

THE VALUE OF CERTAIN PAINT OILS.

BY

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THE recent activity of the paint chemist in searching for oils to partly replace linseed oil, has come not only as a result of the present scarcity of the latter commodity, but through a desire to develop a vehicle that will be for certain technical paints even more satisfactory, if possible, than linseed oil.

It is not the writer's intention, however, to encourage the use of so-called substitutes for linseed oil. The market is flooded with them at the present time, and great danger will lurk in their use until their composition is understood or their value determined in a practical way.

The real object of this paper is to present a summary of the results obtained by the writer from a series of experiments on paint vehicles, which may serve to guide other investigators along similar lines of research. The tests outlined herein, although of interest in pointing out the possibilities of the use of many oils other than linseed, are, nevertheless, tentative in nature and subject to confirmation through practical field exposure tests before they are to be accepted commercially.

It is well known that a most desirable feature of paint oils is their ability to set up in a short period to a hard surface that will not take dust, that will stand abrasion and offer resistance to moisture and gases. This drying property is dependent upon the chemical nature of the oil. If it is an unsaturated compound, like linseed oil, rapid absorption of oxygen will cause the film to dry rapidly and become hard. If the oil be of a fully satisfied nature, like mineral oil, for example, oxygen cannot be taken up to any great extent and drying will not take place. The various animal and vegetable oils differ in their power of oxygen absorption to a lesser or greater extent. This difference is referred to by the chemist in terms of the iodine value. The iodine value of linseed oil is approximately 190, meaning that one gramme of the oil will take up 190 centigrammes of iodine.

Soya bean oil which has presented itself as a claimant for distinction in the list of paint oils, is now being imported into this country in large quantities. It is obtained from the seeds

TABLE I.
CHEMICAL CHARACTERISTICS OF SOYA BEAN OIL.

| Sample No. | Specific gravity | Acid No. | Saponification No. | Iodine No. | Per cent. of foots |
|------------|------------------|----------|--------------------|------------|--------------------|
| 1..... | 0.9233 | 1.87 | 188.4 | 127.8 | 3.81 |
| 2..... | 0.9240 | 1.92 | 188.3 | 127.2 | |
| 3..... | 0.9231 | 1.90 | 187.8 | 131.7 | |
| 4..... | 0.9233 | 1.91 | 188.4 | 129.8 | |
| 5..... | | | | 130.0 | |
| 6..... | | | | 132.6 | |
| 7..... | | | | 136.0 | |
| Average.. | 0.9234 | 1.90 | 188.2 | 130.7 | |

of *Soya Hispida*, a plant indiginous to Manchuria, but raised extensively in our own Southern States as a cattle food.

The writer has examined a number of representative samples of the oil that have come into this country, and the results obtained can be seen in Table I.

TABLE II.
IODINE VALUES OF LINSEED OIL AND MIXED OILS.

| Sample No. | Straight linseed | Soya. 25 per cent.; Linseed. 75 per cent. | Soya. 50 per cent.; Linseed. 50 per cent. | Soya. 75 per cent.; Linseed. 25 per cent. |
|--------------|------------------|--|--|--|
| 1..... | 190.3 | 175.2 | 160.7 | 140.4 |
| 2..... | 189.5 | 175.9 | 161.7 | 140.8 |
| 3..... | 188.0 | 175.4 | 160.3 | 139.0 |
| Average..... | 189.3 | 175.5 | 160.9 | 140.4 |

It is evident that the iodine value of soya bean oil is the only chemical characteristic that markedly differentiates it from linseed oil. Therefore, in the detection of soya bean oil and its estimation, the iodine values of several samples of mixed oils are given, as being of interest in this connection (Table II).

A series of tests were conducted to determine what drier was the most efficient to use with soya bean oil, and the results of these tests indicated that the percentage of lead or manganese, or of lead and manganese, which gave the maximum efficiency in the drying of linseed oil, gave also to soya bean oil the best results. The methods used in carrying out the tests were the same as on linseed oil, referred to later in this paper.

A definite quantity of oil was placed in weighed friction-top can covers, which were re-weighed after receiving the oil, to determine the amount used for the test in each case. The tin covers containing the oil were then placed in a large box under definite temperature control and humidity, for a certain period. Weighings were made at different periods, and the increases in weight, due to absorption of oxygen, was calculated to percentages.

Table III gives the results obtained. The time of drying was somewhat longer than with linseed oil.

