0.1032
7	24	0.0312	0.1084	0.0342	0.1090
10	24	0.0326	0.1131	0.0358	0.1141
21	23	0.0330	0.1145	0.0361	0.1151
24	24	0.0332	0.1152	0.0361	0.1151
28	21.5	0.0332	0.1152	0.0360	0.1148
31	21	0.0332	0.1152	0.0360	0.1148
34	21	0.0329	0.1142	0.0357	0.1138
45	24.5	0.0328	0.1138	0.0356	0.1135
48	23	0.0327	0.1135	0.0355	0.1132
52.5	23	0.0326	0.1131	0.0355	0.1132
57.5	19	0.0324	0.1124	0.0354	0.1128
67.5	22	0.0322	0.1117	0.0352	0.1122
70.5	22	0.0324	0.1124	0.0354	0.1128
79.5	25	0.0325	0.1127	0.0353	0.1125
89.5	25	0.0322	0.1117	0.0350	0.1115
97.5	25	0.0324	0.1124	0.0350	0.1115
101	25	0.0323	0.1120	0.0350	0.1115
112	27	0.0323	0.1120	0.0351	0.1118
125	18	0.0314	0.1089	0.0342	0.1089
139	20	0.0316	0.1096	0.0344	0.1095
150	20	0.0318	0.1102	0.0346	0.1102
167	21	0.0318	0.1102	0.0346	0.1102
209	18	0.0314	0.1088	0.0344	0.1094
259	22	0.0318	0.1102	0.0346	0.1102

CO-SOAP ~~NUMBER~~ 2.

Hrs.	Temp.	Wt. Film A	Wt. A Standard-ized	Wt. Film B	Wt. B Standard-ized
0	23	0.0310	0.1000	0.0326	0.1000
3	24	0.0314	0.1013	0.0328	0.1006
7	24	0.0320	0.1032	0.0334	0.1024
10	24	0.0332	0.1071	0.0346	0.1060
21	23	0.0360	0.1160	0.0378	0.1156
24	24	0.0359	0.1160	0.0378	0.1156
28	21.5	0.0359	0.1157	0.0378	0.1156
31	21	0.0359	0.1157	0.0375	0.1147
34	21	0.0355	0.1144	0.0372	0.1138
45	24.5	0.0350	0.1128	0.0372	0.1138
48	23	0.0352	0.1134	0.0372	0.1138
52.5	23	0.0350	0.1128	0.0367	0.1123
57.5	19	0.0348	0.1122	0.0366	0.1120
67.5	22	0.0346	0.1116	0.0362	0.1108
70.5	22	0.0347	0.1119	0.0364	0.1114
79.5	25	0.0347	0.1119	0.0364	0.1114
89.5	25	0.0346	0.1116	0.0362	0.1108
97.5	25	0.0346	0.1116	0.0360	0.1102
101	25	0.0345	0.1113	0.0360	0.1102
112	27	0.0345	0.1113	0.0362	0.1108
125	18	0.0335	0.1081	0.0352	0.1078
139	20	0.0336	0.1084	0.0354	0.1084
150	20	0.0338	0.1090	0.0354	0.1084
167	21	0.0336	0.1084	0.0354	0.1084
209	18	0.0336	0.1084	0.0354	0.1084
259	22	0.0338	0.1090	0.0354	0.1084

UNTREATED OIL Set .2.

Hrs.	Temp.	Wt. A Film	Wt. A Standardized	Wt. B Film	Wt. B Standardized
0	23	0.0196	0.1000	0.0234	0.1000
3	24	0.0196	0.1000	0.0235	0.1004
7	24	0.0197	0.1005	0.0235	0.1004
10	24	0.0197	0.1005	0.0235	0.1004
21	23	0.0195	0.0995	0.0235	0.1004
24	24	0.0200	0.1020	0.0238	0.1007
28	21.5	0.0200	0.1020	0.0239	0.1021
31	21	0.0200	0.1020	0.0240	0.1026
34	21	0.0200	0.1020	0.0240	0.1026
45	24.5	0.0209	0.1066	0.0248	0.1060
48	23	0.0209	0.1066	0.0248	0.1060
52.5	23	0.0213	0.1087	0.0252	0.1077
57.5	19	0.0218	0.1112	0.0256	0.1094
67.5	22	0.0228	0.1163	0.0263	0.1124
70.5	22	0.0228	0.1163	0.0266	0.1137
79.5	25	0.0230	0.1173	0.0270	0.1154
89.5	25	0.0230	0.1173	0.0272	0.1162
98.5	25	0.0229	0.1168	0.0272	0.1162
101	25	0.0229	0.1168	0.0272	0.1162
112	27	0.0229	0.1168	0.0272	0.1162
125	18	0.0218	0.1112	0.0264	0.1128
139	20	0.0222	0.1132	0.0266	0.1136
150	20	0.0223	0.1137	0.0267	0.1140
167	21	0.0224	0.1143	0.0266	0.1136
209	18	0.0222	0.1132	0.0264	0.1128
259	22	0.0222	0.1132	0.0264	0.1128

PLOTTING OF CURVES

The weight time curves for these films were plotted, using 100 milligrams as the standard initial weight in each case. This standardization of the weight of film disregards the difference in the rate of drying that might be due to different thicknesses of the films. That standardizations of this type were justifiable was shown by the following tests:

Several films of the litharge boiled oil of set II varying greatly in thickness were weighed and allowed to "dry" as in the previous tests. The data for this comparative-thickness drying test is tabulated below (Set 3.)

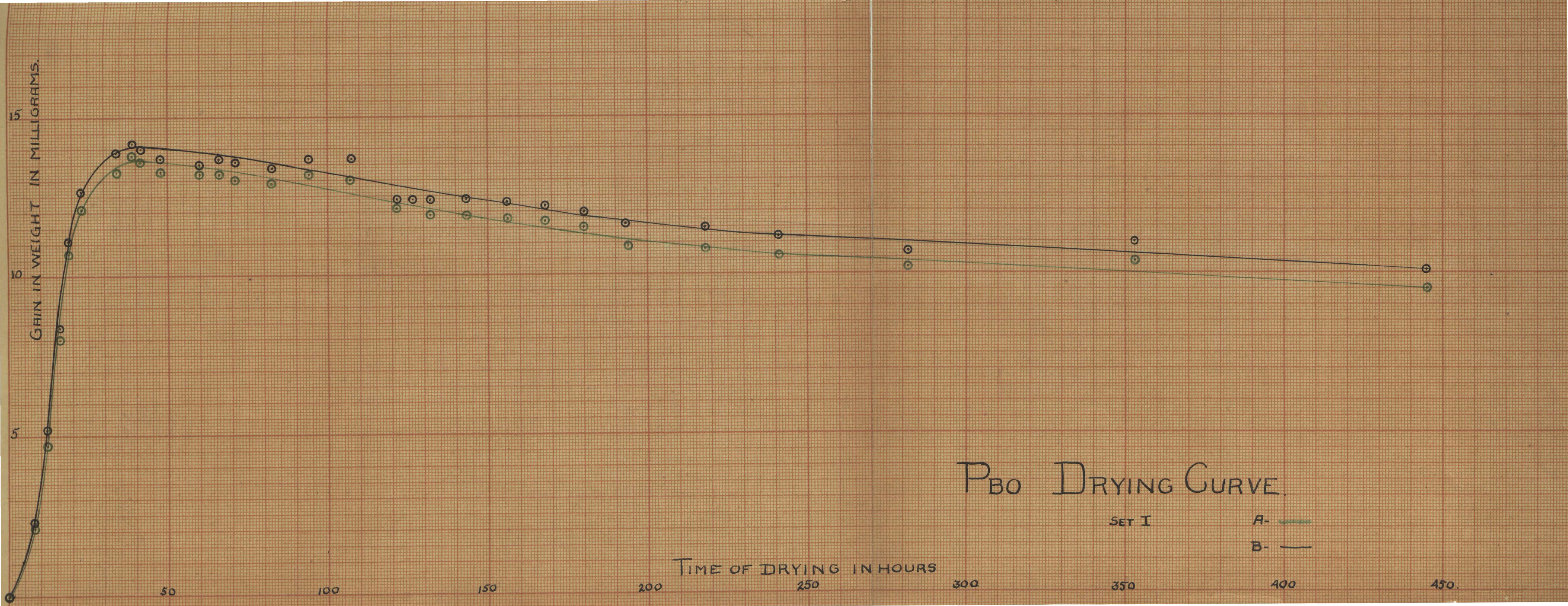
COMPARATIVE DRYING THICKNESS TEST (3)

