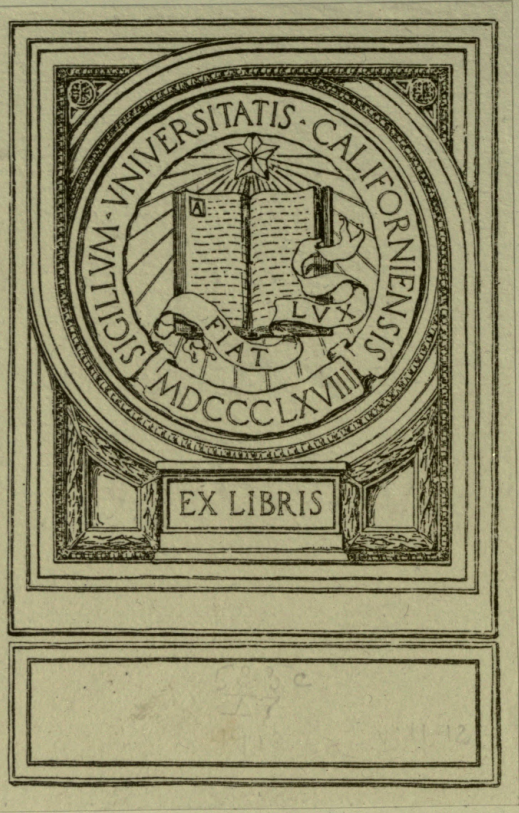


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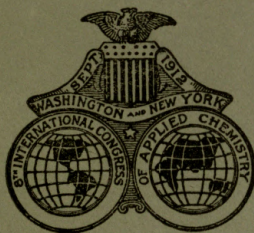


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SECTION Vd: FATS, FATTY OILS AND SOAPS



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## VOLUME XI.

### SECTION Vd: FATS, FATTY OILS AND SOAPS.

#### CONTENTS.

BOELIO, LOUIS AND LOWENSTEIN, ARTHUR	
<i>Experimental Data on the "Cold Test" of Oils</i> .....	17
FAY, IRVING W. AND HAMILTON, S. G.	
✻ <i>Heavy Metal Soaps, Formation, and Solubility in Spirits of Turpentine, Linseed Oil and Petroleum Oils</i> .....	7
HAMILTON, S. G. AND FAY, IRVING W.	
✻✻✻ <i>Heavy Metal Soaps, Formation, and Solubility in Spirits of Turpentine, Linseed Oil and Petroleum Oils</i> .....	7
HEIDUSCHKA, A.	
<i>Über Das Unverseifbare Des Sesamöles</i> .....	13
LOWENSTEIN, ARTHUR AND BOELIO, LOUIS	
<i>Experimental Data on the "Cold Test" of Oils</i> .....	17
SMALLEY, F. N.	
<i>Factory Method for the Determination of Total Fatty Acids in Cotton-Seed Fools</i> .....	27
SMALLEY, FRANK N.	
<i>Investigation of the Methods for the Determinations of Total Fatty Acids in Cotton-Seed Fools</i> .....	31
TANAKA, YOSHIO	
<i>Studies in Lipase</i> .....	37



## HEAVY METAL SOAPS

FORMATION, AND SOLUBILITY IN SPIRITS OF TURPENTINE  
LINSEED OIL AND PETROLEUM OILS

BY IRVING W. FAY AND S. G. HAMILTON

*Brooklyn, N. Y.*

Though the knowledge of soluble soaps is extensive, comparatively little is known of the insoluble soaps of the heavy metals. Zinc and lead stearates find some use in pharmaceutical preparations. Copper stearate is used as an antifouling pigment in paint for ship bottoms. Calcium stearate is mixed with lubricating oils to produce a grease with more body and viscosity. Aluminum palmitate finds application in a secret process for making enamels. The literature affords only meager information upon them.

The object of this work was to prepare and test the solubilities of the soaps of certain heavy metals, e.g., lead, iron, calcium, chromium, etc., in petroleum oils, turpentine, and kerosene. As a preliminary study, various soaps of the heavy metals were made from a common hard soap containing a mixture of sodium salts of stearic, palmitic and oleic acids. Ten grams of this soap was dissolved in 500 c.c. of boiling water and a calculated excess of a soluble salt of the heavy metal in aqueous solution was added with constant stirring. A milky turbidity appeared at once from minute particles of the insoluble soap. Finally the soap would form flocks which rose to the top of the liquid or would form a curdy lump upon the stirring rod. The filtration and washing of the soap separating in flocks was easy, while those in curdy lumps were very difficult to filter and wash and impossible to dry save by great lapse of time. A peculiarity noticed in all these precipitations was in spite of a turbidity on adding the slightest amount of the heavy metal to the solution of soap, no actual separation of any precipitate occurred until in every case an excess of the reagent had been added. The soap

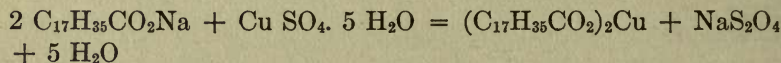
remaining dissolved in the solution, though becoming less and less on continued addition of the reagent, apparently had the power to retain the insoluble stearates, palmitates, and oleates in a pseudo solution or rather as an emulsion. Excess of the reagent always caused a complete separation. When the separation began, it became complete at once. Addition of more reagent to the filtrate gave no additional precipitation or even turbidity.

The precipitates of the heavy metal soaps were filtered off upon linen cloth and washed with hot water and dried in an air bath at temperature below their melting points.

#### PURE STEARATES AND OLEATES

No palmitates were prepared owing to their assumed similarity to the stearates.

**Copper Stearate.** To ten grams of sodium stearate, sold under the mark C.P., dissolved in 500 c.c. boiling water, a calculated excess of copper sulphate based upon the following reaction:



was slowly added with constant stirring. As soon as all of the copper salt was added, and not before, flocks of insoluble blue stearate of copper appeared suspended in the liquid. It was filtered off upon a linen cloth of the texture of a pocket handkerchief. Washing and drying offered no difficulty. The stearate was dried in air bath at 50° C. and then could be pulverized when it formed a greenish blue powder of the fineness of dust and retaining the tallow-like odor of stearic acid.

Lead stearate formed in a similar manner, using an excess of lead nitrate, was when dried at 50° a chalky white powder.

Chromium stearate on its being precipitated in the above manner at 100° C. formed an oily sticky paste, impossible to filter or wash or dry in any satisfactory way. By employing the solutions of sodium stearate and chrome alum at 40° C., the chromium stearate separated from the solution as a flocculent violet colored precipitate which was filtered, washed and dried without difficulty. It formed when dried and pulverised, a light

violet colored powder as fine as dust and of the characteristic odor of tallow.

Iron, calcium, zinc, iron (ferrous), and aluminum stearates were then prepared. All of these stearates were regarded as dry when on cautiously heating a gram of the powders in test tube no trace of moisture was deposited on the clear glass.

The following table shows the colors, temperature of precipitation and the approximate melting points of the stearate prepared.

Stearate	Color	Precipitated at	Melting Point
Copper	Greenish blue	100° C.	106° C.
Lead	Chalk white	100°	102°
Calcium	Chalk white	100°	130-133°
Ferrous	Light brown	100°	89°
Aluminum	Chalk white	100°	108°
Zinc	Chalk white	100°	116°
Chromium	Light violet	40°	61°

**THE OLEATES.** The oleates could not be precipitated at 100° C. on account of their low melting points which at that temperature made them separate as oily or sticky gummy masses impossible to filter, wash, and dry.

By precipitation at about 23° C. it was possible to obtain them as flocculent masses which could be successfully filtered and purified. Chromium was an exception to this for even at 23° C. it was sticky and impossible to wash and purify. Further work had to be abandoned for the time.

Aluminum oleate precipitated at a low temperature showed peculiar behavior. When washed and cut into small pieces for drying, it was a dirty white color and sticky; after standing a few days in the air, the outside positions of the small pieces became gelatinous while the inside remained unchanged, the whole mass resembling frog's eggs. Eventually the whole became gelatinous but after several weeks, the pieces crumbled to a powder when rubbed between the thumb and finger. Though impossible to precipitate aluminum oleate unmelted at 100° C. yet on eight weeks' standing in air, the melting point was found to be between 150°-160°, though even then not completely dried.

The following table shows the color, temperature of precipitation, and approximate melting points of the oleates prepared:

Oleate	Color	Precipitated at	Melting Point
Copper	Light blue	23° C.	50° C.
Lead	Dirty white	100°	95°
Ferrous	Dark brown	25°	82°
Aluminum	Amber	22°	150°-160°
Zinc	Brownish white	23°	84°

From common kerosene oil were separated by four distillations, four fractions, whose boiling points were 175°, 188°, 212°, 229°.

All the stearates, and oleates failed to dissolve to any degree in these four distillates when cold. Copper and iron stearates became suspended only in these oils. Large amounts shaken with the oils formed solid pastes. Cold oils, with which copper stearate had been shaken, showed almost no color on filtering after two days.

All the stearates and some of the oleates formed clear solutions when heated in all fractions of these oils. On standing and cooling, the soaps would separate from the dilute solutions or become pastes or jellies from the more saturated solutions.

To test the degree of solubility, test tubes containing 2 c.c. of the petroleum distillates had .1 gram of the dry soaps added at a time with cautious heating after each addition. These tests showed no distinct point where solubility ceased, but that the hot stearates and hot oils were mutually miscible; the temperature required to make them so, being the melting point of the stearate. To test this, equal amounts of zinc stearate were placed in two test tubes. To one were added three drops of oil. Heated in a sulphuric acid bath, the contents of both tubes liquified at the same time, the one without oil charring first on further heating.

Calcium stearate as an exception, could be made to dissolve only to a 50 per cent. solution without charring.

Iron oleate charred without dissolving at all. Lead oleate was also insoluble but did not char.



### Solubility in Linseed and spirits of Turpentine.

As with the petroleum oils, cold linseed oil and turpentine failed to dissolve either stearates or oleates. All the stearates (save calcium) and oleate of zinc dissolved in all proportions when heated with these oils, lead and iron oleates carbonized when heated with linseed oil and were insoluble in turpentine. Aluminum oleate dissolved in all proportions in linseed oil and was insoluble in turpentine. Copper oleate was quite soluble in hot turpentine but carbonized when 10 per cent. was heated with linseed oil.

Aluminum stearate dissolved in both linseed oil and turpentine remained as clear jellies at the end of five weeks. Calcium stearate jelly under similar conditions becomes opaque.

### CONCLUSIONS

1. Stearates and oleates of calcium, iron, aluminum, zinc, copper, and lead and stearate of chromium may be easily prepared in aqueous solution from alkali salts of these acids.
2. Oleates of these metals have as a rule lower melting points than the stearates and are darker in color.
3. The stearates and oleates are insoluble in cold petroleum oils, linseed oil and turpentine.
4. All the stearates, and oleate of zinc, form clear solutions in hot linseed oil, turpentine and kerosene oils.
5. The stearates and oleates in weak solutions in kerosene oils separate as precipitates when cold. Calcium stearate and aluminum stearate and oleate in hot strong petroleum oils turn to clear jellies on cooling; the other stearates and oleates under similar conditions form pastes.



# ÜBER DAS UNVERSEIFBARE DES SESAMÖLES

VON A. HEIDUSCHKA<sup>1</sup>

*Universität Muenchen, Munich, Germany*

In der heutigen Fettchemie steht das Studium der unverseifbaren Bestandteile mit an erster Stelle. Wir haben z. B. in den unverseifbaren Bestandteilen Phytosterin und Cholesterin vorläufig den einzigen wesentlichen Unterschied zwischen Tier- und Pflanzenfetten, der uns sogar, wie Bömer<sup>2</sup> nachgewiesen hat, ermöglicht, bei den sogenannten gehärteten Fetten zu erkennen, ob sie tierischen oder pflanzlichen Ursprungs sind.

Das Sesamöl, das eine grosse Rolle auf dem Gebiete der Speiseöle spielt, enthält ausser dem Phytosterin noch andere unverseifbare Bestandteile, die besonders charakteristisch für dieses Öl sind. Wir<sup>3</sup> haben uns nun im Nachstehenden speziell mit dem Studium dieser Stoffe befasst. Bisher ist folgendes darüber bekannt:

Zuerst isoliert Villavecchia<sup>4</sup> und Fabris durch Extraktion der Baryumseife mit Alkohol, Phytosterin, Sesamin und ein dickes gelbes Öl, den Träger der Baudouinischen Reaktion. Sie gaben dem Phytosterin die Formel  $C_{25}H_{44}O$ , dem Sesamin die Formel  $(C_{11}H_{12}O_3)_2$ . Etwa um die gleiche Zeit hat J. Tocher<sup>5</sup> aus dem Sesamöl durch Extraktion mit einem Gemisch von Essigsäure und Alkohol einen Stoff mit einem Schmelzpunkt von  $118^\circ$  gewonnen, dem er nach Elementaranalyse und Molekulargewicht die Formel  $C_{18}H_{18}O_5$  gab; ausserdem gewann er noch aus dem Unverseifbaren des Sesamöles ein dickes, braunes Öl von unbekannter Zusammensetzung, das die Baudouinische Reaktion gab. Dann untersuchte Bömer und Winter<sup>6</sup> diese unverseifbaren Bestandteile in eingehender Weise. Dem Phytosterin schrieben

<sup>1</sup>München, Laboratorium für angewandte Chemie der Universität Rav. Ges. 29.

<sup>2</sup>Vortrag im Verein Deutscher Nahrungsmittelchemiker Würzburg 1912.

<sup>3</sup>Die Untersuchungen wurden in Gemeinschaft mit H. Denneler ausgeführt.

<sup>4</sup>Zeitschrift für angewandte Chemie 1893, 505.

<sup>5</sup>Pharm. Journ. and. Trans. 1893, 23, 700. Chem. Zeitg. Rep. 1893, 17, 121.