Several test panels were painted with zinc and lead, alone and in combination, using linseed oil, soya bean oil, and mixtures of the two. No driers were used in these paints, as the object of the tests were to determine the drying action of the oils, without driers. The drying of the linseed oil paints was very good in less than two days, while the straight soya bean oil required nearly four days to set up, and was then tacky for a long period. Laboratory tests of a preliminary nature made with mixtures of the two oils, ground with pigments, so far have indicated that a moderate percentage of soya bean oil is not detrimental when used with linseed oil.

The writer has found that a few drops of soya bean oil placed in a porcelain dish will give with a drop of strong sulphuric acid, faint fluorescent yellow and green colors, forming a pattern distinct from the dark-brown begonia-shaped leaf formed by sulphuric acid with pure linseed oil. Many other qualitative tests have been tried to detect the presence of soya oil in admixture with linseed oil. Soya oil seems, however, not to possess the chromogenetic properties of oils, such as cottonseed oil.

Tung oil, or Chinese wood oil, as it is often termed, has been considered heretofore as an oil most valuable in the manufacture of varnishes, but seldom if ever to be used as a paint

oil. As a matter of fact, however, in manufacturing, certain technical paints for the protection of concrete and steel, the water-proofing of structures, and for other purposes, the manufacturer may find this oil, or its products, most useful, and to be prized very highly. Toch, as well as Lewkovitch, have shown

TABLE III.
SOYA BEAN OIL AND LEAD DRYER.

| Per cent. PbO. | | 0.05 | 0.10 | 0.30 | 0.50 | 0.70 | 1.00 | 1.30 | 1.60 |
|----------------|-----------|------|------|------|------|------|------|------|------|
| Per ct. gain | 1 day.. | | 0.07 | 0.63 | 1.34 | 1.05 | 1.53 | 0.93 | 1.35 |
| | 3 days.. | | 0.07 | 3.54 | 4.31 | 2.75 | 4.86 | 4.82 | 4.12 |
| | 5 days.. | | 0.09 | 5.04 | 6.06 | 6.09 | 6.75 | 6.66 | 5.52 |
| | 12 days.. | | | 6.88 | 7.54 | 7.43 | 7.76 | 7.32 | 6.47 |
| | 15 days.. | | | 8.84 | 8.03 | 8.59 | 8.81 | 8.44 | 7.46 |
| | 20 days.. | 0.05 | 0.20 | 9.02 | 9.08 | 8.00 | 9.03 | 8.65 | 7.83 |

SOYA BEAN OIL AND MANGANESE DRYER.

| Per cent. MnO ₂ | | 0.01 | 0.05 | 0.15 | 0.26 | 0.30 |
|----------------------------|--------------|------|------|------|------|------|
| Per ct. gain | 1 day..... | | | 0.02 | 0.02 | 0.01 |
| | 10 days..... | | 5.06 | 6.48 | 6.10 | 5.97 |
| | 20 days..... | 0.05 | 9.07 | 8.80 | 6.78 | 6.51 |

SOYA BEAN OIL, MANGANESE AND LEAD DRYER.

| Per cent. PbO..... | | 0.20 | 0.30 | 0.50 |
|------------------------|--------------|------|------|------|
| MnO ₂ | | 0.05 | 0.15 | 0.25 |
| Per ct. gain..... | 1 day..... | 3.04 | 3.77 | 3.74 |
| | 8 days..... | 5.96 | 6.43 | 6.47 |
| | 12 days..... | 6.33 | 6.78 | 6.67 |

that metallic tungates are most excellent driers, and the former paint technologist,¹ has indicated their value for certain special purposes. The high iodine number of tung oil makes it a most rapid drier, even faster than linseed oil, but the soft and opaque film it leaves upon oxidation, makes essential its treat-

¹ Toch: "The Newer Paint Materials," The Decorator, London, Nov. 22, 1910, p. 174.

ment by special processes when it is used either for varnishes or for paints, except in special cases.

The writer has prepared the tungate of lead by precipitating saponified tung oil with lead acetate. This tungate after it has been freed from water, may be fused with a small percentage of colophony and borate to produce a rapid drier that gives a perfectly clear film. Experiments with this drier are referred to later.

Menhaden oil, although of marine-animal origin, has a high iodine value, as the following recent tests will show:

| | |
|-----------------------|-------------|
| Sample number 1 | Iodine, 149 |
| Sample number 2 | Iodine, 162 |
| Sample number 3 | Iodine, 164 |
| Sample number 4 | Iodine, 158 |
| Sample number 5 | Iodine, 161 |

The oil obtained from fresh fish is extremely light in color, but the odor is objectionable, when the oil is heated. This oil is a fairly rapid drying oil, and its composition would indicate that it might possess considerable merit. Toch claims that it is of great value for smokestack paints, and for zinc paints exposed at the seashore. Its content of stearine might account for certain waterproofing properties claimed by producers and would suggest its use in paints for the protection of iron and steel.