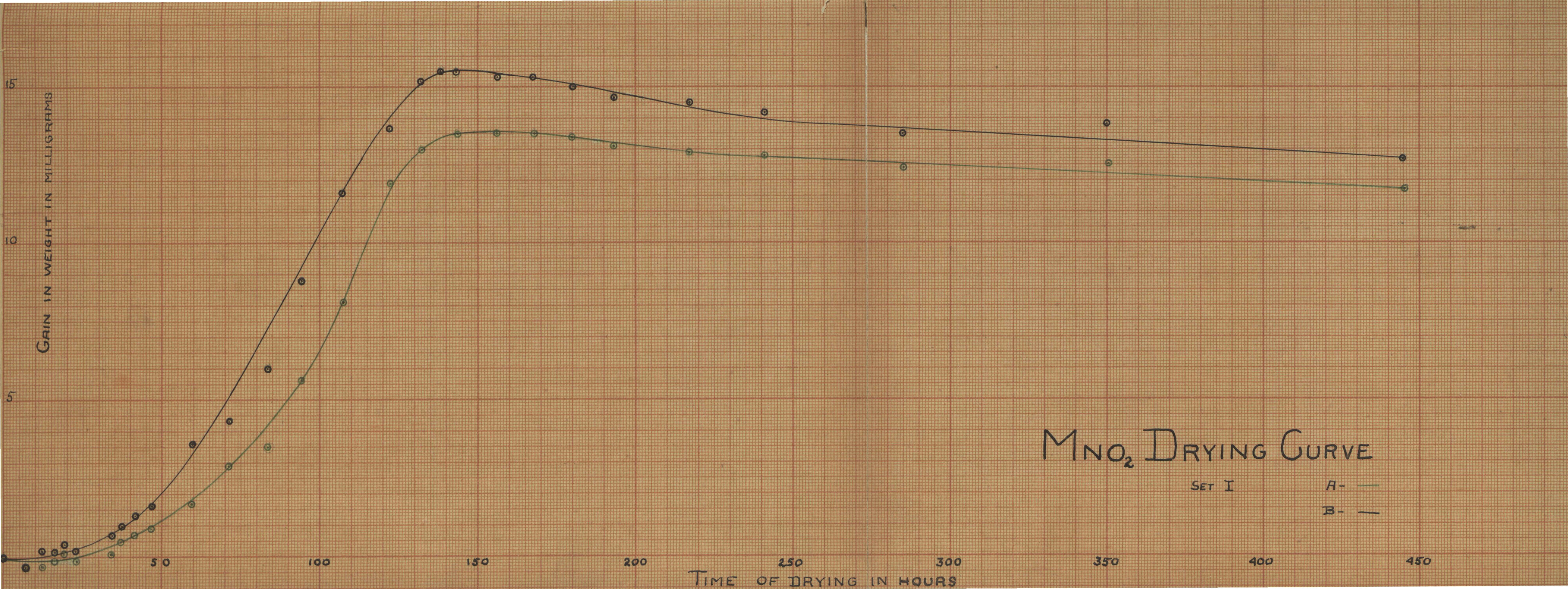
Hrs.	Temp.	Wt. Film 1	Wt. 1 Standard-ized	Wt. Film 2	Wt. 2 Standard-ized
0	23	0.0126	0.1000	0.0221	0.1000
1.5	24	0.0130	0.1032	0.0225	0.1048
5.5	21.5	0.0135	0.1072	0.0231	0.1046
8.5	21	0.0138	0.1096	0.0240	0.1087
11.5	21	0.0143	0.1140	0.0247	0.1119
23	23	0.0146	0.1164	0.0255	0.1156
25	27	0.0146	0.1164	0.0256	0.1161
30	23	0.0146	0.1164	0.0254	0.1152
35.5	19	0.0145	0.1156	0.0251	0.1139
47	22	0.0144	0.1148	0.0250	0.1135
50	22	0.0145	0.1156	0.0253	0.1148
59	25	0.0148	0.1180	0.0253	0.1148
70.5	25	0.0146	0.1164	0.0251	0.1139
79	25	0.0146	0.1164	0.0251	0.1139
84	25	0.0145	0.1156	0.0250	0.1135
95.5	27	0.0146	0.1164	0.0251	0.1139
108	18	0.0137	0.1088	0.0241	0.1093
122	20	0.0140	0.1112	0.0243	0.1102
132.5	20	0.0142	0.1128	0.0245	0.1111
147.5	24	0.0142	0.1128	0.0244	0.1107
180	18	0.0140	0.1112	0.0244	0.1107
250	22	0.0142	0.1128	0.0245	0.1111

COMPARATIVE THICKNESS DRYING TEST (3)