<sup>6</sup>Zeitschrift f. Unters. d. Nahr. u. Genussm. 1899, 705 und 1901, 873.

sie auf Grund ihrer Analysenresultate die Formel  $C_{26}H_{44}O + \frac{1}{2}H_2O$  zu, dem Sesamin die Formel  $C_{33}H_{30}O_{10}$ , dagegen konnten sie aus dem dritten, unverseifbaren Bestandteile des Sesamöls, dem gelben Öl, keine charakteristischen Stoffe isolieren. Kreis,<sup>1</sup> der ebenfalls diesen dritten unverseifbaren Bestandteil des Sesamöls, der vielfach als Sesamol berechnet wird, untersucht hat, glaubt, dass er einen phenolartigen Stoff enthält. In einem in der Societa di Roma am 14. Juli 1907 gehaltenen Vortrag berichten malagnini und Armani<sup>2</sup> über ein Verfahren, nach dem sie den die Furfurolreaktion verursachenden Stoff in kristallinischer Form F. 94° erhalten haben wollen. Ein Spaltungsprodukt desselben sei nach ihren Angaben die von Kreis beschriebene, phenolartige Verbindung, die sie als Methylenäther des Oxyhydrochinons  $C_7H_6O_3$  identifizierten F.57°.

Infolge dieser widersprechenden Angaben der Literatur sahen wir uns veranlasst, die verschiedenen Gewinnungsmethoden dieser unverseifbaren Bestandteile und die erhaltenen Substanzen nach zu prüfen und einer genaueren Untersuchung zu unterziehen. Es ist uns sowohl nach der Methode von Villavecchia und Fabris, als auch nach der von Bömer und Winter gelungen, die drei unverseifbaren Bestandteile des Sesamöls, Phytosterin, Sesamin und das gelbrote Öl, den Träger der Baudouinischen Reakation, zu isolieren. Zur Gewinnung einer grösseren Menge der Stoffe wählten wir die Methode nach Bömer und Winter, da dieselbe eine kontinuierliche Extraktion mit dem von A. Heiduschka und K. Pfizenmaier<sup>3</sup> beschriebenen Apparat zuließ. Derselbe wurde jedesmal mit der 100 g Öl entsprechenden Menge Seife beschickt. Nach 6stündiger Extraktion war die Seife erschöpft. Das auf diese Weise erhaltene Phytosterin verhielt sich genau wie das von Bömer und Winter<sup>4</sup> isolierte. Die Einheitlichkeit dieses Sesamölphytosterins wurde von mir und Klamroth<sup>5</sup> näher untersucht. Das erhaltene Phytosterin hatte den Schmelzpunkt von 136,2 - 136,8°. Es wurde zunächst ver-

<sup>1</sup>Chem. Zeitg. 1903, 1030.

<sup>2</sup>Chem. Zeitg. 1907, 884.

<sup>3</sup>Pharmazeutische Zentralhalle 1909, 333.

<sup>4</sup>Zeitschr. f. Unters. d. Nahr.-und Genussm. 1901, 873.

<sup>5</sup>Dissertation München 1911.

sucht, ob durch fraktioniertes Kristallisieren sich Stoffe von verschiedenem Schmelzpunkt isolieren liessen, doch stets ergab sich ein vollständig gleichbleibendes Produkt. Auch nach der Methode von Windaus<sup>1</sup> und Hauth konnte festgestellt werden, dass nur ein 2 Brom addierendes Phytosterin vorliegt.

Das bei dieser Extraktion in grossen Nadeln erhaltene Sesamin besass nach mehrmaligem Umlösen aus Äthylalkohol einen Schmelzpunkt von 122,5° und gab die von Bömer und Winter<sup>2</sup> beschriebene Farbenreaktion mit einem Gemisch von Essigsäureanhydrid und Schwefelsäure. In seiner Löslichkeit und Kristallform entsprach es ganz den Angaben dieser beiden Autoren, nur fanden wir eine andere elementare Zusammensetzung und ein niedrigeres Molekulargewicht. Die qualitative Analyse zeigte die Anwesenheit von Kohlenstoff, Wasserstoff und Sauerstoff. Die Resultate der quantitativen Analyse ergaben im Mittel: 67,36% C, 5,43% H. Daraus berechnet sich die Formel C<sub>20</sub>H<sub>19</sub>O<sub>6</sub>, der ein Molekulargewicht von 355 entsprechen würde. Die nach dem Beckmann'schen Siedepunkterhöhungsverfahren — reines Chloroform als Lösungsmittel — wiederholt ausgeführte Molekulargewichtsbestimmung gab etwas niedrigere Werte, nämlich 351,85 . 340,9 . 337,01 . 337,45. Die Ausbeute an Sesamin betrug 0,17 %.

Verschiedene Versuche, aus dem gelbroten Öl, genau definierbare, charakteristische Stoffe zu isolieren, gelangen uns ebenso wenig, wie seinerzeit Bömer und Winter. In dem uns über den Vortrag von Malagnini und Armani zur Verfügung stehenden Referat<sup>3</sup> waren leider nähere Angaben über die Gewinnung des kristallisierenden dritten, unverseifbaren Bestandteiles nicht zu finden. Wir haben unter den verschiedensten Bedingungen versucht, kristallisierbare Stoffe aus dem Öl zu gewinnen, doch stets ohne Erfolg. Es resultierte immer ein gelbes Öl, das eine intensive Baudouinische und Soltsiensche Reaktion gab, aber keinerlei Phenolreaktion.

Auf Grund vorstehender Untersuchungen lassen sich die erhaltenen Resultate folgendermassen zusammenfassen.

<sup>1</sup>Berichte d. deutsch. chem. Ges. 39, 4378; 40, 3681.

<sup>2</sup>Zeitschr. f. Unters. Nahr. u. Genussm. 1899, 705; 1901, 873.

<sup>3</sup>Chem. Zeitg. 1907, 884.

Von den drei nach dem Verfahren von Bömer und Winter leicht zu gewinnenden unverseifbaren Bestandteilen des Sesamöles zeigt das Sesamölphytosterin die bekannten Eigenschaften der Phytosterine und es ist als ein einheitliches Produkt anzusprechen.

Der zweite unverseifbare Bestandteil, das Sesamin, wurde in einer Ausbeute von etwa 0,17 % erhalten. Seine Eigenschaften entsprechen den von Bömer und Winter gemachten Angaben. Nach den erhaltenen Analysenresultaten enthält das Sesamin 67,36% C, 5,43% H. Sein mittleres Molekulargewicht (Beckmannsche Siedepunkterhöhungsmehode mit reinem Chloroform) betrug 341,8. Diese Zahlen entsprechen annähernd folgender Formel:  $C_{20}H_{19}O_6$ .

In dem dritten unverseifbaren Bestandteile ist bis jetzt die Isolierung eines charakteristischen, genau definierbaren Bestandteiles nicht gelungen.

## EXPERIMENTAL DATA ON THE "COLD TEST" OF OIL

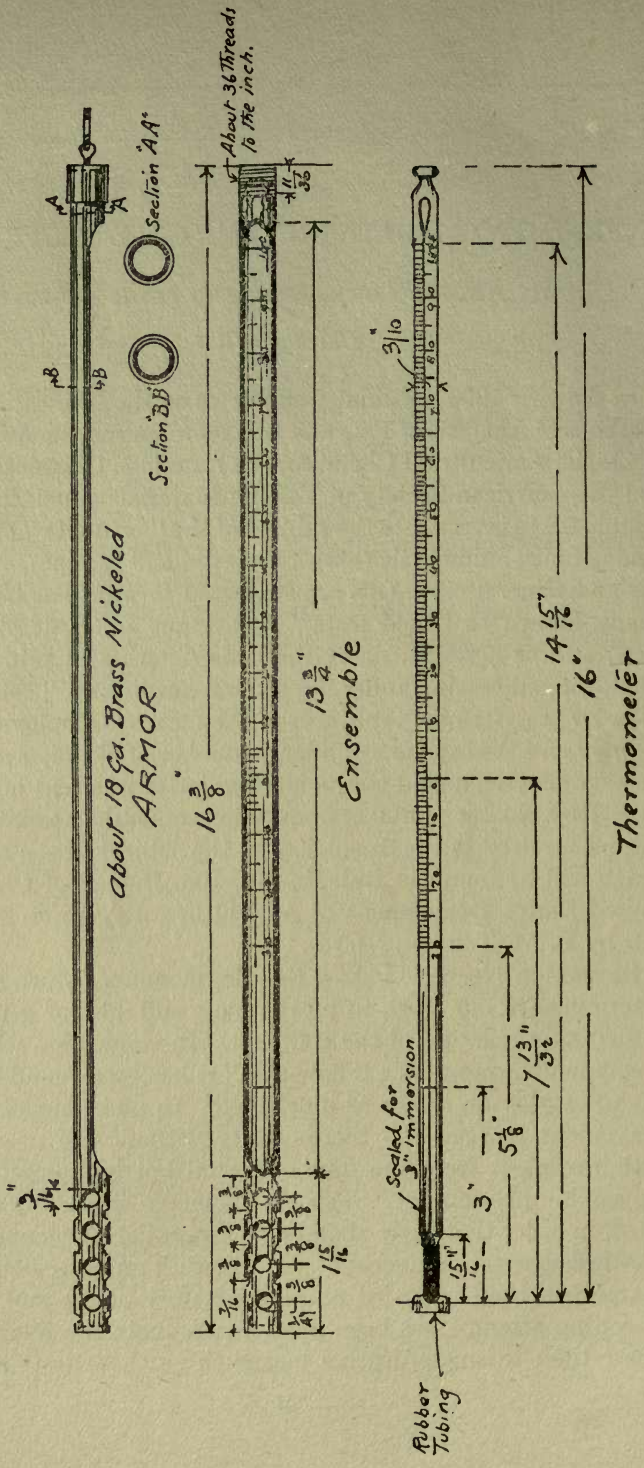
BY ARTHUR LOWENSTEIN AND LOUIS BEOLIO

*Chicago, Ill.*

In the year 1909 the Joint Committee on the Unification of the Methods of Analysis of Fats and Oils representing the Association of Official Agricultural Chemists, the American Chemical Society and the American Society of Testing Materials appointed a subcommittee to investigate the subject of the "cold test" of various kinds of oils, animal oils (both terrestrial and marine), vegetable oils and mineral oils. Oils are subjected to what has been commonly known as "cold tests" with many different objects in view, and as a result, many methods differing in principle are employed, all coming under the general heading of "cold tests." In order to determine the status of the methods employed, in this country and the opinions of a large number of chemists and engineers employing a cold test, a circular letter was sent out in August, 1909, asking a number of questions on various points, which had been raised in the discussion on the subject of the cold test, which will be found in Bulletin No. 105, Bureau of Chemistry, United States Department of Agriculture, Report on Fats and Oils by L. M. Tolman, referee.

Illustration No. 1 will show the thermometer, which we have determined in our work to be the most suitable for general use in the determination of the cold test. In connection with what is commonly known as a "flow test," it has been found convenient to employ an armor as illustrated. In most cases it will be convenient to read the thermometer without the necessity of withdrawing it from the four ounce oil bottles commonly employed in this country. The thermometer should be nitrogen filled, in order that there shall be no separation of mercury when the thermometer is inverted. In this work an agreement of one degree has been regarded as a satisfactory check and for this reason no attempt has been made to graduate the thermometer closer than to single degrees inasmuch as these tests are prin-

PROPOSED THERMOMETER  
FOR THE COLD TEST OF VARIOUS OILS.



SCALE HALF FULL SIZE



cipally for commercial purposes and an agreement of one degree is ordinarily regarded as satisfactory.

Unless otherwise specified, the method outlined in Bulletin No. 99, page 66, Bureau of Chemistry, United States Department of Agriculture, was employed: A pad of hair felt was employed to insulate the testing bottle while making the test. The results are expressed in degrees Fahrenheit, as this is the custom in the United States for expressing results of the cold test. In this paper experimental data only, will be given pertaining to questions asked in the letter referred to above. One of the questions was: "In making tests do you think the samples should be (1st) dried, (2nd) filtered, or (3rd) made on the sample as received?"

In order to determine the effects of varying amounts of water: To one hundred grams of oil 0.05-0.10-0.20-0.30 c.c. of distilled water were added from a burette. In each case the mixture was then shaken vigorously until all of the oil and water were uniformly mixed. Forty cubic centimeters of the emulsion were then put into each of two four ounce oil bottles for check determinations. The bottles and contents were then exposed to a temperature of  $-2^{\circ}$  F. for eighteen hours with the results given in table one.

TABLE I. Influence of Varying Amounts of Water

Amounts of H <sub>2</sub> O	0.05%		0.10%		0.20%		0.30%	
	1	2	1	2	1	2	1	2
Acidless Tallow Oil	70°-71°	69°-70°	70°-71°	69°-70°	68°-69°	68°-69°	67°-68°	67°-68°
Extra Winter Strained Lard Oil	43°-44°	43°-44°	44°-45°	44°-45°	43°-44°	44°-45°	42°-43°	43°-44°
Winter Pressed Extra Prime Neats Foot Oil	23°-24°	24°-25°	25°-26°	25°-26°	25°-26°	25°-26°	26°-27°	26°-27°

It is interesting to note that the influence of the added water seems to have a tendency to bring the flowing point of the oil towards the freezing point of the water. In the case of tallow oil having a high cold test, the addition of water causes a decrease in the cold test proportionate to the amount of water present. In the case of winter pressed neats foot oil having a cold test below that of the freezing point of water, the cold test of the oil is raised upon addition of water. In the case of lard oil where the cold test is but slightly above the freezing point of water, the flowing point is not appreciably affected. In view of this fact it would appear that the samples should be tested as received unless it shows the presence of excessive amounts of water or excessive amounts of foreign solid impurities. Small amounts of foreign impurities did not appear to affect the cold test of the oils. Another question asked was: "A—In methods in which the oil is first frozen solid, should the oil be stirred while freezing or should it be allowed to remain at rest? B—After it is frozen shall it stand a definite length of time and how long?"