Some of the other oils used in these experiments will be considered briefly. Cottonseed oil and corn oil are both light in color, and although greatly inferior to even soya bean oil in their drying action, should merit further investigation.

Rosin oil, the product of the dry distillation of rosin, is dark and viscous. It has a low iodine value, and a high acid number that unfits it for general use as a painting oil.

Sunflower oil is high in iodine number, light in color, but very scarce. There seems to be no reason, however, why the seed should not be grown in larger quantities in this country and the oil produced as a painting oil.

Perilla oil is very high in iodine number, even higher than linseed oil, but it also is very scarce. It is obtained from the *Perilla* nuts, grown in Manchuria and the East Indies. Its iodine number is 206, but Lewkovitz claims that its drying action is accompanied by a peculiar "dropping" of film. This con-

dition might be overcome by special treatment. The writer has not made any experiments on this oil.

Waste oil, or the mixture of fatty acids, and glycerides obtained from the garbage in large cities, is being produced and used in great quantities as soap oils, but the investigations of the writer on several samples, has shown this product to be of small value as a paint oil. Its use in combination with linseed oil to produce a soft, elastic, water repellent film for paints to protect iron and steel submerged in sea water should be studied.

There are several blown and oxidized linseed and other oils upon the market that are so thick that 50 per cent. of benzene or other diluent is required to reduce them to painting con-

TABLE IV.
CONSTANTS OF VARIOUS OILS.

| | Specific gravity | Iodine number | Acid number | Saponification number |
|----------------------|------------------|---------------|-------------|-----------------------|
| Linseed oil | 0.934 | 188 | 3 | 191 |
| China wood oil | 0.942 | 172 | 5 | 190 |
| Soya bean oil | 0.922 | 134 | 2 | 188 |
| Menhaden oil | 0.935 | 160 | 5 | 189 |
| Sunflower oil | 0.929 | 128 | 4 | 188 |
| Cottonseed oil | 0.923 | 110 | 4 | ... |
| Corn oil | 0.924 | 117 | 8 | 190 |
| Rosin oil | 0.989 | 28 | . | ... |
| Waste oil | | 60 | 34 | ... |

sistency. There are also several debloomed mineral oils which resemble linseed oil only in viscosity and their value should be looked into with great care before they are used.

There are on the market many so-called Japan oils. The base of many of these oils is melted rosin, thinned with some linseed oil and large quantities of benzene. Their use is not to be recommended until practical tests of their value have been made.

A table (Table IV) of constants of various oils was made from recent experiments, the oils being subsequently used for the tests referred to in Table V.

The following drying tests (Table V) were made by painting thin films of oil on glass plates, exposing to the atmosphere, and carefully observing the time of the drying. These tests do not indicate the wearing value of the oils tested, but are

simply criterions of their relative drying values. Although sample No. 2, which is untreated tung oil, dried with Drier X, more rapidly than untreated linseed oil with Drier X, it

TABLE V.
DRYING TEST OF OILS.

| Sample | | Hours |
|--------|---|-----------------------|
| No. 1 | *Pine oil with 10 per cent. Drier X..... | 2½ |
| No. 2 | { Tung oil with 10 per cent. Drier X..... | 2½ |
| No. 3 | { Linseed oil with 10 per cent. Drier X..... | 3 |
| No. 4 | { Linseed oil.....25 per cent. | 3 |
| | { Soya bean oil.....25 per cent. | |
| | { Menhaden oil.....25 per cent. | |
| | { Tung oil.....15 per cent. | |
| No. 5 | { Lead tungate.....10 per cent. | 3 |
| | { Linseed oil.....75 per cent. | |
| No. 6 | { Chinese wood oil 25 per cent. } with 10 per cent. Drier X | 3 |
| | { *Pine oil.....25 per cent. } | |
| No. 7 | { Linseed oil.....50 per cent. | 3½ |
| | { Menhaden oil.....25 per cent. | |
| | { Soya bean oil.....15 per cent. | |
| | { Lead tungate.....10 per cent. } | |
| No. 8 | Menhaden oil with 10 per cent. Drier X..... | 3½ |
| No. 9 | Soya bean oil with 10 per cent. Drier X..... | 3½ |
| No. 10 | { Linseed oil.....80 per cent. } | 3½ |
| | { Waste oil.....10 per cent. } | |
| | { Lead tungate.....10 per cent. } | |
| No. 11 | { Linseed oil.....75 per cent. } | 4 |
| | { Soya bean oil.....25 per cent. } | |
| No. 12 | { Linseed oil.....75 per cent. } | 5½ |
| | { Corn oil.....25 per cent. } | |
| No. 13 | { Linseed oil.....75 per cent. } | 6½ |
| | { Cottonseed oil.....25 per cent. } | |
| No. 14 | { Linseed oil.....75 per cent. } | 10 |
| | { Rosin oil.....25 per cent. } | |
| No. 15 | Corn oil with 10 per cent. Drier X..... | 8 |
| No. 16 | Cottonseed oil with 10 per cent. Drier X..... | 9 |
| No. 17 | Rosin oil with 10 per cent. Drier X..... | { Not dry in 2 day |