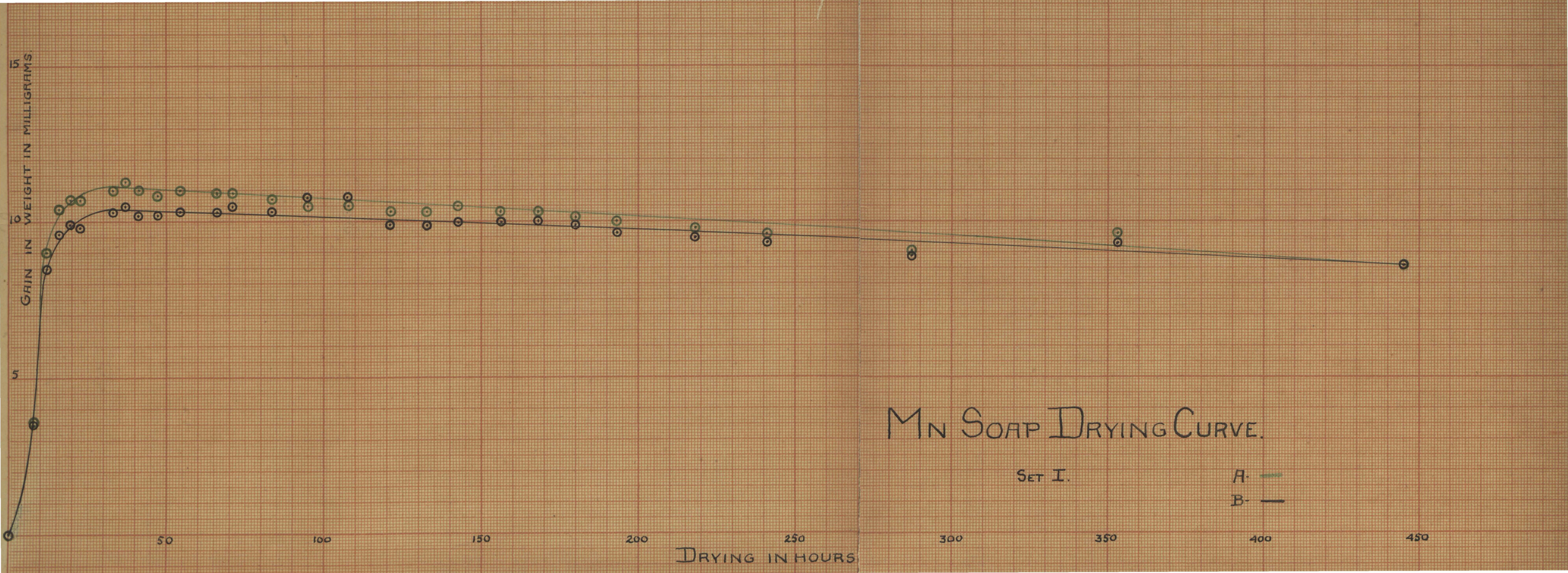
Hrs.	Temp.	Wt. Film 3	Wt. 3 Standard-ized	Wt. Film 4	Wt. 4 Standard-ized
0	23	0.0326	0.1000	0.0485	0.1000
1.5	24	0.0333	0.1021	0.0495	0.1020
5.5	21.5	0.0344	0.1054	0.0510	0.1050
8.5	21	0.0352	0.1078	0.0522	0.1075
11.5	21	0.0364	0.1114	0.0541	0.1113
23	23	0.0379	0.1159	0.0562	0.1158
25	27	0.0377	0.1153	0.0562	0.1158
30	23	0.0376	0.1150	0.0559	0.1152
35.5	19	0.0374	0.1144	0.0555	0.1144
47	22	0.0373	0.1141	0.0554	0.1142
50	22	0.0374	0.1144	0.0556	0.1146
59	25	0.0376	0.1150	0.0557	0.1148
70.5	25	0.0372	0.1138	0.0553	0.1140
79	25	0.0372	0.1138	0.0553	0.1140
84	25	0.0372	0.1138	0.0553	0.1140
95.5	27	0.0370	0.1132	0.0553	0.1140
108	18	0.0361	0.1105	0.0543	0.1118
122	20	0.0364	0.1114	0.0544	0.1120
132.5	20	0.0364	0.1114	0.0545	0.1122
147.5	24	0.0364	0.1114	0.0545	0.1122
180	18	0.0364	0.1114	0.0545	0.1122
250	22	0.0362	0.1108	0.0541	0.1114

It is obvious from this data that the percent gain in weight within the same time limit is practically constant and independent of the thickness of the oil film, and also that the maximum gain is reached in approximately the same time. This confirms the work of Mulder[13] and that of Lippert[9], showing that for thin films the differences of thickness can be disregarded, and that plotting the curves to the same standard is justifiable.


PbO Drying Curve.
Set I
A-
B-
Gain in weight in milligrams.
15
10
5
Time of drying in hours
50
100
150
200
250
300
350
400
450.

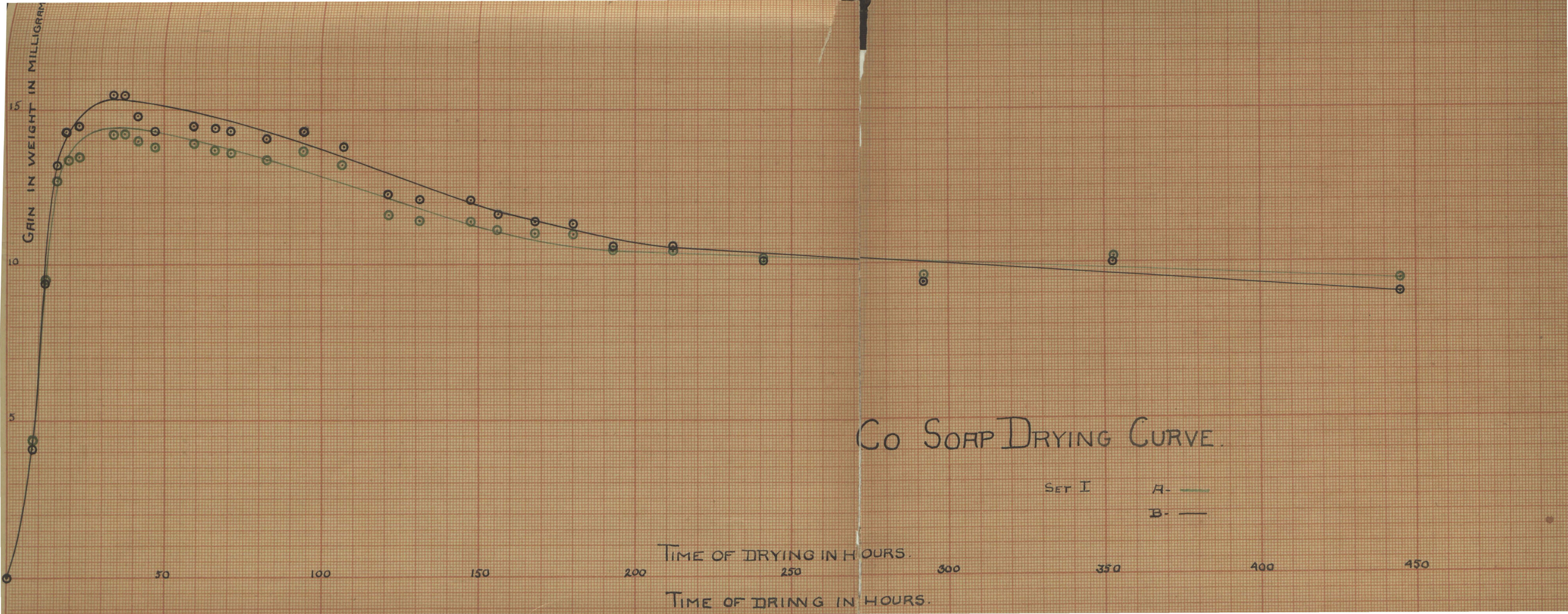


MnO$_2$ Drying Curve
Set I
A-
B-
Gain in weight in milligrams
15
10
5
Time of drying in hours
50
100
150
200
250
300
350
400
450