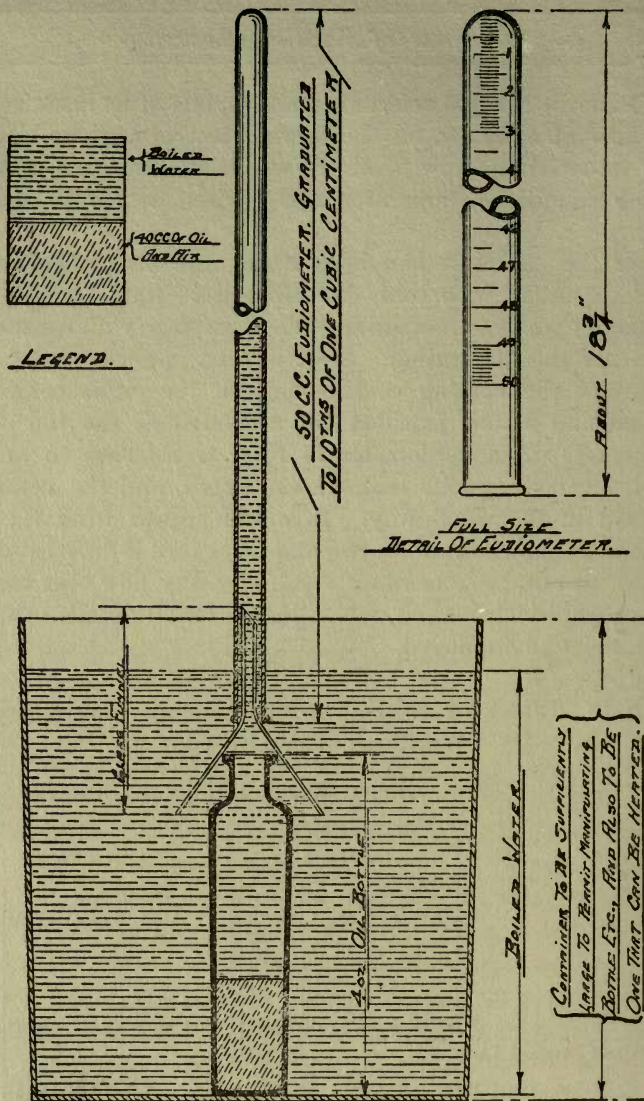
In Bulletin No. 105 referred to above, one of us has discussed the effect of agitation on the flowing test of various oils. In order to determine how much air was stirred into the oil under varying conditions, apparatus was devised as per illustration No. 2.

After the cold test had been made, the testing bottle was completely filled with cold, distilled water—funnel placed over its mouth and a gas measuring tube immediately above the funnel as per the illustration. Heat is then applied to the outer vessel and the heating continued until the oil is completely liquified and all air expelled and collected at the top of the eudiometer. The eudiometer is then transferred to another vessel, levelled, and its temperature noted, and the volume of gas read in the usual way. It would appear from the data obtained as shown in tables two and three that if different operators are to obtain concordant results by any flow test method, that an empirical method, which insists on all details being followed, must be employed.

TABLE 2. Effect of Stirring while Cooling and Subsequent Warming, at two Speeds

Bath —5° F. Speed 60 revolutions per minute

	Test No. 1		Test No. 2		
	Time in Minutes	Flowing Point	Time in Minutes	Flowing Point	c.c. of air on No. 2
Acidless Tallow Oil	While cooling	3	While cooling	3	4.7
	While warming	12	59°-60°	While warming	
Extra Winter Strained Lard Oil	While cooling	6	While cooling	6	1.2
	While warming	4	45°-46°	While warming	
Winter Pressed Extra Prime Neats Foot Oil	Semi-solid	30	Semi-solid	23	2.5
	While warming	4	19°-20°	While warming	



APPARATUS FOR THE ESTIMATION OF THE AIR  
WHICH IS MECHANICALLY MIXED WITH  
OILS IN DETERMINING COLD TEST.

## Speed 250 revolutions per minute

	Test No. 1		Test No. 2		
	Time	Flowing Point	Time	Flowing Point	c.c. air on test No. 2
Acidless Tallow Oil	While cooling 3 While warming 14	65°-66°	While cooling 3 While warming 15	65°-66°	20.5
Extra Winter Strained Lard Oil	While cooling 6 While warming 10	47°-48°	While cooling 6 While warming 10	47°-48°	2.4
Winter Pressed Extra Prime Neats Foot Oil	While cooling 15 While warming 3	21°-22°	While cooling 20 While warming 4	21°-22°	4.8

After stirring, these oils were placed in a bath of  $-8^{\circ}$  F. and allowed to remain 2 hours, then removed and stirred as soon as the solidified oil could be broken up with the thermometer.

TABLE 3. Oils at rest during solidification (18 hours). Stirred only while warming to flowing point.

Speed 60 revolutions per minute. Bath  $-5^{\circ}$  F.

	Test No. 1		Test No. 2	
	Time	Flowing Point	Flowing Point	c.c. of air on test No. 2
Acidless Tallow Oil	15 min.	62° to 63°	63° to 64°	5.6
Winter Strained Lard Oil	8 min.	42° to 43°	42° to 43°	2.6
Winter Pressed E. P. Neats-foot Oil	6 min.	22° to 23°	21° to 22°	0.7



The methods most commonly employed in the United States for the determination of cold tests are a flowing test of the type referred to above. The majority of flow tests employed in this country are modifications in one form or another of the method originally described by the late Dr. Dudley, and described in specification No. 75 A of the Pennsylvania Railroad; a cloud test similar to that described in Bulletin No. 105 referred to above and the official method of the New York Produce Exchange, which is used principally for salad oils. For the sake of comparing the results obtained on the same oils by these different methods, tables 5, 6 and 7 may be of interest.

TABLE 5. Flowing Test (See Bulletin 99, page 66)

40 c.c. of the oil were placed in a four ounce oil bottle, then exposed to a temperature of  $-9^{\circ}$  for eighteen hours.

Description	Test No. 1	Test No. 2
Acidless Tallow Oil	$69^{\circ}$ to $70^{\circ}$	$70^{\circ}$ to $71^{\circ}$
Extra Winter Strained Lard Oil	$42^{\circ}$ to $43^{\circ}$	$43^{\circ}$ to $44^{\circ}$
Grease Oil	$28^{\circ}$ to $29^{\circ}$	$28^{\circ}$ to $29^{\circ}$
Winter Pressed Extra Prime Neats Foot Oil	$22^{\circ}$ to $23^{\circ}$	$22^{\circ}$ to $23^{\circ}$
Winter Cotton-Seed Oil	$18^{\circ}$ to $19^{\circ}$	$17^{\circ}$ to $18^{\circ}$

TABLE 6. Cloud test as given on page 66, Bulletin 99, Bureau of Chemistry, United States Department of Agriculture

Description	Test No. 1		Test No. 2	
	Temp. Bath	Cloud Appears	Temp. Bath	Cloud Appears
Acidless Tallow Oil	$56^{\circ}$	$63.5^{\circ}$	$56^{\circ}$	$63^{\circ}$
Winter Strained Lard Oil	$25^{\circ}$	$32^{\circ}$	$25^{\circ}$	$31.5^{\circ}$
Grease Oil	$25^{\circ}$	$29.5^{\circ}$	$25^{\circ}$	$30.5^{\circ}$
Winter Cotton-Seed Oil	$18^{\circ}$	$25^{\circ}$	$18^{\circ}$	$25^{\circ}$
Winter Pressed Extra Prime Neats Foot Oil	$4^{\circ}$	$10.5^{\circ}$	$4^{\circ}$	$11^{\circ}$

Cloud test made in jacketed test tube—air space between the two tubes. Oil treated same as above

Description	Test No. 1		Test No. 2	
	Temp. Bath	Cloud Appears	Temp. Bath	Cloud Appears
Acidless Tallow Oil	50°	63.5°	51°	64°
Winter Strained Lard Oil	12°	31°	12°	31°
Grease Oil	10°	29°	11°	30°
Winter Cotton-Seed Oil	6°	25°	6°	25°
Winter Pressed Extra Prime Neats Foot Oil	3°	11°	2°	11°

Table six shows results in one case of placing the testing bottle directly into the freezing mixture and in the other case protects the freezing bottle by means of an air jacket. The results were practically the same in both cases, the only advantage of the air jacket being that one is not so apt to pass the initial clouding point. On the other hand, the use of the air jacket consumes considerably more time than where the bottle is placed directly into the freezing mixture.

TABLE 7. Cotton-Seed Oil Test. New York Produce Exchange Method

Time	$\frac{1}{2}$ hr.	1 hr.	$1\frac{1}{2}$ hr.	2 hr.	$2\frac{1}{2}$ hr.
Temperature	32.5°	32.5°	32°	32°	32°
Condition of Oil	Clear	Clear	Clear	Clear	Clear
Time	3 hr.	$3\frac{1}{2}$ hr.	4 hr.	$4\frac{1}{2}$ hr.	5 hr.
Temperature	32°	32°	32°	32°	32°
Condition of Oil	Clear	Clear	Clear	Slightly Cloudy	Cloudy

Further work is in progress employing various grades of mineral oil and also fish oils.



# FACTORY METHOD FOR THE DETERMINATION OF TOTAL FATTY ACIDS IN COTTON-SEED FOOTS

BY F. N. SMALLEY

*Savannah, Ga.*

The method herein described is proposed for a rapid method for the determination of the total fatty acids in cotton-seed foots, or soap stock, and similar materials, by a determination of the iodine number of the same, and its conversion into terms of fatty acids by means of an appropriate factor.

Cotton-seed oil soap stock is the sludge removed from crude oil in the process of refining with caustic soda, and consists of the soda soaps of the fatty acids of the oil, together with some neutral oil, coloring and albuminous matters which are characteristic of crude oil, caustic soda and water.

The most accurate method of the determination of the total fatty acids is the Official Method of the Interstate Cotton-seed Crushers Association, which consists in complete saponification of the fat by means of alcoholic soda, evaporation of the alcohol, solution of the soap in the hot water, decomposition of the soap with dilute mineral acids, melting of the liberated fatty acids, chilling to form a cake, filtering and washing free from mineral acid, extraction of the cake with warm petroleic ether, evaporation of the solvent and weighing of the residual fatty acids.

The method is so long that it is almost useless for factory control, and for that reason after trials of a number of various proposed methods, the iodine method was selected in the summer of 1905, as the best fitted to obtain the most accurate results in the shortest time. Since then it has been in continuous use in the Refinery of the Southern Cotton Oil Company.

The method is carried out as follows: After the sample has been well-mixed, weigh out accurately .5000 grams on to a small square of fat free paper. This is then introduced into a ground glass stoppered bottle with neck so arranged that the joint can be

sealed with the potassium iodid solution. Five c.c. of carbon-tetrachloride and 20 c.c. of Wijs Iodin Solution are added. The bottle is stoppered and the contents gently shaken until the soap stock is in solution. Seal with potassium-iodid solution and allow to stand for thirty minutes.

The determination of the Iodin number is now carried out in the usual Wijs method, and the resultant number is converted by division by 1.24 into per cent. fatty acids.

The factor was arrived at by comparison of the Iodin number with the total fatty acids as determined by the Official method as before outlined. Some one hundred and fifty samples were analyzed by both methods before the final selection of the factor was made.

The following table shows the closeness of the two methods.

Sample Number	F. F. A. by Official Method	I. No.	F. F. A. by Calculated for I. No.
2171	43.39	53.53	43.17
72	40.70	50.90	41.05
75	47.35	58.68	47.32
76	46.70	57.64	46.48
77	49.34	60.71	48.96
78	47.13	58.16	46.90
79	46.51	57.13	46.07
81	48.48	58.88	47.48
84	51.52	61.19	47.31
87	49.30	61.0	49.20
88	46.67	47.34	38.18
90	47.45	58.66	47.31
91	49.31	61.48	49.58
92	47.03	58.16	46.90
94	49.29	61.19	49.35

The above represented one day's work, and the results are typical of all work done. The three samples 2181-84-88, which show the greatest difference, were several weeks old and fermentation was in an advanced stage.

The results showed that the conversion factor could not be depended on if the soap stock was more than a week old, but as

the whole purpose was to obtain results as soon as possible after the refining was made, this was no serious objection.

The six years' use has proven that the method as used gave on the whole extremely satisfactory results, and it has only received minor modifications, consisting in using special strength of Sodium Thio-sulphate and iodine solution, so as to simplify the calculation.



# INVESTIGATION OF THE METHODS FOR THE DETERMINATIONS OF TOTAL FATTY ACIDS IN COTTON-SEED FOOTS

BY FRANK N. SMALLEY

*Savannah, Ga.*

Recent co-operative work conducted by the Society of Cotton Products Analysts on the relative solvent power of gasoline of different boiling points when used in the determination of total fatty acids of cotton-seed foots by the Official Method of the Interstate Crushers Association, show such non-agreeing results, that the author believed that an investigation of the Official Method to determine the reason for the wide discrepancies between the different chemists, and a study of the proposed substitute methods for the same, would be of value.

It might be well to state that the co-operative work brought forth the fact that all gasoline whose boiling points did not exceed 75° Cent. showed no differences in their solvent power. And as the greatest differences between any one chemist's reported values using the three grades of gasoline (Boiling under 50°, from 50° to 65°, from 65° to 75°) was fifty-six hundredths of one per cent., while the greatest difference between the different chemists using the same grade of gasoline was 5.34%, the author believed that the differences were due to the different chemists using different modifications of the Official Method.

The following is the Official Interstate Method. Weigh out eight to ten grams of the well-mixed sample into a small extraction flask. Saponify with an alcoholic solution of a sodium hydroxide over a steam bath and heat with occasional stirring until all the alcohol is driven off.

Wash out the soap with about 400cc. of hot water into a beaker and digest on a water bath until complete solution of the soap is effected. Acidify with dilute sulphuric acid and continue heating on the water bath until the layer of fatty acids has melted

clear. Cool and filter off the liquid from the cake of fatty acids, washing with cold water until no traces of sulphuric acid are left. Allow the fatty acids to dry, most conveniently over night. Transfer the fatty acids to a folded filter paper and place in a Soxhlet extraction apparatus and dissolve the fatty acids adhering to the beaker with warm petrolic ether boiling below 50 degrees Centigrade and extract with petrolic ether boiling below 50 degrees Centigrade for three hours. Evaporate off the ether and heat to constant weight. Calculate percentage on original weight.