* Pine oil referred to is not rosin oil but the high-boiling-point distillate of wood turpentine.

is the writer's opinion that the linseed oil would be the more serviceable. The pine oil referred to in these tests is not the pine oil of commerce, but a product of the refining of wood

turpentine. 'Drier X' referred to was a strong lead and manganese linoleate drier.

The only practical field tests made by the writer thus far on the value of oils, other than linseed oil, are those at Nashville, Tenn., where a fence has been erected, consisting of 42 tests of white paints. In these tests pure linseed oil was used, except in formulas 31 to 42.

On these tests there have been placed one formula which has given satisfaction on the various other test fences erected, and this formula has been made up with combinations of linseed oil and other oils. One of the oils tested is called pine oil, a high-boiling-point product obtained from the manufacture of wood turpentine from sawdust. This has a boiling point of over 210° C. as against 150°, the boiling point of ordinary gum spirits. It is almost water white and has the same penetrating qualities as the pure gum spirits, and is almost free from that objectionable odor characteristic of so many low-boiling-point products. When mixed with 50 per cent. linseed oil, this product forms a paint oil of extremely light color, and most excellent properties, producing a semi-flat paint of great whiteness. If exposure tests prove this oil as worthy as the tests thus far show, it would appear to be of great importance to the Southern manufacturers to produce this material in quantity, by fractional distillation of the crude spirits. Its iodine number is high and its oxygen carrying properties are good. Its evaporation leaves a durable film.

The tests referred to on the Southern Test Fence are as follows:

COMPOSITION OF FORMULAS.

| | | |
|--------|---|------------------------------------|
| No. 31 | Corroded white lead...45 per cent. Zinc oxide45 per cent. Asbestine 5 per cent. Calcium carbonate 5 per cent. | } Ground in pure } linseed oil. |
| | 100 per cent. | |

No. 38—Same as No. 31 but ground in 50 per cent. raw linseed oil, 50 per cent. soya bean oil.

No. 39—Same as No. 31 but ground in 50 per cent. raw linseed oil, 50 per cent. corn oil.

No. 40—Same as No. 31 but ground in 50 per cent. raw linseed oil, 50 per cent. cotton seed oil.

No. 41—Same as No. 31 but ground in 50 per cent. raw linseed oil, 50 per cent. rosin oil.

No. 42—Same as No. 31 but ground in 50 per cent. raw linseed oil, 50 per cent. pine oil.

Driers.—The problem of drying of oils and their behavior with various siccatives in varying quantity is an interesting one, and, obviously, of considerable importance from a practical standpoint. Unfortunately there is a decided scarcity of reliable literature dealing with the subject for the guidance of those concerned in the manufacture or application of siccative products. Furthermore, when the problem is investigated, it is not difficult to see why this is so.

At a glance, it is evident that a decided obstacle in experimentation on the drying properties of oils, is the difficulty in obtaining identical conditions for comparative purposes. Inasmuch as a multitude of factors, such as uniformity and homogeneity of the driers and the oils themselves, intensity and source of light, temperature, uniformity of application, and many others, play a decisive part in the siccative tendencies of oils, the resources and ingenuity of the chemist engaged in the research are severely taxed.

It is a well-known fact that linseed oil, when applied to a clean surface, such as a glass plate, will undergo oxidation and take up oxygen to the extent of about 16 per cent., forming a hard, elastic, non-sticky product which has been called linoxyn. This material, unlike the oil from which it has been formed, is insoluble in most solvents. Other oils, such as cottonseed, hemp, rape, olive, etc., are more fully satisfied in nature and have not the power to absorb the amount of oxygen taken up by linseed oil. It is said that perilla oil, however, will absorb as high as 20 per cent. of oxygen.