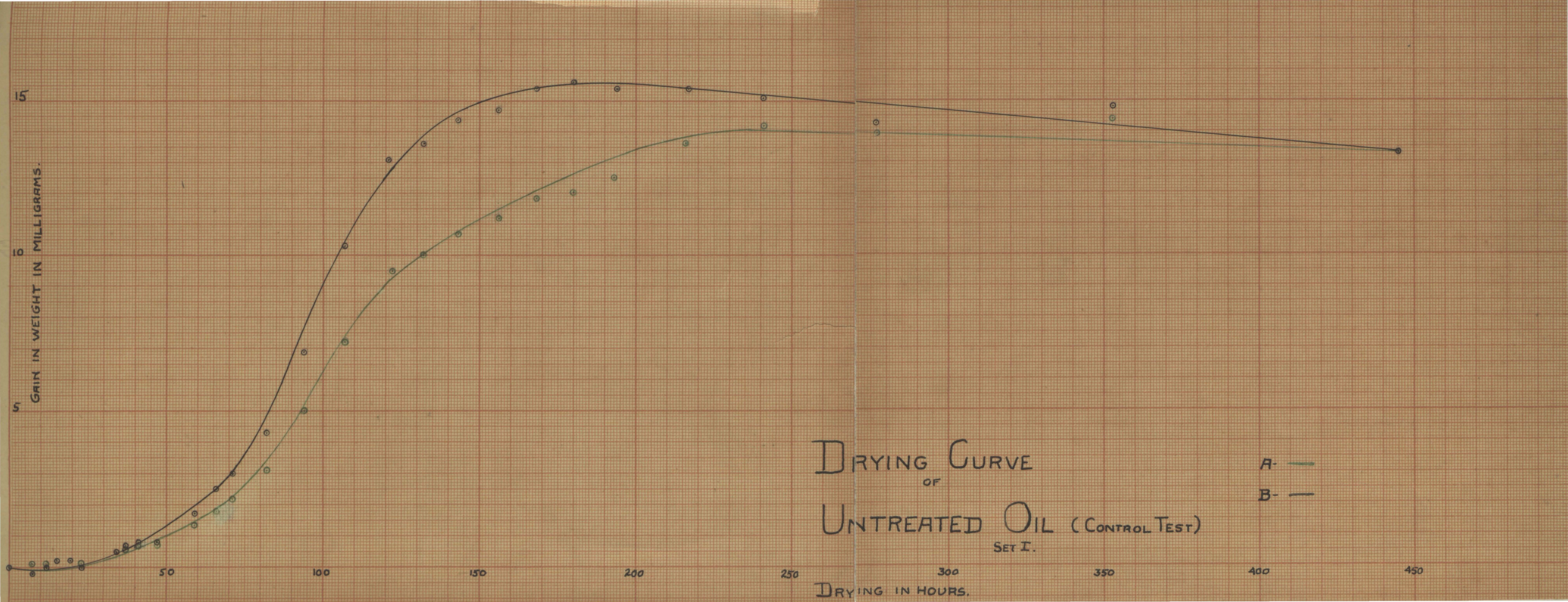


Mn Soap Drying Curve.
Set I.
A-
B-
Gain in weight in milligrams.
15
10
5
Drying in hours
50
100
150
200
250
300
350
400
450

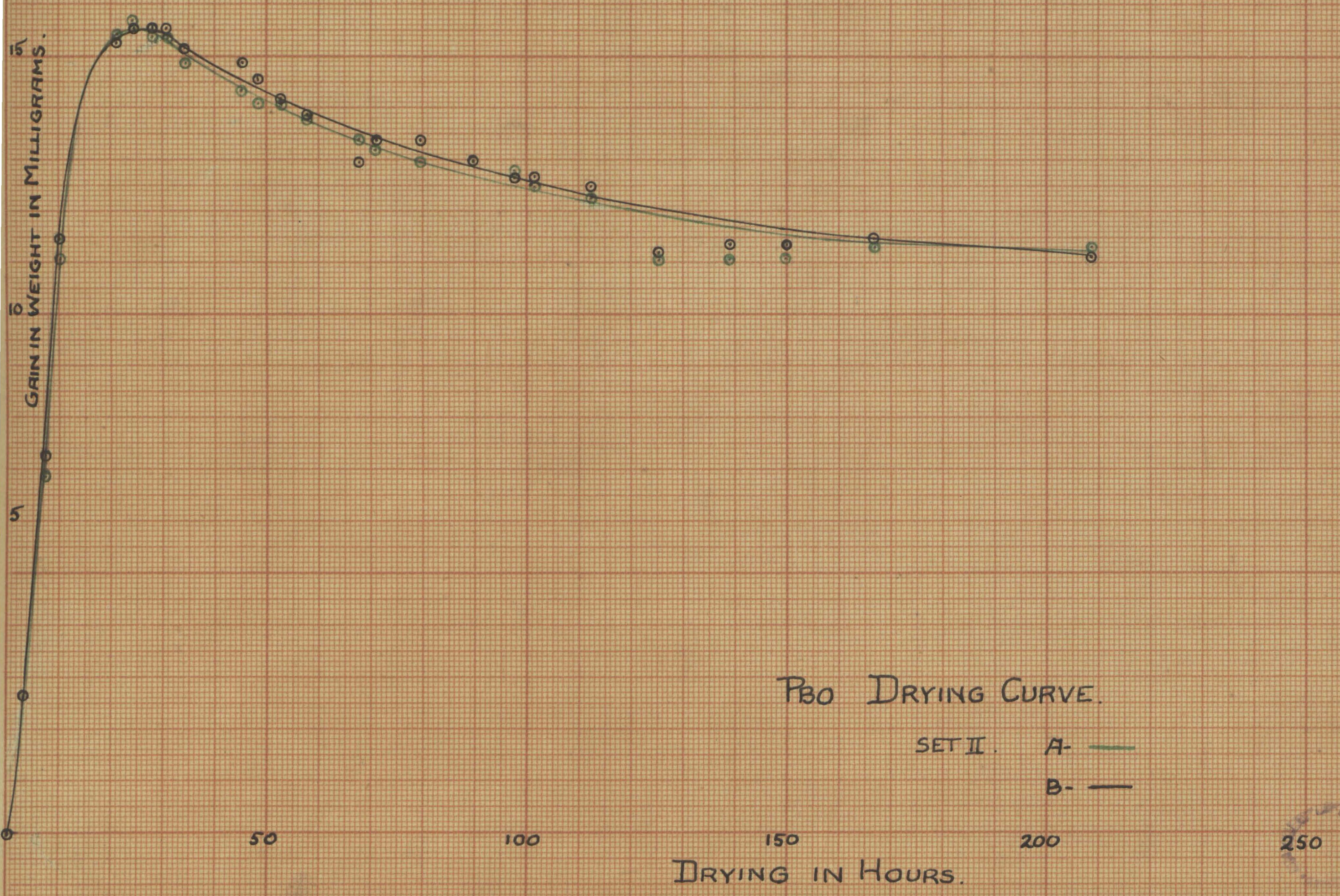

Pb Soap Drying Curve
Set I.
A-
B-
Gain in weight in milligrams
5
10
15
Drying in hours
50
100
150
200
250
300
350
400
450