When this method was followed as closely as possible the author obtained values of 95.70 and 95.63 average of 95.66%. In this method the cake of crude fat was dissolved by extraction, care being taken to transfer from the beaker as much as possible of the same to the filter paper.

A modification of the method of extracting was carried out as follows; the bulk of the crude fat was retained in the beaker and successively treated with 25cc. portion of warm gasoline each portion being filtered through the original filter paper, into the extraction flask, until the beaker was thoroughly cleaned; the filter paper now extracted in a Soxhlet apparatus, as before, gave the values of 95.33 and 95.38 average of 95.36%.

A third method of extracting was carried out as follows. The whole of the crude fat, filter paper included, was treated with 100cc. of gasoline in the original beaker and complete solution obtained by a few minutes' boiling over an electric hot plate. This was then filtered through a fresh filter paper into the extraction flask and the residue treated in the same manner with a fresh portion of gasoline and finally transferred to the filter paper which was extracted as before. This method gave results of 94.55 and 94.63 average of 94.59%.

In the first two extraction methods it was noticed that in the extracted solutions before evaporation there was a flocculent precipitate while the solution from the last method was perfectly clear, showing that a saturated solution of the crude fat in gasoline dissolves resins and coloring matter which is precipitated out on dilution of the same. While the differences between these three methods is only one and seven hundredths per cent. the

author believes that this is the particular point in the method which has caused the wide differences in the results of the previously mentioned co-operative work.

The following is one of the methods which has been proposed as a substitute. Weigh out accurately into a tared beaker of 300cc. capacity four to five grams of the thoroughly mixed sample and treat as follows. 10 to 12cc. of 40 degrees Be. Caustic Soda and 15 to 20c.c. of 95% alcohol are added and the whole mass thoroughly stirred. The beaker is then placed on a sand bath, the temperature of which is so regulated that the evaporation is not too rapid or violent and the mass stirred repeatedly. When the mass is nearly dry the sides of the beaker are washed down with a few c.c. of alcohol and the evaporation continued until the alcohol is expelled and the soap nearly dry. The beaker and contents are then removed from the sand bath and allowed to cool. The soap is then thoroughly dissolved in about 200 c.c. of boiling water and decomposed by adding dilute sulphuric acid in considerable excess. The beaker and contents are again heated on the sand bath until the fatty acids become clear. While still hot the contents of the beaker are filtered through a filter, previously wet with hot water, care being taken to hold back the larger part of the fatty acids until the water has filtered through. The fatty acids are then transferred to the filter, the beaker and fatty acids thoroughly washed with boiling water. The filter is allowed to drain ten or fifteen minutes and is then transferred to the original beaker in which the saponification was made and the whole set in a steam oven for 15 or 20 minutes to expel moisture. When thoroughly dry, which is shown by the saturation of the filter paper by the fatty acids, the fatty acids are dissolved in gasoline (distilling under 50 degrees Cent.) and filtered through a clean dry filter (but using the same funnel used in the previous filtration of the fatty acids from the acid solution) into a 6oz. flask, care being taken to wash beaker and funnel free from fatty acids. At least 100 to 125c.c. of gasoline should be used in dissolving the fatty acids and washing the beaker and funnel. The solution of fatty acids in gasoline is then placed on a steam bath (with air jet) until the gasoline is completely expelled after which the flask and fatty acids are dried in an oven at 105 degrees

C. for 15 minutes. The flask is then removed from the oven and allowed to cool (the fatty acids crystallizing) after which the whole is weighed. From these weights the percentage of fatty acids is calculated. Two tests on each sample are run and the duplicate results should check within 0.25% or less. The essential difference is the manner of separating fatty acids from the solution from which they were precipitated. It has been the author's experience that it is almost impossible to sufficiently wash the fat free from mineral acid without a small portion of the same passing through the filter paper. Oftentimes even an apparently clear filtrate when allowed to stand on the steam bath for some time will show small globules of fat. This as well as the fact that drying in the oven with the mineral acid not thoroughly removed causes error, condemns the method in the opinion of the author.

A separatory funnel method was also tried in which the saponification, solution, and throwing out of the fatty acids was conducted the same as in the Official Method. The solution was then placed in a separatory funnel and the extraction of the crude fat made by repeated treatments of gasoline, the various gasoline portions collected, filtered through dry paper and the fat thoroughly removed from the same, and the gasoline evaporated and residual fat weighed. This method gave results as follows, 93.28-92.10-92.50-92.98-92.50-93.48. As these values show such differences amongst themselves, the highest showing much lower than our other method, the author considers the method one which requires extreme care and considerable skill to manipulate, so that checking results may be obtained. With the best of care losses occur, and furthermore the actual manipulating time is considerably increased. On these grounds the author considers that the method need not be considered as a substitute for the Official Method.

A number of other modifications of the Official Method consist of methods of saponification, and of solution.

Therefore, the author concludes that the most accurate method is that of the Official Interstate Method with the following modification.

For the solution of the crude fat, transfer the fatty acids on



the filter paper back to the original beaker and dissolve by the addition of 100 c.c. of gasoline with a few minutes' boiling on the electric hot plate. This is then filtered through dry paper and the residue treated with successive smaller portions of gasoline until the fat is thoroughly dissolved. In case only two such extractions are given, it is recommended the filter paper with the residue be given an extraction in a Soxhlet apparatus.



## STUDIES ON LIPASE

BY YOSHIO TANAKA

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Lipase has been made the subject of detailed studies by recent investigators, and it has been shown that the addition of acid is essential to lipolytic hydrolysis by castor seeds.

But scarcely any careful consideration has been given to the role played by the acid that is used in the hydrolysis of oil by castor seeds. Green<sup>1</sup> presumes that the acid liberates the active lipase from the zymogen which exists in the castor seeds. Connstein, Hoyer and Wartenberg<sup>2</sup> contend, on the other hand, that the acid acts as a catalytic agent for the active enzyme, without functioning as an activator of the zymogen. H. E. Armstrong<sup>3</sup> finds that hydrolysis by lipase can be brought about only in the presence of acid and that the acid does not act to liberate the enzyme. The majority of recent investigators maintain that the castor seed lipase acts only in the presence of acid.

The author<sup>4</sup> found in his previous research that the addition of a definite quantity of acid for a definite quantity of castor seeds is necessary for the hydrolysis of fats by the latter, and that the concentration of the acid added is not the main factor of the lipolytic action.

From these facts, it appeared probable that the acid added does not act merely by making the medium acid, but that it must act chemically upon the constituents of the castor seeds.

The object of the present paper is to record a number of experiments which have been made with the object of ascertaining the correctness of the above view, and which have cleared up the nature and mode of action of lipase. The preparation of a lipolytic powder, which is eminently suitable for industrial purposes, is also described.

<sup>1</sup>R. Green's *Soluble Ferments and Fermentation*, 2nd ed., 1901, 243.

<sup>2</sup>Connstein, etc.; *Berichte*, 1902, 3968-4006.

<sup>3</sup>H. E. Armstrong; *Jour. Chem. Soc.*, 1906, Abstr. i. 126.

<sup>4</sup>Y. Tanaka; *Jour. Coll. Engin. Imp. Univ. Tokyo*, 1910, V. 25.

### NON-NECESSITY OF FREE ACID IN LIPOLYTIC MEDIUM

Experiments were first made to test the acidity of the watery medium in which the enzyme was at work. The author found that the extract made from the ground castor seed cake by triturating it with the optimum quantity of N/10 sulphuric acid was indifferent to methyl-orange. From this, it is evident that the acid added in the optimum quantity does not exist in the free state in the medium, and that the acidity of the lipolytic medium is not necessary for the hydrolysis.

The following experiment gave a further confirmation on this point:

5 grams of the pressed cake of castor seeds were triturated with 30 c.c. of N/20 sulphuric acid for 30 minutes and the milky liquid was filtered. The insoluble residue was washed until it was completely free from acid and other soluble matters. The final product, which was now in a pasty condition, was triturated in a porcelain mortar with 50 grams of soja bean oil and about 10 c.c. of water, and allowed to stand for about 18 hours at the room temperature. Analysis showed that about 76,5% of the oil had been decomposed, though no free acid was added in this case.

The results prove that, as suggested by Green, lipase exists in the state of an inactive zymogen in castor seeds and that, by the action of dilute acids, the latter can readily develop the active enzyme. It is also to be observed that the liberated lipase is most active in a neutral medium and that, contrary to the opinion of Green, the enzyme is insoluble in water. The author, therefore, can not agree with the generally accepted view that the castor seed lipase acts only in the presence of acid.

### PREPARATION OF "LIPASE POWDER"

Based upon the results of the above experiments, the author has prepared an active product from castor seeds and in a convenient form. The method is as follows:

100 grams of pressed or extracted castor seeds are triturated with 600-700 c.c. of N/10 acetic acid (or about 500 c.c. of

N/10 sulphuric acid) for 30 minutes at 30°-35° C. The milky mixture thus obtained is filtered, and the residue washed thoroughly with water and dried at temperatures not exceeding 40° C.

The lipolytic product thus obtained is termed "Lipase powder" by the author. It is an odourless, white powder, containing no soluble matter. Its chemical composition varies with the pressed castor seeds used. One sample had the following composition:

Water	5.3 per cent.
Crude fatty matter	37.2 per cent.
Nitrogenous matter	46.3 per cent.
Mineral matter	1.2 per cent.
Non-nitrogenous organic matter	10.0 per cent.

Hydrolysis of fats and fatty oils can be rapidly brought about by a small quantity of the "lipase powder" in the presence of water alone, as may be seen from the following experiments, in which 25 grams of fats or fatty oils were mixed with one gram of the "lipase powder" and 8 c.c. of water, and allowed to stand at 38° C. The percentages of oils and fats hydrolysed in one and in six hours were:

Oil or Fat	Per cent. of Oil or Fat decomposed in	
	One hour	Six hours
Soja bean oil	44.4	81.7
Groundnut oil	49.8	84.7
Cocoanut oil	40.4	70.8
Lard	51.7	85.9
Tallow	50.6	84.4

The great purity of the hydrolysed products makes any further treatment unnecessary.

#### KEEPING QUALITY OF "LIPASE POWDER"

The keeping quality of the "lipase powder" has been tested during a period of six months. As can be seen from the data adduced, it has shown no appreciable change in its lipolytic activity for a moderately long time.

Twenty-five grams of soja bean oil were decomposed by one gram of the "lipase powder" and 8 c.c. of water at 38° C.:

Time of keeping in days	Per cent. of oil decomposed in one hour
1	45.4
60	45.0
120	43.5
180	40.0

Hoyer's "ferment," which is at present being manufactured in a marketable quantity, rapidly loses its lipolytic power on keeping. Moreover, the glycerine resulting from its use contains impurities derived from the "ferment." All these disadvantages may be avoided by the use of the present preparation of "lipase powder," which is thus eminently suitable for industrial purposes.

#### INFLUENCE OF SOME NEUTRAL SALTS ON LIPASE

R. Green<sup>1</sup> has shown that a neutral salt, such as sodium chloride, impedes the action of lipase. Connstein, Hoyer, and Wartenberg,<sup>2</sup> on the other hand, have held that ferrous sulphate, sodium chloride, sodium sulphate, magnesium sulphate and ammonium sulphate have no effect on its action. Further, K. Braun and E. C. Behrendt<sup>3</sup> have found that compounds of magnesium, alkali-metals and tungsten have no influence on the activity of lipase, but that even a small amount of mercury, copper and iron salts checks the enzymic activity, while E. Hoyer<sup>4</sup> maintains that an addition of 0,15 to 0,2 per cent. (of the weight of the fat) of manganese sulphate helps to increase the activity of lipase.

These contradictory results appeared to the present author to be due to the disturbing influence of the salts and protein substances naturally present in the castor seeds or castor seeds cake, and he has, therefore, undertaken the study of the influence of

<sup>1</sup>Green's *The Soluble Ferments and Fermentation*, 1901, 244.

<sup>2</sup>Connstein, etc.; *Ber. Deutsch. Chem. Ges.*, 1902, 4004.

<sup>3</sup>Braun & Behrendt; *Ber. Deutsch. Chem. Ges.*, 1903, 1905.

<sup>4</sup>E. Hoyer; *Chem. Centr.*, 1905, 2. 582.

some neutral salts on "lipase powder," which contains no soluble matter and is active in the presence of water alone.

For this purpose, 25 grams of soja bean oil were rubbed up with one gram of the "lipase powder" together with 6 c.c. of water and, after adding varying amounts of some neutral salts, allowed to stand for 90 minutes at 38° C. The following percentages of oil were found to be hydrolysed:

Grams of salt added	Per cent. of oil decomposed in 90 minutes
No salt added	59.8
0.3 gram of NaCl	65.9
0.5 gram of NaCl	62.7
0.3 gram of KCl	65.2
0.6 gram of KCl	64.0
0.3 gram of K <sub>2</sub> SO <sub>4</sub>	66.8
0.6 gram of K <sub>2</sub> SO <sub>4</sub>	62.7
0.3 gram of LiCl	65.9
0.3 gram of NH <sub>4</sub> Cl	65.5
0.01 gram of Mg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	57.1
0.12 gram of Mg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	45.4
0.02 gram of CaCl <sub>2</sub>	56.5
0.08 gram of CaCl <sub>2</sub>	48.8
0.02 gram of BaCl <sub>2</sub>	45.0
0.05 gram of MnSO <sub>4</sub>	65.1
0.25 gram of MnSO <sub>4</sub>	62.7
0.003 gram of CuSO <sub>4</sub>	11.7
0.02 gram of CuSO <sub>4</sub>	8.0

Thus it is evident that the lipase greatly increases its activity by the addition of a small quantity of the neutral salts of alkali metals. The salts of magnesium, calcium, barium and, especially, copper have an inhibitory influence on lipase. That manganese sulphate produces an accelerating action, as was already observed by Hoyer, is worthy of remark.