In carrying out the following tests, on the drying of oils, a quantity of pure linseed oil of the following analysis was secured:

| | |
|---------------------------------|-------|
| Specific gravity at 15° C. | 0.934 |
| Acid number | 5 |
| Saponification number | 191½ |
| Iodine number | 188 |

This oil was distributed into a number of 8 oz. oil sample bottles, and to a series of these bottles was added varying quan-

tities of a very concentrated drier made by boiling oil to 400° C. in an open kettle, with the subsequent addition of lead oxide. The amount of drier added to each bottle varied according to the percentage desired; being calculated on the lead content of the drier, which was very accurately determined by analysis.

There was secured in this manner a series of oils containing varying amounts of lead oxide, and from this lot was selected a certain number of samples which would be representative and typical of paint vehicles now found in the market.

Another series of tests were made by combining with a large number of samples of pure linseed oil as used above, various percentages of a manganese drier made by boiling oil at 400 degrees and incorporating therewith manganese dioxide.

Still another series of tests were made upon a number of oils into which were incorporated various small quantities of lead oxide and manganese oxide together, using the standard driers made in the above manner, all of which were carefully analyzed to determine their contents.

In view of the errors in manipulation that could occur where so many tests were made, it was not deemed advisable, in carrying out the tests, to use glass plates, on which only a minute quantity of oil could be maintained. A much better solution of the difficulty presented itself in using a series of small, round, crimped-edge tin plates about three inches in diameter, such as are used for lids of friction-top cans.

With paints it is impossible to secure films as thin as those presented by layers of oil on glass, nor would it be desirable to secure films of this same relative thickness. For this reason, an endeavor was made to conduct the following tests with films of the same relative thickness as that possessed by the average coating of paint. The drying of the films did not take place in the same short period, nor in the same ratio as with the thin layer that is secured by flowing oil upon glass. The results, however, are more practical, and of greater value to the manufacturer.

The cans were carefully numbered in consecutive order, corresponding to the numbers on the various samples of oil. A very small quantity of oil was placed in each of the can covers, which were previously weighed, and allowed to dis-

tribute itself over the bottom surface thereof. Re-weighing of the covers gave the amount of oil which was taken for each test. The test samples in the covers were all placed in a large box with glass sides, having a series of perforated shelves. In the side of this box as an opening through which a tube was passed, carrying a continual current of air washed and dried in sulphuric acid. Oxidation of the oil films commenced at once, and the amount of oxygen absorbed was determined at suitable periods, by weighing, the increase in weight giving this factor. This test was kept up for a period of twenty days.

A test was also made in the same manner with a current of damp air passing into the box, to observe the relative oxidation under such conditions.

The experiments consumed considerable time and effort. A chart of the results obtained have been made (Table VI), to show the effect of the various driers.

The following outline will present to the mind of the reader the most salient points which have been gleaned from these experiments, and which should give the manufacturer definite knowledge as to the best percentage of oxides to use either in boiled oil, paints or varnishes.

In the case of lead oxide, an increase in the percentage of lead oxide in the oil causes a relative increase in the oxygen absorption, but when a very large percentage of lead has been added, the film of oil dries to a leathery skin.

In the case of manganese oxide, the increase in oxygen absorption on the first day is much more pronounced than is the case with lead oxides. Furthermore, the oxidation of manganese oils seems to be relative to the increase in manganese up to a certain period, when the reverse of this law seems to take place, and beyond a certain definite percentage of manganese, added percentages seem to be of no value. It was furthermore observed that the films dry to a more brittle and harder skin than is the case with lead oxide. The oxygen absorption with oils high in manganese has been noticed to be excessive, and the film of oil becomes surface-coated, drying beneath in a very slow manner, a condition that often leads to checking. The critical percentage where the amount of manganese appears to be most propitious and renders the greatest efficiency seems to be 0.02 per cent. This critical percentage,

TABLE VI.
LANSBED OIL AND MnO_2 (Manganese) DRYER—TEST No. I.