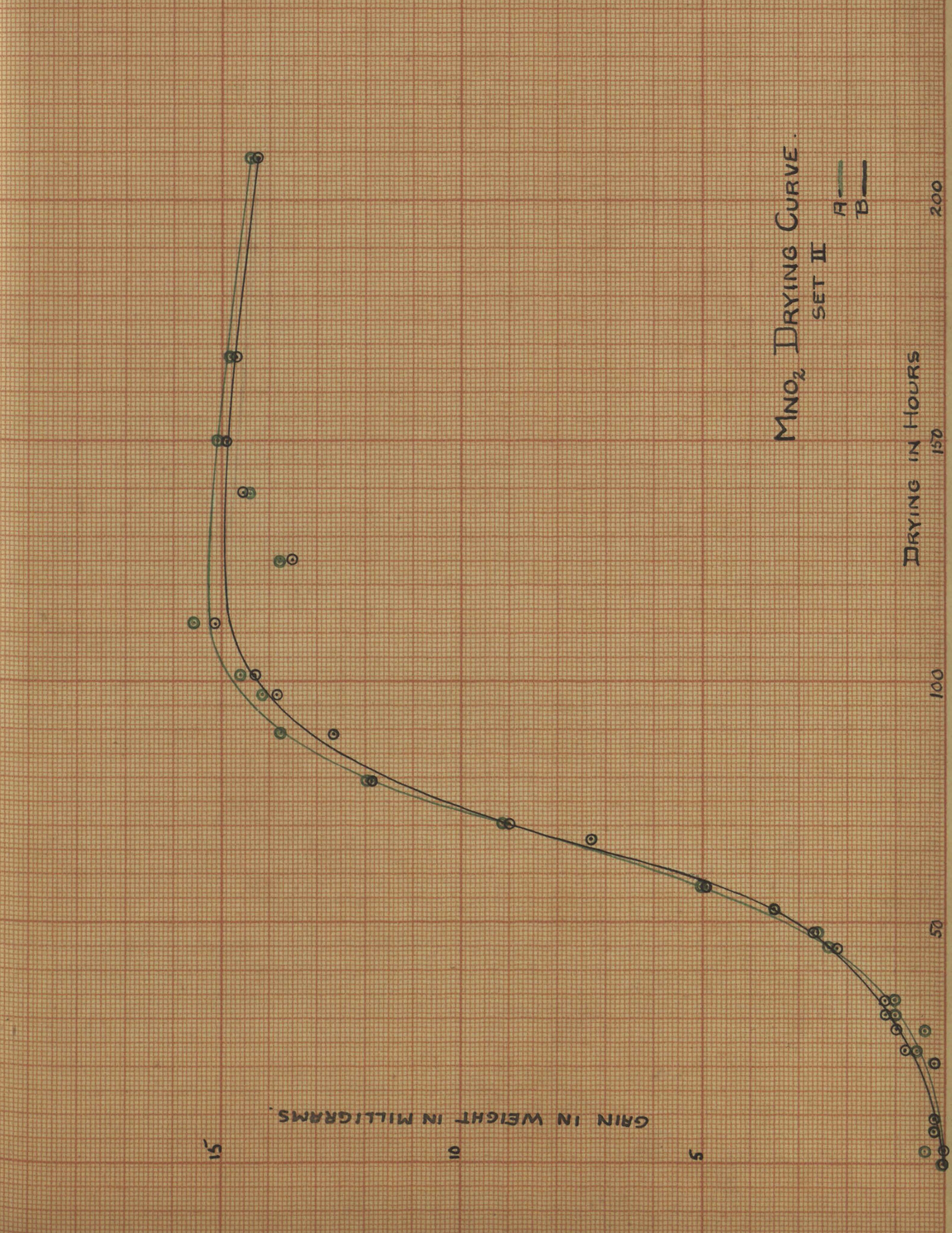
Co Soap Drying Curve.
Set I
A-
B-
Gain in Weight in Milligram
5
10
15
50
100
150
200
250
300
350
400
450
Time of Drying in Hours.
Time of Drinng in Hours.



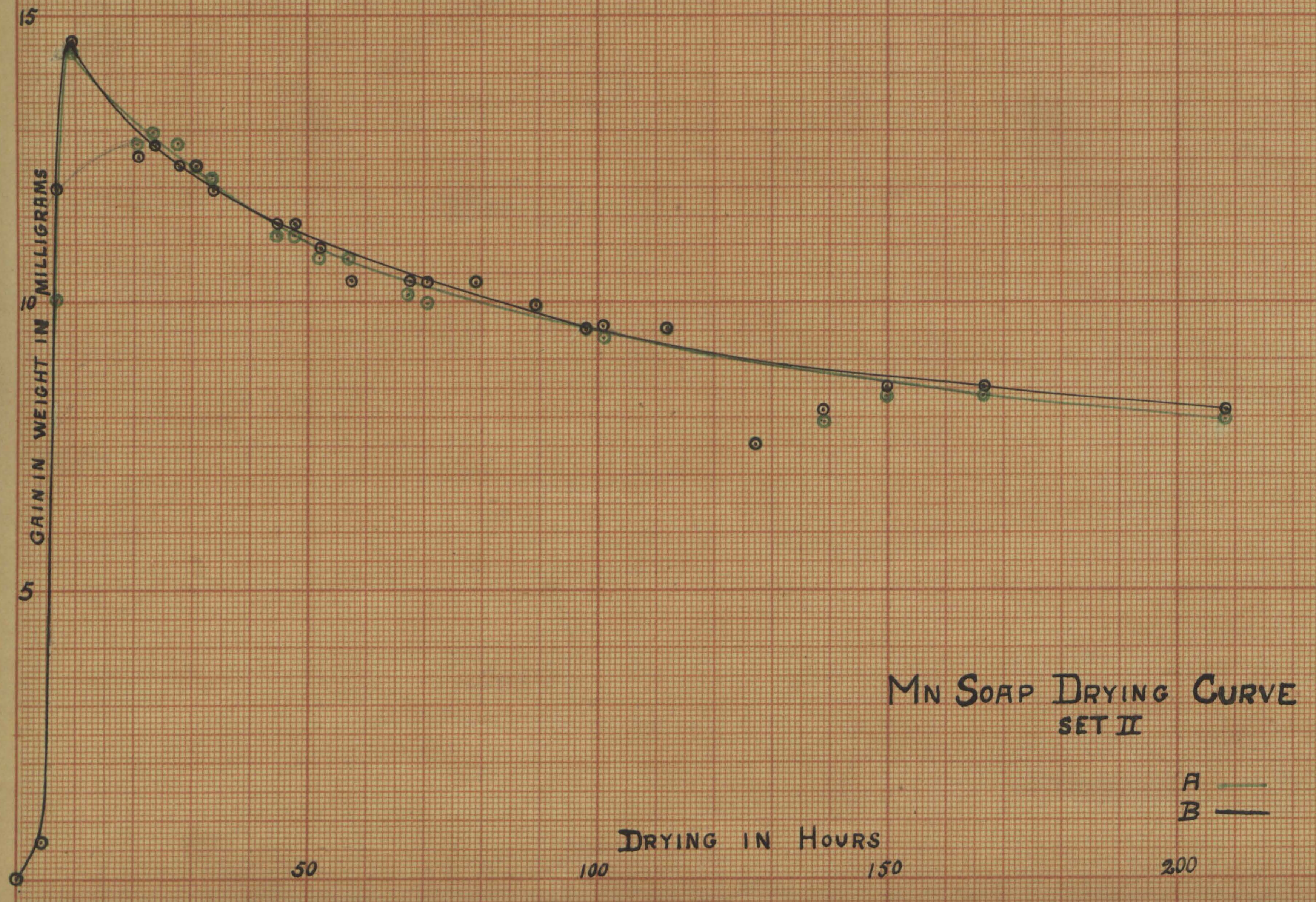
Drying Curve of Untreated Oil (Control Test)
Set I.
A-
B-
Gain in weight in milligrams.
5
10
15
50
100
150
200
250
300
350
400
450
Drying in hours.