#### INFLUENCE OF CASTOR SEEDS EXTRACT AND SOME PROTEINS ON LIPASE

That castor seeds extract has also a favourable effect on the activity of lipase may be seen from the following experiment.

Two samples of 25 grams each of soja bean oil were hydrolysed for one hour at 38° C. with one gram of the "lipase powder," and adding 7 c.c. of castor seeds extract to the one but not to the other. The extract was made by triturating 100 grams of the pressed castor seeds with 700 c.c. of water for an hour. The results were as follows:

	Per cent. of oil decomposed in one hour
Without extract	40.5
With extract	46.0

The influence of the mineral constituents and protein matters isolated from castor seeds extract has next been separately studied, and the results show that the accelerating effect of the castor seeds extract is to be ascribed both to its mineral constituents (dialysate) and proteose, but not to globulin and other coagulable albumines.

In the following series of experiments, fifty grams of soja bean oil were mixed with two grams of the "lipase powder" with the addition of the substance named dissolved in 12 c.c. of water:

Grams of substance added	Per cent. of oil decomposed in one hour
0	41.5
0.12 gram of leucine	44.2
0.12 gram of asparagine	45.4
0.06 gram of gelatine	41.2

From these results, it may be seen that the decomposition products of protein, such as leucine and asparagine, have also an accelerating effect on lipase, while gelatin does not appear to promote the lipase action. Neutralised egg albumin behaves like gelatin in this respect.

#### SUMMARY

1. It is shown that the acid added to the castor seeds in its optimum quantity does not go to acidify the lipolytic medium and that, therefore, acidity of the medium is non-essential to lipolytic hydrolysis.



2. An active lipolytic powder has been prepared by treating pressed castor seeds with the optimum amount of acid, completely washing out all the soluble matters with water and drying the pasty mass thus obtained. This product which is an odourless, tasteless, white powder and contains no soluble matter, hydrolyses fats and fatty oils very rapidly in the absence of any acid. From this it follows necessarily that lipase exists in castor seeds as zymogen, from which the active enzyme is developed on the addition of an acid, that lipase is absolutely insoluble in water and that it is active in a neutral medium. The above lipolytic product has been named "Lipase Powder."

3. Not only can the "lipase powder" be kept for a long time without showing an appreciable change in its activity, but also the products of hydrolysis resulting from its use are exceedingly pure. It is, therefore, eminently suitable for industrial purposes.

4. The activity of lipase is shown to be greatly increased by the addition of the neutral salts of alkali-metals, while the salts of magnesium, calcium, barium and, especially, copper exert a retarding influence. That manganese salts should greatly accelerate the activity of lipase, a fact already observed by Hoyer and confirmed by the present author, is clearly exceptional.

5. The hydrolysing power of "lipase powder" is also shown to be remarkably increased by the addition of castor seeds extract. This behavior is ascribed to the accelerating influence of the mineral salts of alkali-metals and proteose contained in the extract; globulin and other coagulable albumins also contained in the castor seeds extract do not appear to exert any influence.

6. The decomposition products of protein, such as leucine and asparagine, are also found to exert a pronounced stimulative effect on lipase action.









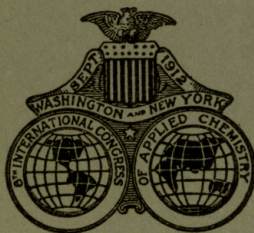


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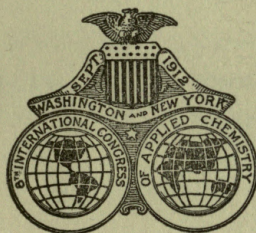


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VARNISHES



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## VOLUME XII

### SECTION Ve: PAINTS, DRYING OILS AND VARNISHES

#### CONTENTS

	PAGE
BOCHAND, G. AND GILLET, P. <i>Essai &amp; Critique de la Methode McIlhiney pour l'Analyse de Vernis Gras</i> .....	7
CABOT, G. L. <i>Lamp Black and Carbon Black</i> .....	13
GARDNER, HENRY A. <i>The Rarer Paint Oils</i> .....	33
GILLET, P. (see BOCHAND, G.)	
HAWLEY, L. F. <i>Wood Turpentine—Their Analysis, Refining, Composition and Properties</i> .....	41
HERTY, CHAS. H. <i>The Past, Present and Future of the Naval Stores Industry</i> .....	101
HICKS, EDWIN F. <i>Shellac Analysis and the Detection of Small Amounts of Colophony in Shellac</i> .....	115
KLATZ, JOHN M. <i>Benzol and the Coal Tar Distillates and Their Application in the Paint Trade</i> .....	123
KRAUSS, V. P. <i>Cobalt Driers</i> .....	127
LAWRIE, J. W. <i>Theory and Practice of the Painting of the Modern Steel Passenger Car</i> .....	133
LIEBREICH, ERIK <i>Können Anstriche Rostfördernd Wirken?</i> .....	143
LUSSKIN, ABRAHAM <i>Herring Oil</i> .....	155
MANNHARDT, HANS <i>Moisture and the Drying of the Linseed Oil Film</i> .....	159
OLSEN, J. C. AND RATNER, A. E. <i>The Decomposition of Linseed Oil During Drying</i> .....	165

	PAGE
PIERRES, GASTON DE (see SMITH, J. CRUICKSHANK)	
RATNER, A. E. (see OLSEN, J. C.)	
SCHAEFFER, JOHN A.	
<i>The Manufacture and Properties of Sublimed White Lead</i> . . . . .	175
SCHORGER, A. W.	
<i>The Examination of the Oleoresins from Several Species of Pine     Native to the Western States</i> . . . . .	181
SMITH, J. CRUICKSHANK AND PIERRES, GASTON DE	
<i>The Technology of Varnish Manufacture with Notes on an     Improved Scientific Process</i> . . . . .	185
TOCH, MAXIMILIAN	
<i>The Permanency of Painting</i> . . . . .	195
WILLIAMS, HENRY	
<i>Modern Painting Methods in the Navy</i> . . . . .	203
VÉZES, M.	
<i>Sur deux Nouvelles Sources de Pinène</i> . . . . .	211

ESSAI & CRITIQUE DE LA METHODE McILHINEY  
POUR L'ANALYSE DE VERNIS GRAS

G. BOCHAND AND P. GILLET  
*Puteaux, France*

TABLEAU  
VERNIS GRAS

*Distillation par la Vapeur d'Eau.*

GROUP I	GROUP II
Partie volatile	Partie non volatile
Solvants volatils	Solvants fixes
	Résines
	Gommes dures
	Huiles
	Matières siccativantes (pour mémoire).

*Saponification Alcoolique suivie d'un Traitement Acide.*

GROUP III (insoluble A)	Soluble A
Solvants fixes	Glycérine
Résines	
Gommes dures	
Acides gras	

*Traitement par l'Ether de Petrole*

GROUP IV (Insoluble B)	GROUP V (Soluble B)
Acides oxydés	Solvants fixes
Gommes dures	Résines
	Acides gras inoxydés
	Acides gras incomplètement oxydés

<i>Traitement par Alcool A 85°</i>		<i>Nouvelle Saponification</i>	
Insoluble C	Soluble C	Insoluble D	Soluble D
Gommes dures	Acides oxydés	Solvants fixes	Acides gras inoxydés d° incompl. oxydés
			Résines
			<i>Determinees par la Methode Twitchell</i>
			Résines
			Acides gras inoxydés and incomplet oxydés.

Pour fournir sur la méthode des critiques raisonnées, nous en avons fait l'application à l'analyse d'un vernis de composition rigoureusement connue & rentrant dans la série des fabrications courantes.

Voici quels ont été les résultats sur une prise d'essai de 13 gr., 616 de vernis:

Solvants volatils . . . . .	44,70%
Glycérine . . . . .	1,80
Gommes dures . . . . .	10,13
Acides oxydés . . . . .	7,06
Ac. inoxydés ou incomp. oxydés . . . . .	10,81
Solvants fixes . . . . .	4,50
Résines . . . . .	11,56
 Total . . . . .	 90,56

Nous avons seulement remplacé la méthode de TWITCHELL par le procédé de HÜBL & STADLER qui nous semble d'exécution plus aisée & plus sûre.



Voici la composition initiale du vernis soumis à l'analyse :

Gomme dure, variété de Pontaniak cuite avec 17%	
de perte . . . . .	12,50%
Résine . . . . .	12,50
Huile de lin crue . . . . .	12,50
Huile de bois polymérisée . . . . .	12,50
Essence de térébenthine . . . . .	45,00
Huile minérale légère . . . . .	5,00
<hr/>	
Total . . . . .	100,00

La perte d'environ 10% dans l'analyse se retrouve d'une façon assez constante dans le dosage de certains éléments :

Gommes dures, 10,13 au lieu de 12,50%			
Résine	11,56	d°	12,50
Solvants fixes,	4,50	d°	5,00

L'analyse est très suffisamment approximative en ce qui concerne les solvants volatils (44,70% au lieu de 45%); pour les huiles l'erreur est grande, car nous trouvons 19,50% au lieu de 25,00%. Cela provient principalement de la nature des corps examinés & des difficultés matérielles des séparations par l'entonnoir à robinet, (gouttes huileuses que l'on ne peut détacher, émulsions partielles, difficultés de distillation des solvants, suintements sur les parois des vases, etc., etc.), toutes causes de pertes lorsqu'on effectue les pesées. Aucune des méthodes d'analyse proposées, soit pour le dosage de tous les éléments, soit pour la séparation de deux ou plusieurs d'entre eux, ne signale ces causes d'erreur dues aux difficultés de manipulation.

Un autre point faible du procédé McIlhiney réside dans ce fait que les gommes dures cuites ne sont point complètement insolubles dans l'éther de pétrole. Lorsque la gomme dure est faiblement pyrogénée, comme c'est le cas du vernis examiné, le pouvoir dissolvant de l'éther de pétrole est nul ou à peu près. Au contraire lorsque la pyrogénéation du copal est poussée assez loin, comme cela est souvent nécessaire, pour les gommes manilles, par exemple, la proportion de pyrocopal soluble dans l'éther de

pétrole croit dans de notables proportions; il s'ensuit que l'on pèse plus tard de la gomme dure comme résine.

### ETUDE DU GROUPE I

#### *Solvants Volatils Entraînés par la Vapeur d'Eau*

On recherche généralement ces solvants ramenés aux 3 formes: carbures aromatiques, carbures terpéniques, carbures pétroliques.

Les solvants séchés aussi exactement que possible, sont traités par HCl gazeux sec qui fournit le mélange de chlorhydrates de térébenthènes solides & liquides que l'on peut aisément séparer des carbures benziniques & pétroliques.

Les carbures benziniques par un traitement acide nitrique & réduction ultérieure, permettent, par reprise acide, de donner des sels d'amine solubles dans l'eau, tandis que les carbures pétroliques résistant à cette action, se retrouvent à l'état insoluble.

Fréquemment les carbures pétroliques employés sous la dénomination de "White Spirit" proviennent des pétroles de Galicie & renferment une certaine quantité de carbures benzéniques ou cycliques. Dans ce cas, il y aura attaque nitrique partielle & incertitude dans le dosage.

Disons toutefois que la nature du solvant volatil entrant dans la composition du vernis est la chose qui intéresse le moins le fabricant, en ce sens qu'elle n'influe que très peu sur la valeur finale du produit: brillant, durée, souplesse ou dureté.

### ETUDE DU GROUPE II

#### *Residus de la Distillation à la Vapeur d'Eau.—Saponification Alcoolique Suivant d'un Traitement Acide*

La saponification s'effectue normalement. Le traitement acide par HCl de préférence, permet une séparation facile de l'Insoluble A (Acides gras, résines, gommes dures) d'avec le soluble A (eaux glycérineuses).

Dans le soluble A on dose la glycérine. Ce dosage est considéré actuellement comme sans intérêt par l'industrie.

## ETUDE DU GROUPE III

*Insoluble A du Groupe II.—Traitement par l'Ether de Pétrôle*

Ce traitement se fait facilement dans un appareil à épuisement, mais l'évaporation de la solution éthérée pour obtenir le soluble B est une opération fort délicate.

La grande cause d'insuccès est le suintement des parties solubles entraînées sur les parois intérieures & extérieures par l'évaporation de l'éther. Etude à faire: Méthode d'évaporation ou recherche d'appareil évaporatoire approprié supprimant les pertes par suintement.

## ETUDE DU GROUPE IV

*Insoluble B du Groupe III.—Traitement par l'Alcool à 85°*  
(On obtient l'insoluble C & le soluble C)

Ce traitement ne laisse pas complètement insolubles les gommes dures & dissoud incomplètement les acides oxydés. La variation dans le pourcentage peut aller de 5 à 6 en plus ou en moins, ce qui empêche de dire nettement si le vernis est à base d'huiles pures ou contient de la gomme.

La connaissance exacte du rapport des quantités d'huiles & de gommes contenues dans un vernis est de la plus haute importance pour le fabricant. C'est là le point faible de la méthode. De nouvelles études pour le dosage de ces deux éléments sont de toute nécessité.

## ETUDE DU GROUPE V

*Soluble B du Groupe III*

Une nouvelle saponification alcoolique du soluble B séparera les solvants fixes (Insoluble D) des résines acides gras inoxydés & acides gras incomplètement oxydés (soluble D).

Cette séparation se fait assez facilement, mais ce 2ème traitement alcoolique donne des savons inconnus, près de leur point limite de solubilité & empêchant une séparation nette dans l'entonnoir à robinet.

*Insoluble D.* Les solvants fixes extraits par cette saponification comportent les huiles minérales. Etant donné le groupe très

restreint de ces huiles employé dans l'industrie, il ne paraît pas utile de spécifier à quel genre d'huile minérale on a affaire.

*Soluble D.* Méthode TWITCHELL. A cette méthode d'une exécution fort délicate, nous préférons le procédé HÜBL & STADLER basé sur la solubilité du résinate d'argent dans l'éther, tandis que l'oléate d'argent y est insoluble. Cette méthode donne des résultats assez précis.