| Per cent. MnO_2 | 0.02 | 0.05 | 0.15 | 0.25 | 0.35 | 0.45 | 0.55 | 0.70 | 1.00 |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 day. | 0.08 | 0.11 | 0.16 | | 3.21 | 3.46 | 3.27 | 3.01 | 2.76 |
| 2 days. | 0.16 | 5.88 | 4.48 | | 3.61 | 3.66 | 3.79 | 3.51 | 3.18 |
| 3 days. | 0.21 | 6.79 | 4.61 | | 3.83 | 4.31 | | 3.51 | |
| 4 days. | | | 4.64 | | | | | | |
| 5 days. | 3.01 | 6.84 | | | 4.13 | 4.68 | 4.19 | 3.01 | 3.90 |
| 6 days. | 8.00 | | 4.88 | | 4.37 | | 4.51 | 4.32 | 4.13 |
| 7 days. | 8.58 | 6.02 | 4.90 | | 4.48 | | 4.61 | 4.52 | 4.23 |
| 8 days. | 9.06 | | 5.03 | | 4.55 | 5.23 | 4.77 | 4.62 | 4.44 |
| 9 days. | | 6.80 | 5.18 | | 4.83 | 5.40 | 4.94 | 4.79 | 4.51 |
| 10 days. | 0.07 | 7.03 | | | 4.81 | 5.47 | | 4.98 | 4.73 |
| 11 days. | 0.15 | 7.03 | | | 4.98 | | 5.45 | 5.32 | 5.22 |
| 12 days. | | | | | 5.25 | | 5.60 | 5.49 | 5.33 |
| 13 days. | 0.22 | 7.17 | | | 5.25 | 6.00 | 5.60 | 5.49 | 5.33 |
| 14 days. | 9.25 | 7.18 | 5.81 | | | | | | |
| 20 days. | | 7.21 | 5.81 | | 5.84 | 6.70 | 5.94 | 5.84 | 5.77 |

Above percentages of drier reclaimed to metallic content.

Per cent. gain.....

TABLE VII.
LINSBRO OH AND MnO₂ (MANGANESE) DRYER—TEST No. 2 (CHECK).

| Per cent MnO ₂ | 1 day | 2 days | 3 days | 4 days | 5 days | 6 days | 7 days | 9 days | 11 days | 12 days | 16 days |
|---------------------------|-------|--------|--------|--------|--------|--------|--------|--------|---------|---------|---------|
| 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 |
| 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 | 0.55 |
| 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 | 0.70 |
| 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

TABLE VIII.
LINSBRO OH AND PbO (LEAD) DRYER.

| Per cent PbO | 0.00 | 0.03 | 0.10 | 0.30 | 0.50 | 0.70 | 1.00 | 1.30 | 1.60 | 1.90 | 1.60 |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|------|
| 1 day | 0.042 | 0.049 | 0.092 | 0.098 | 0.066 | 0.062 | 0.062 | 0.079 | 0.079 | 0.14 | 0.72 |
| 2 days | 0.098 | 0.104 | 0.153 | 0.116 | 0.138 | 0.185 | 0.194 | 4.83 | 4.79 | 5.27 | 6.11 |
| 3 days | 0.128 | 0.159 | 0.179 | 0.137 | 0.279 | 0.185 | 7.11 | 8.60 | 5.35 | 7.89 | 8.28 |
| 4 days | 0.104 | 0.214 | 0.206 | 0.178 | 0.178 | 4.07 | 7.39 | 9.55 | 8.53 | 7.93 | 8.68 |
| 5 days | 0.179 | 0.211 | 0.300 | 0.243 | 0.340 | 7.00 | 7.47 | 9.87 | 8.78 | 8.18 | 9.09 |
| 6 days | 0.108 | 0.281 | 0.281 | 0.243 | 0.340 | 9.30 | 7.64 | 10.01 | 9.00 | 8.24 | 9.09 |
| 7 days | 0.179 | 0.281 | 0.281 | 0.243 | 0.340 | 7.00 | 7.47 | 9.87 | 8.78 | 8.18 | 9.09 |
| 8 days | 0.212 | 0.281 | 0.281 | 0.243 | 0.340 | 7.00 | 7.47 | 9.87 | 8.78 | 8.18 | 9.09 |
| 9 days | 0.226 | 0.281 | 0.281 | 0.243 | 0.340 | 7.00 | 7.47 | 9.87 | 8.78 | 8.18 | 9.09 |
| 13 days | 0.327 | 0.448 | 0.306 | 0.331 | 7.36 | 7.36 | 7.36 | 10.41 | 9.07 | 8.62 | 9.09 |
| 15 days | 0.466 | 0.448 | 0.510 | 0.574 | 11.05 | 11.05 | 7.01 | 10.67 | 9.20 | 8.62 | 9.09 |
| 20 days | 0.521 | 1.08 | 0.650 | 8.76 | 11.25 | 10.67 | 7.98 | 10.52 | 9.36 | 8.62 | 9.09 |

TABLE IX.
LINSEED OIL AND PbO (LEAD AND MnO₂ (MANGANESE)—COMBINATION DRYER.