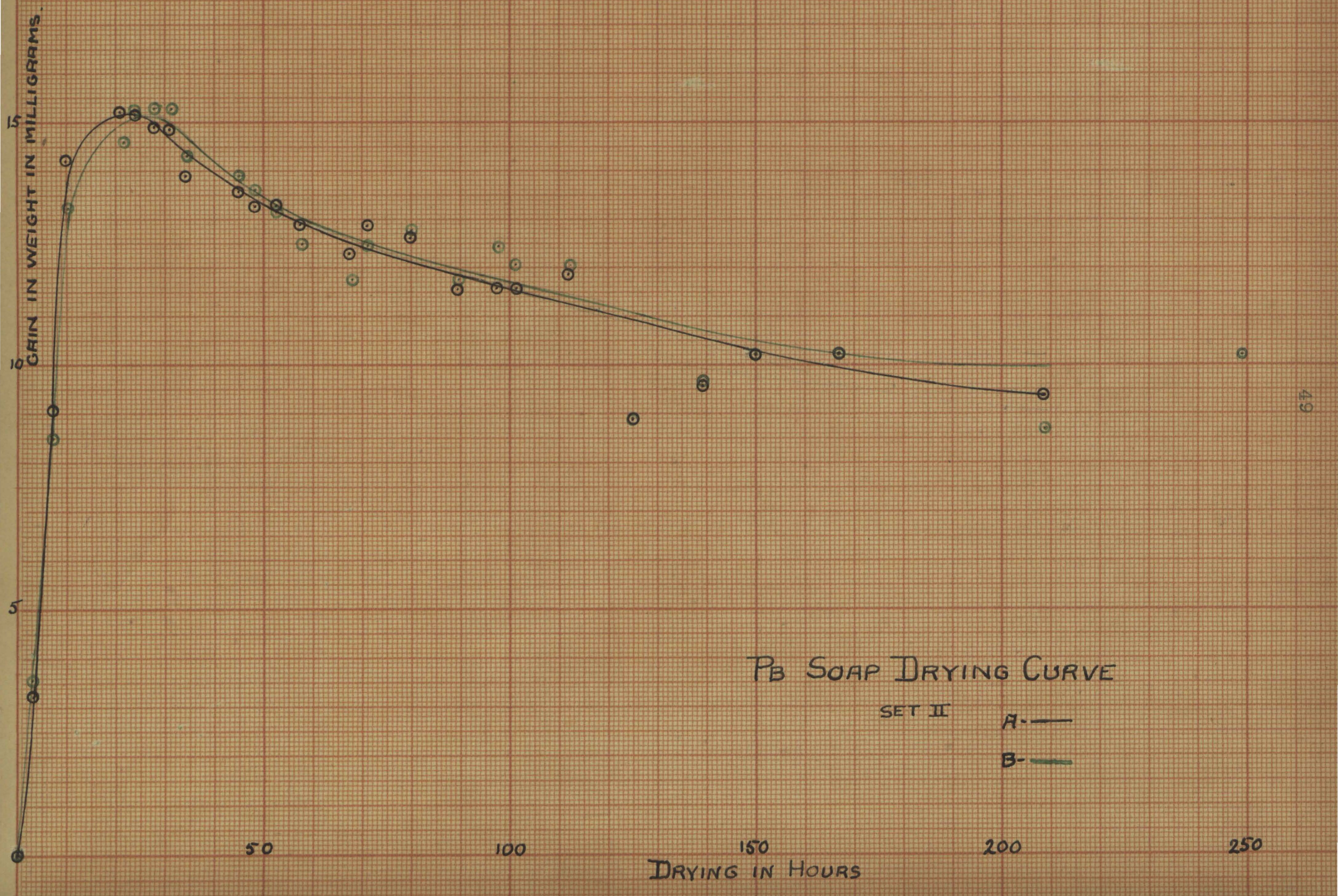


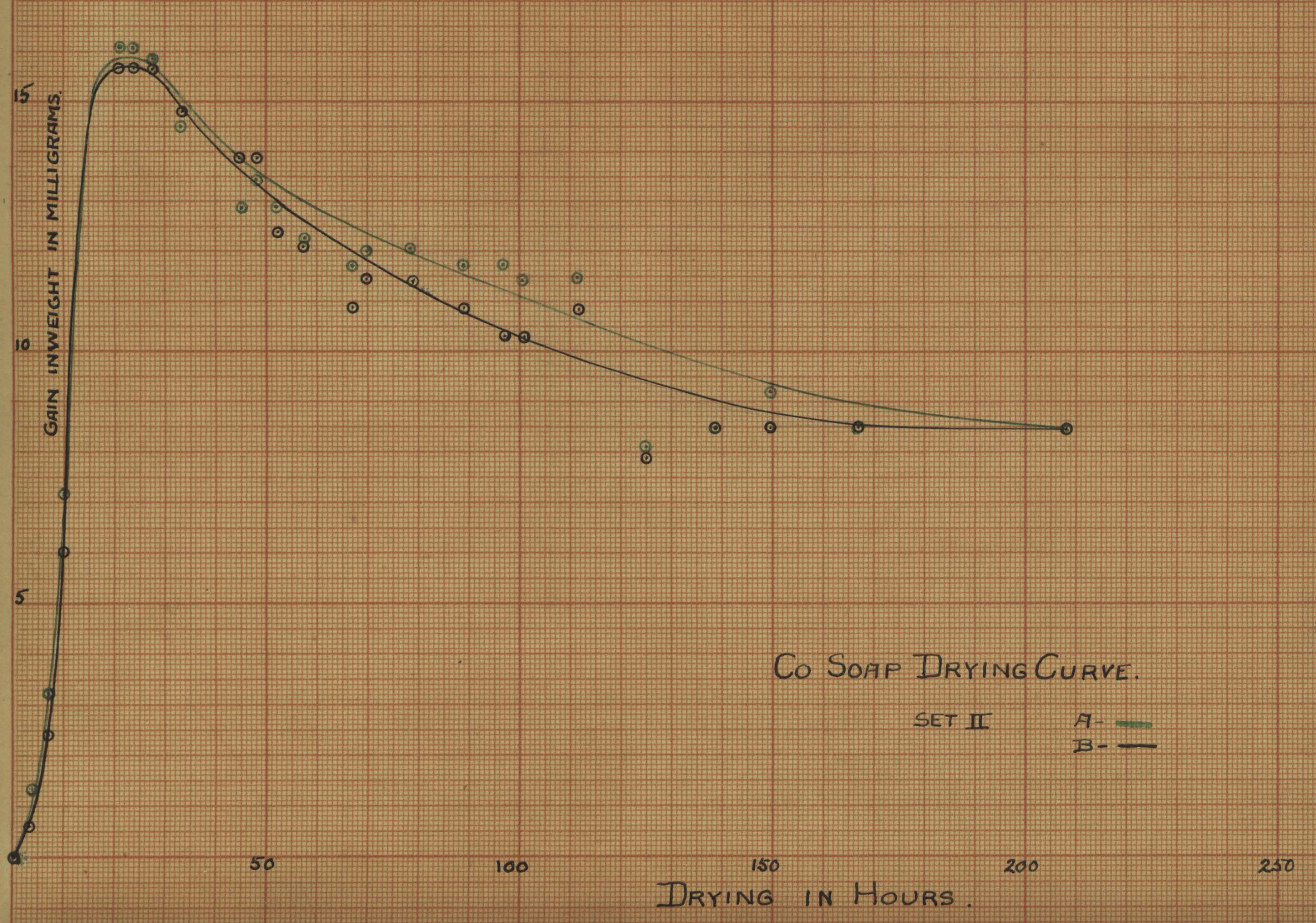
PbO Drying Curve.
Set II. A-
B-
Gain in Weight in Milligrams.
15
10
5
50
100
150
200
250
Drying in Hours.