#### MATIÈRES SICCATIVANTES

Nous passons à dessein sous silence la recherche des composés minéraux introduits dans les vernis pour la siccativation des huiles. La quantité restant dans le vernis est pour la plupart des cas très inférieure aux proportions mises en oeuvre à la fabrication. Leur recherche & leur dosage sont du domaine de la chimie minérale.

#### CONCLUSIONS

Nous estimons que le procédé de Mr. McIlhiney ne permet pas de déterminer d'une façon suffisamment précise les constituants d'un vernis.

Les études à faire doivent porter sur les points suivants & dans l'ordre où nous les indiquons :

Connaissance exacte de la nature de la gomme dure employée, ce qui implique l'étude des propriétés des différentes gommes aux différents de rés de pyrogénéation.

Séparation exacte de la résine ordinaire d'avec le pyrocopal, quel que soit le degré de pyrogénéation de ce dernier.

Nature exacte de l'huile végétale employée et *accessoirement* :

Nature des huiles minérales.

Analyse complète des solvants volatils.

Ces études ne devront se terminer, en aucun cas par l'adoption de formules types de vernis, formules très appréciées des administrations. Si de telles formules étaient adoptées, il y aurait souvent présomption de fraude sur un vernis possédant toutes les qualités requises pour l'emploi que l'on en veut faire, si ses constituants ne correspondaient pas à la formule d'adjudication.

Les différentes proportions des constituants [répondent à des nécessités industrielles & actuellement sont souvent les seules caractéristiques de la fabrication d'une marque connue.

## LAMP BLACK AND CARBON BLACK

GODFREY L. CABOT

*Boston, Mass.*

Lamp Black is defined in Webster's Dictionary as the fine, impalpable soot obtained from the smoke of carbonaceous substances which have been only partly burnt, as in the flame of a smoking lamp. This definition is correct from the chemist's point of view and covers also the substance that is known to the trade in this country and elsewhere as "Carbon Black." Nevertheless, I have given both names in the title to this paper, because in the American trade the term "Lamp Black" is usually understood to be a soot deposited by the smudge process and made from oil, resin or some other solid or liquid raw material; whereas Carbon Black is the term applied to a black deposited by actual contact of a flame upon a metallic surface.

Using the name "Lamp Black" in its wider sense as any commercial form of soot, it may be prepared in three different ways,—1st, by the combustion of dead oil of tar, pitch, resin or some other carbonaceous raw material with an inadequate supply of air and the collection of the floating particles of soot that escape unburned from the flame and slowly deposit themselves on the walls and floors of the collecting chambers.

2nd,—it may be formed by the direct impact of a flame upon a collecting surface and 3rd, it may be formed by heating carbonaceous vapors to a decomposing point, apart from the air or flame.

From time immemorial soot has been used by some savage tribes to paint their faces with and color other objects that they might wish to beautify in this way, but the civilized man has long since discarded ordinary soot as being too impure, gritty and weak in coloring power and to the best of my knowledge, there is no market for ordinary soot for paints, printing ink or any of the uses to which Lamp Black is commonly applied.

Ordinary soot contains 50% of grit, empyreumatic matter and other impurities.

Considering Lamp Black in the more restricted sense to which it is known to the American trade, of a commercial soot, deposited by the smudge process, the starting point is usually the dead oil of tar, an oil containing a large amount of naphthalene, a certain amount of phenol and various aromatic hydrocarbons particularly suited to the manufacture of Lamp Black by reason of the large percentage of carbon therein contained, the effect of which is that when burnt with an inadequate supply of air, a very considerable proportion, to wit, from 15 to 35% of its weight, can be obtained in the form of Lamp Black by deposition in suitably arranged chambers.

The quality of the black is determined by the size and shape of the furnaces in which the oil is burned; by the heat to which it is subjected in the process of manufacture; by the position in which the black is deposited and by the care that is exercised in the process of manufacture and in the selection and preparation of the raw materials.

The oil is usually allowed to flow in a sluggish stream into an earthenware or iron pot or pan, in which it burns and from which the smoke passes through flues into the chambers in which it is deposited.

To absorb and utilize commercially some of the heat, boilers are often placed within reach of the flame and the steam thus generated is used for the industrial processes that may take place in the same factory. Care is necessary to entirely free from water whatever raw material may be employed and also to protect the reservoirs and the pipes from them to the burners from excessive cold in the wintertime, which might cause a stoppage by the coagulation of naphthalene and anthracene or other solid matter in the pipes. A screen is often used at the final exit from the black-condensing chambers in order to hold back the last traces of the black, both on account of its value and because the smoke that passes from a lamp black factory is very annoying to neighbors.

The best grades of black, generally speaking, are obtained in furnaces of moderate size, so built that the black is prac-

tically calcined at the time it is deposited and carries down with it but very little empyreumatic matter. The products of combustion are usually carried through a series of chambers and the black is assorted according to its distance from the point of origin, the lightest being that furthest from the flame and for this reason commands better prices for certain purposes.

These chambers are periodically emptied and before doing so, it is needful to be sure that the black is thoroughly cold and is not afire, for if too much oxygen comes into the chambers it sometimes happens that the black gets afire and the fire may lurk undetected unless great care be exercised. Generally speaking, an experienced workman can detect fire by the smell of the carbonic oxide and the workmen are thus put on their guard to hunt out and extinguish the fire. It sometimes happens the amount of carbonic oxide gas is dangerous to the workmen and this danger should be borne in mind. This gas is very poisonous.

It has been observed that the smokiness of a flame can be increased by artificial cooling, for instance, if you bring a coarse wire grating into an ordinary gas flame, it immediately begins to smoke and various attempts have been made to utilize this principle to increase the yield of Lamp Black, but so far as I know, the only practical application has been the generation of steam in boilers by the heat of the Lamp Black furnaces.

It is good practice to introduce partition walls in the chambers used for deposition, thereby increasing the distance that the products of combustion must travel before they finally escape in the open air, with a view to increasing the percentage of deposition, but this practice can easily be overdone, for if you divide up your chambers too much, you do more harm, by increasing the speed with which the products of combustion travel; than you do good by increasing the distance.

Mechanical devices have been used in the form of stirrers, which churn the air and cause the condensation of the smoke in masses sufficiently large for it to deposit itself. I do not know whether any of these devices are now in use on a commercial scale. The soot thus obtained contains in the neighborhood of 80% of carbon, the rest being chiefly oxygen and hydrogen, with traces of grit on the walls and floors of the collecting cham-

bers and a greater or less percentage of oil or other empyreumatic matter.

This oil or empyreumatic matter can be driven off by heating the black in sheet iron boxes, care being taken, on the one hand, to heat it sufficiently to drive off the oil, and on the other, not so hot as to affect the mixing strength and it is possible, as already stated, by a proper proportioning of the fireplace, flues and the supply of raw material and a proper arrangement of the temperature and other conditions, to cause a deposition of a certain amount of black practically free from empyreumatic matter from the start.

Resin, resinous woods, tar, pitch and other raw materials have been and still are, to a certain extent, used in the manufacture of Lamp Black, but generally speaking, the quality thus obtained is less good than that obtained from the dead oil of tar and other distillates and such inferior raw materials are comparatively unimportant as a commercial source of Lamp Black.

There is not time here to enter into the great variety of different shapes and sizes of ovens, collecting chambers, various devices for regulating and controlling the draft and the many different complications of detail that have been and are still used in this business.

Before passing on to Carbon Black, I will briefly mention the methods of making Lamp Black by the heating of hydrocarbon vapors out of contact with air. For a typical instance of this see Patent No. 866883, by Albert D. Purtle and Irving E. Rowland of Salem, W. Va., These gentlemen have described their patent as a process of making Carbon Black, but this is a misnomer, for the resulting pigment has nothing like the strength of Carbon Black obtained by the depositing process and in appearance and properties more nearly resembles the ordinary Lamp Black of commerce.

For years a similar process was used to extract carbon from natural gas to be used in the manufacture of electric light pencils near Red Bank in the Alleghany Valley, Pa., but the carbon thus obtained cost too much to compete in the long run with coke, which is now the chief raw material for these pencils. For some reason which I do not pretend to understand, Lamp Black thus



obtained is apt to contain particles of adamantine carbon, so hard that they will scratch glass.

Another commercial obstacle is the high cost of the apparatus and the large expense from deterioration as compared with the value of the finished product. Therefore, although a much larger proportion of carbon can be obtained from natural gas by this than by any other known process, all such efforts have, up to this time, failed to show a commercial profit, but I believe that this method of making Carbon Black will sometime be successfully applied.

Attempts have been made to first volatilize the raw material and secondly burn the resulting vapor on the smudge system with an insufficient supply of air and collect the resulting soot, but I do not know that any such attempts have proved profitable on a commercial scale. I should hardly think they would.

Various devices have been adopted to perfect the separation of the soot from the air and I may say that both in the manufacture of Lamp Black by the ordinary smudge process and in the manufacture of Carbon Black by the contact process, one of the most difficult problems is the proper separation of the black from the air in which it floats or which it holds mechanically when it settles.

In the case of the smudge process, are some times used adjustable blinds by which the black enters the chimney and which can be worked just like the adjustable slats on an ordinary window-blind, although they are best made of iron. Thus the draft is regulated and eddies are formed which help to cause the black to unite in larger pieces and settle out.

High pressure electric discharges of a static machine have been used experimentally for causing this separation of the black from the air, but this is too expensive and cumbersome a method to have proved profitable on a commercial scale, and, of course, on a large scale high pressure discharges are dangerous. The best material for the chambers in which the black settles, is masonry with cement floors and a brick roof put together with cement mortar.

When a new plant is put in operation, the black first made is apt to contain moisture, condensed by the coldness of the walls;

empyreumatic matter which has not been calcined out for the same reason, and grit, which at first comes off the walls to an annoying extent, even when great care is exercised in construction. This black is sold, usually at a cheap price, to those who are willing to use a black containing grit and only after the operation has been carried on for some time, so that everything is warm and in good running order and the loose grit has fallen, can the best results as to quality be obtained.

The Lamp Black which is thus precipitated, can be freed from empyreumatic matter by calcining, as already stated, or by washing with alkali or acid. So far as I know, there is practically none of it ever washed with alkali or acid, the expense of drying being very material and in general, the handling of black is a difficult and expensive process, owing to its great bulk and extreme lightness, which means a great deal of loss and much dirt and disagreeable work, and it is more and more the aim of lamp black manufacturers to so conduct their process that the black is calcined in the process of making, at least, to an extent satisfactory to most buyers.

In the case of Carbon Black, the black when first scraped from the plates is so light that 30 pounds will fill a sugar barrel. When you consider that the specific gravity of Carbon Black is about 1.7 (that is, very much heavier than water) you will perceive that 95% of the bulk of black as it comes from the plates is air and the problem of packing is to separate this black from the air so far as is commercially feasible.

This can be done by screw-packers, similar to those used for packing flour, but different in detail and run at a very much lower rate of speed, or it can be done by a plunger, lined with sheepskin, the wool side out, worked up and down vertically by a ratchet or screw.

An essential element is time. You cannot hurry the process of packing Carbon Black without much loss by spurting of the black through the air and many other evils not needful here to mention.

As it comes into the market, a sugar barrel will hold from 75 to 80 pounds. In fact, we get 80 lbs. into a barrel of less than sugar barrel size; which means that the black has been compressed

to about one-third of its original bulk and that about 88% of its bulk is still air. Under these conditions, it is very hard and many buyers insist on its being less hard pressed, owing to the greater difficulty of grinding, but its ultimate quality for most uses is not affected by this pressure.

In Koehler's book on the Manufacture of Black, are mentioned four different firms that at one time had factories for the manufacture of contact black from oil, using for this purpose a heavy mineral oil burned in burners beneath a plate on the upper surface of which was water and around the rim below a shield to protect the burners from side-draft.

The capacity of these factories, if I correctly understand this article, would be about 170,000 pounds a year, but I do not think anywhere near this amount was ever made. The apparatus was very expensive in proportion to the output and the price at which the black was sold forbade direct competition with American natural gas black, of which probably more is made in a day than was ever made of this other black in a year.

The raw material used in this European process was a heavy shale oil and I believe in actual practice they volatilized it and scrubbed the gas to remove the impurities.

There is still another source of Lamp Black, to wit, Acetylene Gas, obtained from the refuse of Carbide of Calcium factories, namely, those grades of Carbide of Calcium, containing too small an amount to be merchantable.

This acetylene gas possesses the remarkable quality of exploding by itself alone without the admixture of air and Jaenecke & Schneemann were in the habit of making black by exploding it under 5 atmospheres, either by compression or by an electric spark.

The great trouble is, first, that it is very hard on the apparatus and second, a black thus obtained is very inferior in color and strength to Carbon Blacks from natural gas. It is essentially a by-product; the supply is very uncertain and the price very irregular, but always averages very much higher than that of Carbon Black. Therefore, it can only be used where its bluish tinge gives it the preference in certain trades.

Carbon Black is the trade name given in this country, and to

a certain extent abroad, to Lamp Black made upon the surfaces of metal or stone by direct impact of flame.

The first Carbon Black ever made in this country and sold in a commercial way seems to have been made in the year 1864 by J. K. Wright, an ink maker of Philadelphia, Pa., for use in printing ink.

This industry is, therefore, a comparatively new one in this country, and it certainly never attained any great importance abroad, although I cannot say when it was first made in other countries. Mr. Wright made Black on sheet iron cylinders revolved over gas jets, from which the Black was removed by stationary scrapers. This process was used by other ink makers for making Carbon Black from artificial gas in a small way for use in printing ink, and a very glossy, high-priced ink, of intense color, was obtained.