| | 0.1 | 0.3 | 0.5 | 0.7 | 0.9 | 1.1 | 1.4 |
|----------------------------|-------|-------|-------|-------|-------|-------|-------|
| Per cent. PbO | | | | | | | |
| Per cent. MnO ₂ | .005 | .015 | 0.015 | 0.35 | 0.45 | 0.55 | 0.7 |
| 1 day..... | 0.026 | 0.061 | 0.055 | 0.022 | 0.16 | 0.11 | 1.06 |
| 2 days.... | 0.094 | 0.087 | 0.143 | 0.16 | 5.21 | 6.28 | 3.37 |
| 3 days.... | 0.118 | | 0.17 | 4.23 | 7.63 | 8.31 | 3.74 |
| 4 days.... | | | 0.23 | 7.36 | 8.87 | 9.20 | 4.02 |
| 5 days.... | 0.120 | 0.12 | 0.29 | 9.04 | 9.13 | 9.37 | 4.17 |
| 6 days.... | 0.17 | 0.13 | 1.44 | 9.88 | 9.26 | 9.51 | 4.34 |
| 7 days.... | 0.21 | 0.18 | 4.65 | 10.11 | 9.28 | | 4.45 |
| 8 days.... | 0.30 | 0.20 | 10.03 | 10.35 | 9.61 | | 5.11 |
| 9 days.... | | | | 10.15 | 9.67 | | 5.11 |
| 10 days.... | 0.35 | 0.54 | 10.37 | 10.51 | 9.67 | 10.03 | 5.11 |
| 11 days.... | | | | 10.62 | 9.68 | | 5.73 |
| 12 days.... | 0.40 | 3.43 | 10.38 | | | | |
| 13 days.... | | | | | | | |
| 14 days.... | | | | | | | |
| 15 days.... | | | | | | | |
| 16 days.... | | | | | | | |
| 17 days.... | | | | | | | |
| 18 days.... | | | | | | | |
| Per cent. gain.... | | | | | | | |

as it may be termed, should not be exceeded, and any added amount of manganese has the effect of making the film much more brittle and causes the so-called "burning up" of the paint. The loading of paint with drier and the bad result therefrom, may be explained to some extent from the above results.

In the same way with lead driers, excessive amounts of lead oxide seems to have no beneficial effect on the drying of an oil, and when the percentage which seems to be the most beneficial, namely 0.5 per cent. lead oxide, is exceeded, the film is apt to become brittle.

Oils containing lead oxide driers are less influenced in their drying tendencies by conditions of moisture in the atmosphere than oils containing manganese, but frequently, however, the former dry much better in a dry atmosphere. As a general rule, varnishes rich in manganese dry more quickly in a dry atmosphere, while those containing small quantities dry more quickly in a damp atmosphere.

It was furthermore noticed in these tests that sulphuric acid, placed in dishes on the bottom of the large box in which the samples of oil were drying, were discolored and turned brown after several days, showing that the acid had taken up some material of a volatile nature that was a product of the oxidation.

Another curious feature of these tests was the development of a peculiar aromatic odor which was given off by the oils upon their drying in dry air. When the oils were dried in moist air, a rank odor resembling propionic acid was observed, and this led the observer to believe that a reaction was effected by the absorbed oxygen, that caused the glycerin combined with the linoleic acid as linolein to split up into evil-smelling compounds. It has been suggested that the oxygen first attacks the glycerin, transforming it into carbonic acid, water and other volatile compounds, which are eliminated before the oil is dried to linoxyn. Toch,² however, has shown that the drying of linseed oil gives off only very small percentages of carbon dioxide. Mulder has observed that in the process of linseed oil being oxidized, glycerin is set free, which becomes oxidized to formic, acetic and other acids, while the acid radicals are

² Toch: *The Chem. and Tech. of Mixed Paints*, p. 89. D. Van Nostrand, N. Y.

set free and are converted by oxygen into the anhydrides from which they pass by further oxidation into linoxyn.

The theory of auto-oxidation of linseed oil has been very ably treated by Blackler, whose experiments indicated that during the drying process the slow absorption of oxygen was, at a critical period, followed by a rapid absorption which he attributes to the presence of peroxides which accelerate oxidation. The materials produced by this peroxide formation may act as catalyzers and accelerate the formation of more peroxide. Lead and manganese oxides may also be oxidized to peroxides by the action of oxygen and in this event might act as very active catalyzing agents or carriers of oxygen. Blackler's statement that the presence of driers do not increase, but have a tendency to decrease the initial velocity of oxygen absorption, has been confirmed by these experiments, but it has been noticed throughout the tests that the driers have an accelerative action at a later period.

Some most interesting results were secured by dipping extremely fine copper gauze into linseed oil, and then suspending the gauze in the air. The adhesion of the oil to the copper caused the formation of films between the network, and remarkable drying action was observed. The copper or any superficial coating of copper oxide which may have been present on the metal, undoubtedly effected the result to some extent. It has been found that metallic lead is even more efficient than copper in this respect, but this may be due to the action of free acid in the linseed oil, forming lead linoleates, products that greatly accelerate drying. Another interesting experiment was made by taking pieces of gauze cloth and immersing in linseed oil. After the excess oil had been removed, by pressing, the cloth was again weighed to determine the amount of oil used for the experiment. The increase in oxygen absorption in this case was very rapid and the result obtained confirmed the results in the other experiments.