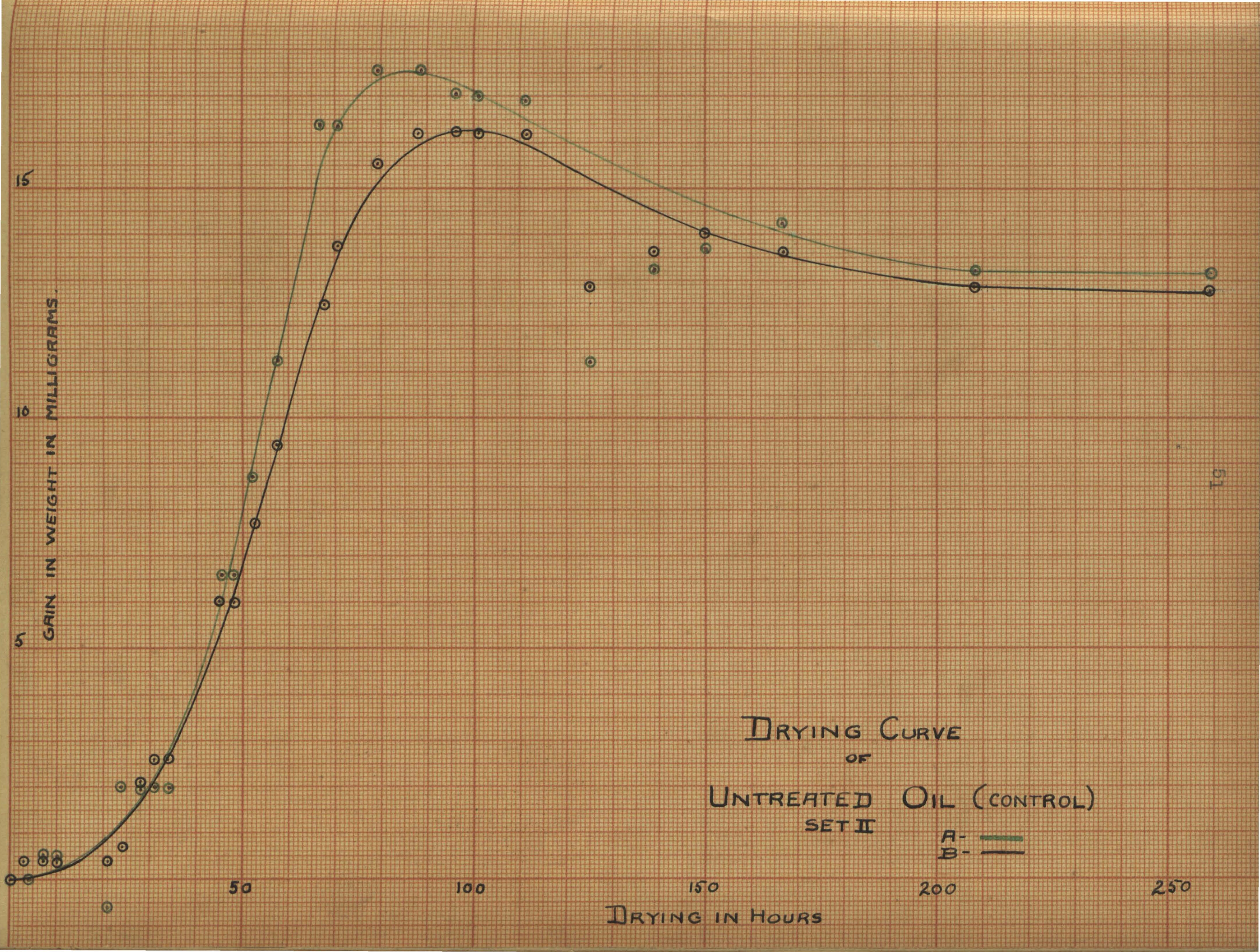


MnO2 Drying Curve.
Set II
A—
B—
Drying in Hours
50
100
150
200
Gain in Weight in Milligrams.
5
10
15