These pioneers in the Carbon Black industry apparently did not consider the process of sufficient importance to patent it, for the first patent granted in this country was issued Dec. 10th, 1867, to A. Millochan, New York, for a process which proved to be of no value, and it was not until the year 1872 that any process was patented that was subsequently used on a regular commercial scale. It had attracted the attention of many different people, among others, Peter Neff, Gambier, Ohio, and John Howarth, Salem, Mass., that large quantities of natural gas going to waste in the gas regions offered a cheap and abundant raw material for this manufacture, and on Sept. 17th, 1872, John Howarth received a patent for the manufacture of Carbon Black from Natural Carbureted Hydrogen Gas, claiming the production of Carbon Black from a natural carbureted hydrogen gas issuing from the earth, etc. His plan was to connect the gas well with a gas-holder, such as is used in artificial gas works, and with a blow-off from which might escape the surplus flow of the well not required in the process of manufacture. As the natural pressure of gas in the rock sometimes exceeds five hundred pounds on the horizon from which he derived the supply of his factory and there was at that time no method of regulating the flow, this waste of gas was a necessary feature of his enterprise. From the gas-holder, the gas passed through pipe to ordinary gas jets

arranged in the same horizontal plane beneath slabs of soapstone. These slabs of soapstone were provided with holes for ventilating, without which the carbonic acid gas, and other inert products of combustion, would have formed a layer about the middle of the slabs and kept the flame away from the surface, thereby diminishing the yield and impairing the color of the resulting product. Above these slabs of soapstone rose, in an arch, an iron dome or hood with a chimney at the top of this arch, and in this chimney a damper that could be set to give the right amount of draft. On the slabs rested pans of water closed in and kept cool by a continuous circulation. The edges of this arch descended below the edges of the soapstone slabs and were grooved longitudinally with horizontal grooves in which ran a scraper that could be pulled to and fro by hand with a long handle. This scraper removed, from time to time, the deposited soot which fell into the sheet iron aprons or troughs which hung from the burner pipe. From these again the Black fell through discharge pipes into receptacles which could be changed by hand when full. This was a very crude, clumsy and expensive way of making Carbon Black, decidedly less advantageous than that previously employed in making Black from artificial gas, but, nevertheless, owing to the cheapness of the raw material, the price, which had been \$3.00 to \$5.00, was immediately dropped to \$2.50, and then to \$1.50, and shortly after to \$1.25 per pound. It is, however, a curious fact that the Black from natural gas does not possess all the qualities of that made from artificial gas.

The next patent granted for Carbon Black was for a cylinder cooled externally by water and slowly revolving over burners placed on its interior, but I am not aware that this process was ever used.

On March 23rd, 1875, John Howarth received a further patent on a travelling car which hung from rails running length-wise of the bench or row of slabs, and these rails also held between them the slabs themselves. This car carried a scraper, a shallow frame, and, hanging to that frame on each side, two deep receptacles of sheet iron which could be detached at will and emptied. These receptacles were joined together over the burners by a narrow arch of sheet iron, just wide enough to allow

the apparatus to pass over the single row of burners without striking. The car was drawn by an endless rope passing over pulleys and pulled first in one direction and then the reverse. The scrapers were held against the plates by wire springs and were only in contact with the plate when passing toward the end at which the receptacles were removed. The dome was a superfluous adjunct. Cast-iron was better than soapstone and there was no need of water cooling. Indeed, Mr. Howarth never used water cooling on a commercial scale. Obviously, its effect would hardly be felt through such a non-conductor as soapstone.

The first factory was located at New Cumberland, West Virginia, and the gas came from what is known as the salt sand, and was very rich in carbon and made an excellent Black. The factory was made of wood and before long it burned down and the business was removed to Saxonburg Station, Pennsylvania. In two or three years, competition sprang up at Gambier, Ohio, where a small factory was erected by Mr. Peter Neff, who made Black by a somewhat similar process for something like ten or twelve years. He had as many patents for Carbon Black apparatus as all the other inventors put together, or thereabout, but most of them were fantastic and useless. His factory reached an output at one time, of 125 pounds per day.

The next important competition was by a Mr. A. V. Nolen, who, in the year 1879, built a factory at New Cumberland, West Virginia, and made Black on cast iron pans holding water. By this time the price of Black had gone down to about 60 cts. per pound, but nevertheless where the two pioneers had met with little pecuniary success, Mr. Nolen, by superior ability, made a good deal of money, and bought out the original company. Various other small factories were started from time to time, but it was not until the year 1883 that any considerable advance was made, when the firm of L. Martin & Co., of Philadelphia, became interested in a small and struggling enterprise at Foster's Mills, Pennsylvania, and there erected five plates 24 feet in diameter, cast in segments and suspended on a central mast which rotated with it upon a bronze bed plate. Beneath this was fixed a stationary burner of parallel, horizontal iron pipe, 1 1-4"

in diameter, branching from a central supply 3 3-4" inside diameter, and this, in turn, connected suitably with the well.

Incredible as it may seem, even at this time, after ten years of experience, no attempt had been made by either of these three leading manufacturers to control the flow of gas from the wells, although this was then quite possible with available appliances, and a blazing torch at each gas well, wasting daily millions of feet, was a feature at the principal factories, including that at Foster's Mills, Pa. About the same time a factory was started by Samuel Cabot in the adjacent village of Worthington, at which some efforts were made to confine and economize the gas, but it remained in large part fruitless for some years, owing to the inefficiency of the foreman. At the factory at Foster's Mills, the idea of a travelling box and scraper was discarded and a plan for the first time successfully adopted on a commercial scale of a horizontally rotated collecting surface. The same principle was adopted at Worthington at about the same time, but failed of success owing to purely mechanical imperfections. At first blush, it would seem as if the original idea of moving only the scraper box was the correct principle, and yet it is now entirely abandoned, and about two-thirds of all the Black that is made today is made on surfaces which are moved over a stationary scraper box and stationary burners.

The first decade of the manufacture of Carbon Black from natural gas on a commercial scale was the epoch of factories in which the collecting surfaces were arranged in rectangular shapes, placed end to end to form what the workmen call "benches."

The details whereby the Black was collected, the dimensions of the different parts and the arrangements of the size of the burners varied in different factories; but four-fifths of all the Black made was made on benches, and the rest was made on the external surfaces of rotating cylinders. Various efforts were made to use petroleum oil and the firm of Carnahan & Swan, of Duke's Center, Pennsylvania, made a very fine Black by this method for several years.

Various other manufacturers of Carbon Black tried to use oil, and were tempted thereto by the greater amount of Black deposited by a flame of a given size on a given surface; but one and

all of them found it unprofitable, owing to the great expense of oil and the danger of fire, which increased very greatly with any increase in the size of the apparatus. An apparatus which worked perfectly well on a laboratory scale was quite unsafe on a commercial scale. At the end of this epoch, Mr. A. V. Nolen was the largest manufacturer and the total output was probably ten hundred to fifteen hundred pounds a day. The year 1883 brought with it the introduction of large rotating plates, which replaced at Foster's Mills, a factory in which benches had been used. A scraper box and scraper was placed radially so that in revolving the scrapers were at right angles to the direction in which the surfaces passed across them. The Black was removed by a screw conveyor in the bottom of the scraper box which carried it outward to a longer conveyor which ran tangential to five plates in a row and carried the Black to a rotating bolt through which it went into the bin. It was then lifted from the bin by hand in large scoops and packed by hand with a screw press, but the Black is very light and the handling of it was very dirty, unhealthy work, involving considerable loss in raw material. In the earlier factories it had been the habit to brush the Black through a fine horizontal sieve by means of brushes rotating on a vertical axis. A bolt revolving on a horizontal axis which discharged the coarser particles of Black at one end and allowed only the finer particles to fall through it, was a decided improvement. In the same year, a very able young man, named A. R. Blood, of Warren, Pennsylvania, devised a method in which a small plate about 3 feet in diameter was used. The advantage of this was that no ventilation holes were needed, as in the case of the larger plates, excepting, however, that this small plate was cast in the form of a ring with an opening in the center. This plate was moved by means of a ratchet at the center. This ratchet was worked by a lever, and this by another lever revolved on a shaft. Every time the shaft came around it would give the plate a little shove which would move it 1 1-2 inches. Beneath the plate was a scraper in the mouth of a radial hopper, through which the Black fell into a longitudinal conveyor running beneath the row of plates. There were sixteen plates in a row and five rows in the building. The building was of sheet iron on a



framework of pipe and angle iron and was pierced with small holes near the bottom to give the needful supply of air. Along the ridge pole was an opening about 30" wide and about 6" above this, a little pent roof, to prevent the entrance of rain. The space between was something like 6" through which the products of combustion passed. All of these factories used gas jets either of iron or steatite, such as are ordinarily used in houses. There was one factory which used Argand burners but it did not last many years. About this same year 1883, E. R. Blood, the father of this A. R. Blood, began making Black on the roller process, and using a burner with a small hole in the point of the tip giving a round flame. This Black was at first very unprofitable owing to the small yield and comparatively poor color, but the successors of Mr. A. R. Blood improved the details of manufacturing and experience has shown this Black to possess some valuable qualities and in spite of its inferior color it sells for a high price and is very profitable to the owners, the Peerless Carbon Black Co., of Pittsburg.

This company was for many years the only company making Carbon Black in this country from natural gas on revolving cylinders, although in earlier days there were two or three factories on this principle, and are now three such factories.

In the second decade the process of making Carbon Black introduced by Mr. A. R. Blood became the most important as to output and total value of Black produced. The prices of Black fell rapidly and reached 7 cts. per pound by the year 1887 and 4 cts. per pound by 1889. After this there was a considerable improvement in prices, followed by a further rapid increase in output and by the close of the second decade the total output had reached about 10,000 pounds per day, worth at that time about 6 cts. per pound on an average. Toward the end of the second decade two new processes began to become an appreciable factor in the total output. The first of these was our process whereby, under 24 foot plates, similar to those previously mentioned, though varying somewhat in details, was rotated a burner and black box radially placed. The burner was made up of parallel 1 1-4" pipe inserted in a central supply pipe 3 3-4" diameter. As first used the radial black box discharged into

a hopper placed at the side of the plate by means of a little trap door with a lever which was pressed in such a way as to open the trap door every time it passed over the hopper and after the discharge the trap door closed again by means of a counterpoise. This method of a rotating burner was introduced at Worthington somewhere about the year 1884, but did not become a commercial success until the year 1887. The factory changed hands and the new owner changed the method to that of a central discharge whereby the Black was continuously discharged downward by a vertical spout at the inner end of the radial black box into a circular ring-shaped box; thence it went through a hole in the bottom into a long conveyor. By the former method, the long conveyor had been tangent to the ring and by this it went within two feet of the center. A cover was hung above this round box in such a way as to exclude air and rotate with the burners, black collecting box, etc. The bottom of the vertical spout above alluded to pushed the black in front as it slowly swung around the ring until it reached the orifice through which the Black fell. One great advantage of this method was that the Black was not exposed to the air. By the former method whenever the box emptied, a cloud of Black arose, making a nuisance and a great loss of output. As rebuilt, the Black was kept under cover and carried to a bolt, also shut in, and raised from beneath this bolt in an elevator into a bin. From this bin, it was packed by machinery in either sacks or barrels, always under cover, so that from the time the Black was made until it was used by the consumer, it was never touched by hand and was always under cover and protected from all appreciable drafts of air.

The other process above referred to was introduced about the year 1891 at a place called Gallagher, Pennsylvania, and consisted of a system of channel beams turned with flat side downward over horizontal rows of stationary burners and black boxes. By a reciprocating mechanism, these beams slowly moved back and forth and the Black was scraped and removed by a screw conveyor in the usual manner. This Black was packed direct without bolting.

The chief advantage of this system is the perfection of the surfaces, which are smoother than the surfaces of cast-iron plates.

In the beginning of the third decade of this industry, another attempt was made to manufacture Carbon Black with the help of petroleum and under a somewhat new principle by evaporating petroleum and burning its vapor through gas burners. The cost of making this Black was probably less than that of any other Black made from petroleum by the contact process; still more than could be realized by its sale. One great difficulty was the formation of adamantine carbon in the Black. These particles were so hard that they would scratch glass and the manufacturer was unable to discover a method of removing them. Since that time there has been no Carbon Black made from oil on a commercial scale in this country, although there is a small amount of a very expensive grade made in Europe from what are known as gas oils, a heavy oil obtained in the distillation of shale and chiefly used by manufacturers of illuminating gas. No important improvement in Carbon Black making appeared in the third decade. The output steadily increased and reached 20,000 pounds a day.

The price fluctuated a good deal, the average for the decade (1893-1902) being about 6 cts. The amount of Black produced with rotating burners and with the reciprocating channel beams very considerably increased. There were also modifications made in the process of the small stationary plate, and the amount made on this general principle increased. In 1902, about one-quarter of all the Carbon Black was made with rotating burners; and something like one-fifth with reciprocating channel beams; not quite one-half on rotating cast-iron plates, mostly with the smaller sizes; and the rest chiefly with rollers. There was only one factory in existence which operated on the bench principle.

In the year 1899, the construction at the Grantsville factory was begun, operating on the principle of 24 foot plates, with revolving burners and black-box, etc., beneath them.

By the end of the third decade, namely, about the year 1902, this had become the largest factory in existence and has since been still further increased until it is making about 10,000 pounds a day. Possibly a brief description of this factory may be of interest.

It lies on the right bank of the Little Kanawha River and com-

prises 113 plates, each 24 ft. in diameter and surrounded by protecting rings of corrugated iron, 26 ft. in diameter. Above these plates is a roof made partly of diagonal sheets of sheet iron and partly of rectangular sheets of corrugated iron and reaching about two-thirds of the way to the top of the 16 ft. mast on which these plates are hung, leaving, therefore, in the center a space having about one-third the diameter of the plate, through which the products of combustion can escape upward.

These plates are arranged in rows about parallel to the river and disposed on two side of a central avenue which runs from the river to the road, at right angles to both.

The Black is collected by long conveyors running through the center of the rows of plates, toward the central avenue, where it passes into larger conveyors, which bring it to the packing-house; elevate it into bins and from them the black is packed partly by sack packers and partly by barrel packers, which work with a plunger.

The black is carried down the Little Kanawha River in gasoline boats whenever there is water in the river. Large tanks, containing about a thousand barrels of water, stand on the hillside above the factory and the factory is adequately piped in every part over an area of about 6 acres, whereby water can be turned on, either for the purpose of putting out fire or for the purpose of knocking black out of the ventilator holes in the rings on which the black is deposited.