In order to secure a more evenly distributed state of the oil, tests were conducted by saturating pieces of stiff blotting papers and after exposure, weighing as usual.

The influence of light on the drying of oils is unquestionably a potent one. The practical painter knows that a certain varnish will dry quicker when exposed to the light than when in the dark.

Chevreul was one of the first pioneers in this field of research to observe the effects of colored lights on drying, and he claimed that oil exposed under white glass dried more rapidly than when exposed under red glass which eliminates all light of short wave lengths.

Genthe obtained interesting results in the drying of oil submitted to the effect of the mercury lamp. Oxidation without driers was effected probably through the formation of peroxides. In commenting on this subject, Blacker³ gives a description of the use of the Uveol Lamp, which is similar to the mercury lamp, but has instead of a glass casing which cuts off the valuable rays, a fused quartz casing which allows their passage.

In the boiling of linseed oil, by certain processes the oil is heated to 250 degrees and manganese resinate is incorporated therein. It goes into solution quite rapidly. In other processes the oil is heated to 400 degrees or over, and manganese as an oxide is boiled into the oil. Although it is unsafe to say that a small percentage of rosin such as would be introduced by the use of resinate driers, is not harmful, yet it appears that this process should give a good oil, inasmuch as it has been found that no matter whether the manganese is added to the oil, as a resinate, borate or oxide, practically the same drying effect is noticed in every case where the percentage of manganese is the same. It is the opinion of some, however, that the resinate driers are not as well suited for durability as oxide driers. However, if a boiled oil is found to contain on analysis a small percentage of rosin (less than 0.5 per cent.) it should not be suspected of adulteration. Practical tests, however, should be made with such oil along with an oil made with an oxide drier, before pronouncing on their relative values. Inasmuch as the addition of certain driers to linseed oil lessens the durability of the film, it is more practical to use the smallest amount of drier that will serve the purpose desired, that is, set the oil up in a paint to a hard condition which will not take dust and which will stand abrasion.

The results of this investigation would indicate that when lead or manganese linoleates are used, the most efficient results may be obtained with 0.5 per cent. lead or with 0.05 per cent.

³M. B. Blacker: "The Use and Abuse of Driers," P. and V. Society, London, Sept. 9, 1909.

manganese or with a combination of 0.5 per cent. lead and 0.02 per cent. manganese.

Until more definite results have been obtained with the *tungates*, which will probably prove of exceptional interest as driers, the above driers will probably be used to the greatest extent.

An Enormous Anchor. (*La Nature*, No. 1948, 130.)—In the Engineering and Machinery Exhibition opened in September at Olympia in London, there is to be seen an enormous ship's anchor which was forged by N. Hingley and Sons, of Dudley, for the "Olympic," the new giant White Star steamer. It weighs 15 tons, is nearly 20 ft. long, and its greatest thickness is 10 ft. The shank is 4 ft. 6 in. thick. It is furnished with a chain of three links each weighing 880 lbs. Twelve horses were required to drag it from Paddington to the exhibition. Another attraction is offered by Messrs. Siebe, Gorman & Co., in the demonstration of its new helmet which allows a man to plunge into water, or through flames or through noxious gases, with impunity. Men provided with this helmet walk at the bottom of a huge vat, filled with water, with glass sides, which allow their least motion to be seen clearly. Their only communication with the outside world is a telephone wire, through which they converse with the spectators.

Crystal Forms which are Stable only at High Pressures. A. SKRABAL. (*Zeit. Phys. Chem.*, lxxiii, 171.)—Tammann has stated that at present no rules can be formulated as to the separation of crystal forms of varying stability and that Ostwald's theory of successive reactions, when so applied, leads to conclusions at variance with the facts. The author believes that his statement of Ostwald's rule that the stability of thermal products is in inverse ratio to the speed of the reaction is in accord with the facts of crystallization. Hence the formation of diamonds by the crystallization of carbon from molten cast iron would be the result of rapid cooling, while graphite would result from slow cooling.

Boroid, a Substitute for Celluloid. ANON. (*Electrician*, lxxv, 533.)—A new substance named boroid has been found in commerce recently, which is completely nonflammable. Its use as an insulator and especially as a substitute for celluloid in cinematograph films is to be recommended. On account of its nonflammability its superiority to celluloid for cinematograph films is beyond question.