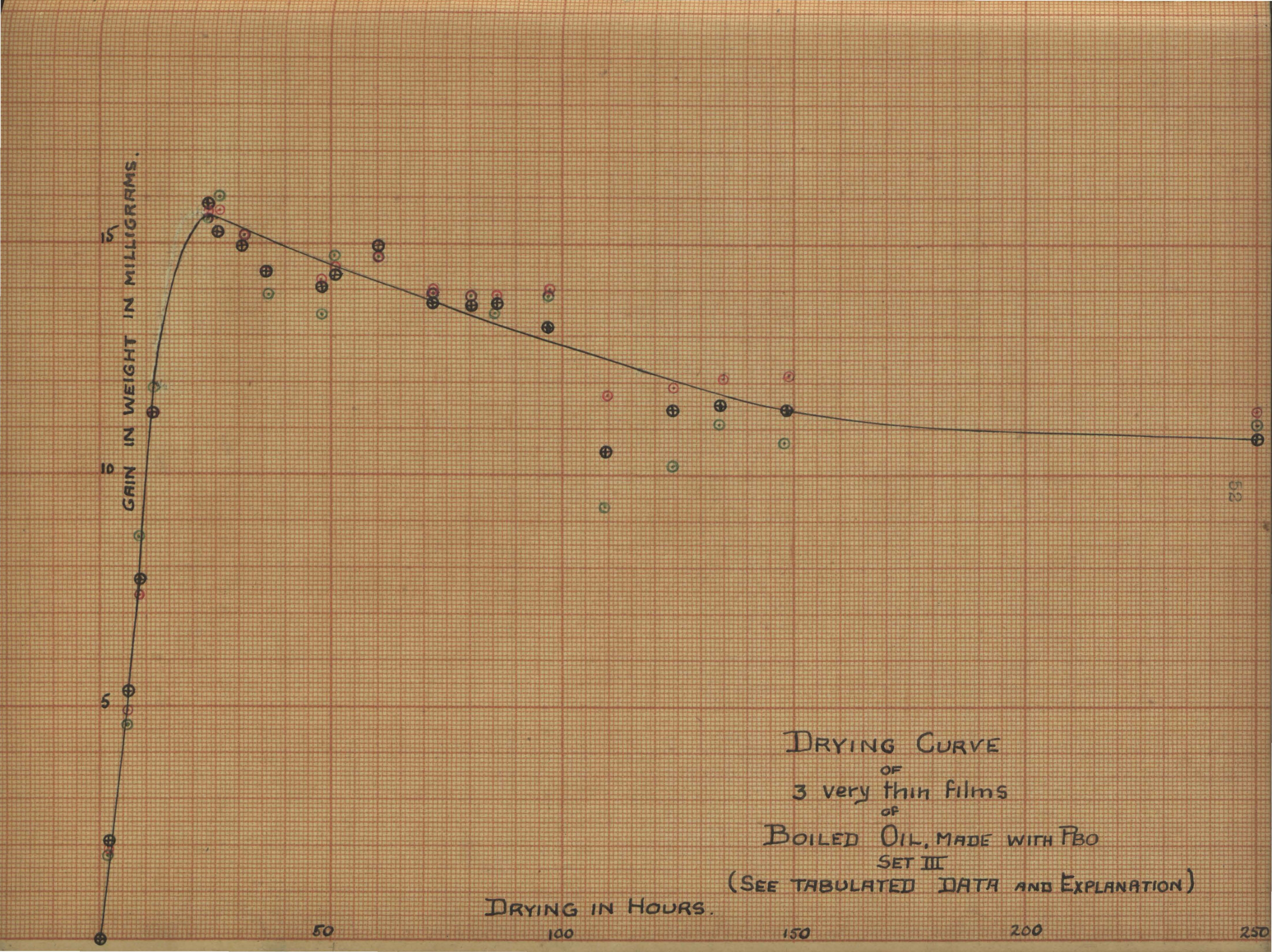

Mn Soap Drying Curve
Set II
A
B
Gain in Weight in Milligrams
Drying in Hours
15
10
5
50
100
150
200


PB SOAP DRYING CURVE
SET II
A-
B-
GAIN IN WEIGHT IN MILLIGRAMS.
15
10
5
50
100
150
200
250
DRYING IN HOURS


Co Soap Drying Curve.
Set II
A-
B-
Gain in weight in milligrams.
15
10
5
50
100
150
200
250
Drying in Hours.



Drying Curve
of
Untreated Oil (control)
Set II
A-
B-
Gain in weight in milligrams.
5
10
15
50
100
150
200
250
Drying in Hours
51


DRYING CURVE
OF
3 very thin films
OF
BOILED OIL, MADE WITH PbO
SET III
(SEE TABULATED DATA AND EXPLANATION)
GAIN IN WEIGHT IN MILLIGRAMS.
5
10
15
DRYING IN HOURS.
50
100
150
200
250
52

D I S C U S S I O N O F C U R V E S

The above curves were drawn to represent the weight changes under average, constant atmospheric conditions and minor irregularities believed to be due to changes in these conditions have been neglected. The sudden drop in all of the curves of set II at 125 hours was simultaneous with a sudden temperature change, and occurs in set III at 108 hours, (the two sets not having been started simultaneously). Set I was not weighed at this time. There is every evidence that this drop was due to meteorological changes and need not be considered in the curves of sets II and III.

Film 1 of set III was not plotted, Because of its extreme lightness it was believed that all errors would be unduly magnified in standardization. However, a single curve serves very well for any of the three curves plotted, and this curve corresponds closely to those of the same oil in set II.

On the whole, it seems that the duplicates of the fastest drying oils give the more closely checking curves, but it must be remembered that each division on the vertical scale corresponds to a weight of but 0.0001 gm., and that in the majority of cases all errors have been increased by standardization.

Altho there is probably no definite point on any of the curves at which the drying action of the oil can be said to be complete, we are inclined to agree with Lippert(9) that the

point showing maximum gain, i.e., the highest point on the curve, may be used in judging the relative rate of drying. In other words, the time required to reach the ~~point~~ maximum weight is shortest in the case of the most rapidly drying oil film.

No equation for the above curves has yet been derived, but owing to the many factors involved, the equation is probably very complex.

S U M M A R Y   A N D   C O N C L U S I O N S

The conclusions drawn from this investigation are the following:

(1) That the manganese, lead, and cobalt α-elaeostearates cannot be prepared in the pure state by the ordinary methods, even with unusual precautions in preparation.

(2) That the soaps made in the manner described contain a percentage of metal that is somewhat higher or lower than the theoretical percent of metal in the corresponding elaeostearates, depending on the nature of the soap.

(3) That the manganese, lead, and cobalt soaps herein described are "driers" and resemble the corresponding isomeric linoleates in their drying action.

(4) That since the maximum absorption in the case of the linseed oil treated with the manganese soap is reached more rapidly than in the case of the "boiled oil" made with the equivalent amount of litharge, the manganese soap may be considered a more efficient drying agent.

(5) That the lead and cobalt soaps, judging from the drying curves, are approximately equal to litharge as driers.

(6) That the "boiled oils" made from the lead, manganese, and cobalt soaps may be, owing to their lighter color, commercially more valuable than that made from litharge.

(7) That the shape of the curves of the boiled oils depends partly on the manner, i.e., temperature, etc., of boiling.

B I B L I O G R P H Y

(1) Cloez, Comtes Rendus, 81, 469

(2) Ibid 82, 501

(3) Ibid 83, 934

(4) Marquenne, Comtes Rendus, 135, 696

(5) Kamataka, Journal of the Chemical Soc. 1903, 83, 1042.

(6) Majima, Berichte der Deutschen Chemischen Gesellschaft, 42, 674

(7) Lewkowitsch, Chemical Technology and Analysis of Oils, Fats, and Waxes, Vol. II, 60

(8) Kissling, Journal of the Society of Chemical Industry 1891, 778

(9) Lippert, Zeitschrift für angewandte Chemie, 1898, 412

(10) Sabin, Journal of Industrial and Engineering Chemistry 1911, 3, 84.

(11) Gardner, Journal of Industrial and Engineering Chemistry 1914, 6, 91

(12) Andés, Oil Colors and Printers Inks p. 40

(13) Mulder, Die Chemie der anstrockenen Oele