These rings are of two patterns,—one of them made with 14 radial arms in the shape of T-rails, which support 70 cast iron plates, 5 between each pair of arms. The other pattern has for each plate 48 segments, 16 in the inner row and 32 in the outer row, which are supported directly by guys. In each case the plate is supported by guys which are screwed into a cap, which has approximately the shape of a very blunt, truncated cone. This cap rests upon the top of the hollow mast and the joint between the cap and the mast is made good with asbestos board.

The mast stands in a bed-plate on the upper surface of which is a groove, in which run  $1\frac{1}{2}$ " steel balls. Upon these steel balls rests a casting, having 8 horns, projecting outward and upward and fixed in the lower ends of struts made of 2" pipe. On the

outer end of these struts of 2" pipe, is an angle-casting into which the 2" pipe fits and through which a horizontal hole accommodates a horizontal guy-rod, attached at the inner end to an octagonal plate, which rotates with the burner around the central mast.

On the outer end of these horizontal guy-rods, are 3-4" nuts, and by screwing these up, the struts can be raised to the correct position, thus regulating the height of the burners beneath the plate. On the face of these angle-castings, supported by the 2" struts, is bolted an iron-bar, hanging vertically down from these angle-castings and to this iron-bar is attached an angle iron, in which runs the chain that rotates the burners, black-box, etc.

Against these angle-castings is also bolted a horizontal ring, made of bars  $4\frac{1}{4}$ " x 1-4", forming a circle around the plate and on this ring is supported the grid-iron of burner pipe. This grid-iron of burner pipe has as its central supply a piece of 3 3-4" casing, 22 ft. 6" long, and this casing, in its turn, is fed with gas by  $21\frac{1}{2}$ " pipes, connected with the help of 4 ells and a union to an octagonal gas-box, at the top and bottom of which sit glands. This gas-box is fed through holes in the mast. The glands are stuffed with asbestos so that the gas cannot escape as the black-box revolves around the mast.

I have mentioned at an earlier period in this paper that the black is removed from the plates by scrapers, placed radially to the mast above a black-box, in the bottom of which lies a screw conveyor, which in its turn is actuated by a pinion, on its inner end, which engages a bevel fixed to the central mast. Beneath the octagonal plate, to which the horizontal guys are fastened, is bolted a hanger in which turns the shaft of the conveyor which carries the pinion just mentioned.

On the inner end of this black-box, the black descends in a vertical 3" pipe through the rotating cover into the circular box from which it discharges downward into the long conveyor, which runs tangent to this circular box and two feet from the center of the ring.

In the last decade the factories in Pennsylvania have all of them been moved to West Virginia, with three unimportant exceptions, to wit, two factories not in use and the third, a factory producing only 50 lbs. a day.

A new factory has been started in Oklahoma and the total output of Carbon Black has risen to about 65,000 lbs. a day. Certain new processes have come into use which are, however, only modifications of those previously mentioned. In one factory, namely, that of the Bristol Oil & Gas Co., the black is collected on a hollow channel iron, flat beneath, and through which a blast of air is blown, with a view of cooling the plates.

The question is often asked whether the heat of the gas used in the manufacture of Carbon Black is saved or lost and why. It is always lost and for the reason that the expense of utilizing this heat would greatly exceed the value of the power to be obtained. Our Grantsville Works, producing about 10,000 pounds of black a day, are operated by five gas engines, which probably do not consume fifty cents worth of gas a day at the price which I am paying for gas.

If these works were in the immediate vicinity of a large city, it is probable that it would pay to circulate water underneath them in an immense coil and heat the neighboring quarter of the city with hot water. Located as they are in a sparsely settled country, 30 miles from our railroad terminus, there is no practical way of saving this heat. Wasteful as this operation seems, it is better than that all of this gas or a great part of it, should pass into the atmosphere through the numerous oil wells of the Yellow Creek and other adjoining fields. A much larger quantity of gas has been wasted than all that we have consumed in the Little Kanawha Valley since we have been there.

Another source of waste in this manufacture is the smoke, which ascends day and night to a very great height in the atmosphere and can sometimes be seen at a distance of 18 miles, but this consists of a lamp black, rather than Carbon Black and would probably only sell for two or three cents a pound if it could be collected and the task of collecting, even one-half of it, would probably be much more expensive than the whole maintenance of the factory and its fuel supply.

I have personally no doubt that great economies are possible and would not for one moment wish to convey the impression that the Grantsville factory or any factory now in existence, is the last word, but at the same time, they are the result of many

hundreds of experiments by myself and others and we still peg away, trying every year to learn something and make some improvement and it is to me surprising that considering all of the thought that has been given to the matters involved, so little progress has been made in the last twenty years.

The total value of Carbon Black made in a year would somewhat exceed one million (\$1,000,000.) dollars and the total value of the world's output of Lamp Black would probably be two or three times as much, but the real importance of these two commodities to humanity is inadequately represented by these figures.

They form the basis of the black printing inks, with which all of our printing is done and are also largely used in black paints, stove polish; for coloring rubber, oil cloth, leather and many other substances too numerous to mention.

It is rather a curious fact that the uses of Carbon Black and Lamp Black are separately defined and quite sharply defined at that, so that the market price of each commodity fluctuates with little reference to the market price of the other.

Carbon Black is much better for black ink, stove polish, vulcanized rubber. Lamp Black is much better for coloring oil cloth, leather and other forms of rubber and is much more widely used in paint, although Carbon Black is better for certain kinds of paint and varnish.

Generally speaking, if a buyer is using a black made on the smudge process, or by the heating or explosion of hydrocarbon vapors, he does not wish to change and take the black made on the contact process, and if a buyer is using a black made on the contact process, he cannot safely switch over onto a black made on the smudge process or the explosion process.

The gradual diminution of the margin between the cost of making black and the average selling price goes on and there seems to be no reason why it shouldn't continue through the present decade. There seems no likelihood of any shortage of Carbon Black, excepting from some temporary cause, or any great and permanent enhancement in the price during the life of any one now living.





## THE RARER PAINT OILS

BY HENRY A. GARDNER

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On account of its present scarcity, linseed oil might be classed as the most prominent of the so-called rarer paint oils. The subject of this paper, however, is meant to include only those oils which have been under test or which have come into general use to make up for the shortage of linseed oil. This paper will not go into the chemistry of the oils considered, as it is based upon a series of empirical tests primarily intended to afford to the paint grinder definite information as to the relative suitability and durability of certain oils as constituents of paint vehicles.

Among the newer oils, the one used to the greatest extent is that produced from the soya bean, a legume grown in Manchuria for its oil content and food value. Although the soya bean has been grown extensively in America as a forage crop, it is only within the last year or two that it has been cultivated in this country as a source for paint oil. Quantities of soya beans have recently been crushed by the cottonseed mills in several of the Southern States, and American grown soya oil is now available to the trade. Whether this oil will be used as a source for soap stock or for paint oil, is a question which will ultimately be determined by the cost and quantity produced. On account of its iodine value, which is much lower than that of linseed oil, soya oil has been classed as a semi-drying oil. From the standpoint of actual drying, however, it is a much better paint oil than other semi-drying oils of like iodine value. Probably its first application in the paint industry was in admixture with linseed oil, in the grinding of colors. Some manufacturers claim that certain pigments are less liable to harden in the package when ground in an oil mixture containing soya oil than with straight linseed oil. Later on soya oil was admixed in quantities up to

about 25% with linseed oil, and used in the manufacture of general mixed paints. There is no doubt but that some manufacturers have used it to a greater extent, but the mixture based upon the above percentage has been the one most favored, showing constants similar to La Plata and some other pure linseed oils. It has been stated that of the various types of soya beans which are grown, only a few yield an oil which is suitable for paint making purposes. Many authorities, however, are inclined to doubt this statement, as practical tests upon several types of oil produced from various varieties of beans, have shown good results. The importance of using a rapid drier with some grades of soya oil, has, however, been shown by Toch.<sup>1</sup> Very recently heat treated and bodied soya oils have come into the market. These oils have been subjected to high temperatures in the presence of driers and with the introduction of air. Such treatment not only raises the gravity and the general drying properties of the oil, but, at the same time, lightens its color and makes it more suitable for use in paint. Some very important heat treatment tests on soya oil are now being conducted by sub-committee C on Paint Vehicles, of the American Society for Testing Materials. The object of these tests is to set up standards that may be used in determining the quality of various samples of soya oil offered to the trade.

Perilla oil, which in chemical constants, color, drying and general properties is similar to linseed oil, has never been imported in sufficient quantities to come into general use. It should, however, find favor among the trade, and it will undoubtedly become one of the newer oils to be used in the general manufacture of paints and varnishes.

Menhaden oil has been so refined as to become of fairly good odor and of a color even lighter than linseed oil. Its rapid drying and ability to form a waterproof film well fit it for use in many technical paints, and especially for marine compounds. In combination with linseed oil paint designed for the protection of exterior wooden surfaces, it has shown good weather resisting properties. Its most prominent defect is that of taking dust and becoming dark. These latter features are shown to some extent

<sup>1</sup> New Paint Materials. Proc. Paint & Varn. Soc., London, May 1911.

by all marine animal oils, and probably to the greatest extent by whale oil, one of the newer oils which was recently proposed as a partial substitute for linseed oil.

Corn oil and cottonseed oil are both very slow drying oils, and recent attempts to heat treat them in the presence of a current of air and drier failed to accelerate their drying character materially. When either of these oils are ground into paint and applied to wood, the film remains rather tacky for a long time, and prone to take dust. This slow setting is, however, said to be beneficial, as the film generally remains very elastic and less subject to the checking that is sometimes shown by very rapid drying oils.

Chinese wood oil has already found its place in the paint and varnish world, having become a most important constituent of several of the highest grade varnishes, enamels, floor paints etc. This statement refers to wood oil that has been heat treated (boiled with litharge and resins) to overcome the opaque, crystalline character of film with which the raw oil dries. The ability of the treated Chinese wood oil to dry to a film of high gloss and great hardness, has well fitted it for the protection of cement and concrete surfaces. For the protection of iron and steel, paints are now upon the market, containing small percentages of treated Chinese wood oil in combination with linseed oil. So far these paints have given excellent results. The rosin content of treated wood oil is, however, apt to cause checking when it is used to any extent in paints for the protection of wooden surfaces.

Rosin oil and mineral oil have places of their own in certain grades of paint, but their use in the highest grade paints for the protection of wood should be discouraged.

The writer has made several interesting exposure tests with wooden panels painted with paints made up with various percentages of the rarer paint oils. These tests have already thrown considerable light upon the wearing of such oils, and will in the future afford further information of a reliable nature. The first series of tests made were at Nashville, Tenn., upon a test fence especially designed for paint exposures. The second series of tests, which is probably the most comprehensive series of practical paint vehicle tests ever made, is at Washington, D. C. A brief



Test No. 40 Vehicle Formula: 50% Linseed Oil  
50% Cottonseed Oil

Chalking: Medium

Checking: Very slight

General Condition: Good

Remarks: Darker than No. 31 and softer

Similar to No. 38.

Test No. 41 Vehicle formula: 50% Linseed Oil  
50% Rosin Oil

Entirely disintegrated.

When applied, it dried slowly, with a yellowish color which later on was bleached white by the sun. Rapid chalking followed, and alligatoring soon appeared, accompanied by a partial return to the yellowish tint observed at the start of the test. Cracking and scaling has removed most of the paint.

Test No. 42 Vehicle formula: 50% Linseed Oil  
50% Pine Oil

Chalking: Considerable

Checking: Considerable lateral checking. Tendency to scale

General Condition: Fair

Remarks: Quite white

Dried rapidly, when applied, to a semi-flat surface of great whiteness. Probably used in too large percentage for efficient results.

#### *Washington Test Fence*

Painted in April, 1911, and exposed in May, 1911. Inspected May, 1912.

#### Pigment formula used

Basic carbonate-white lead.....	20%
Basic sulphate-white lead.....	30%
Zinc Oxide.....	35%
Magnesium silicate.....	10%
Barytes.....	5%

Test No. 1 Vehicle formula: 100% Raw Linseed Oil

Chalking: Very slight

Checking: None

General Condition: Excellent

Remarks: Paint is very white and in excellent condition.

Test No. 2 Vehicle formula: 100% Soya Bean Oil

Chalking: Very slight

Checking: Fine matt checking evident in a few places

General Condition: Very good

Remarks: Panel is slightly darker than No. 1

Test No. 3 Vehicle Formula: 100% Menhaden Oil

Chalking: Very slight

Checking: None

General Condition: Very good

Remarks: Panel very dark. Color noticeable from distance.

Test No. 8 Vehicle formula: 50% Raw Linseed Oil

50% Blown Linseed Oil

Chalking: Considerable

Checking: Evident in a few places. Of fine lateral order.

General Condition: Good

Remarks: Panel has an excellent gloss and resembles an enamel.  
The paint is very white in appearance.

Test No. 10 Vehicle formula: 50% Raw Linseed Oil

50% Soya Bean Oil

Chalking: Medium

Checking: Very slight and of lateral order

General Condition: Good

Test No. 11 Vehicle formula: 50% Raw Linseed Oil

50% Menhaden Oil

Chalking: Medium

Checking: None

General Condition: Very good

Remarks: Panel slightly dark.







# WOOD TURPENTINES—THEIR ANALYSIS, REFINING, COMPOSITION AND PROPERTIES

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## CONTENTS

	PAGE
Introduction.....	45
Method of analysis.....	46
Need for a new method.....	46
Description of method.....	47
Fractional distillation.....	47
Examination of fractions.....	48
Boiling point.....	49
Specific gravity.....	49
Index of refraction.....	49
Recording data.....	50
Interpretation of distillation curves.....	50
Discussion of theoretical boiling point curves.....	50
Fractionation by ordinary distillation.....	50
Fractionation by dephlegmation.....	52
Summary.....	52
Distillation curves of a gum turpentine.....	52
Distillation curves of a wood turpentine.....	54
Chemical identification of dipentene.....	55
Completeness of separation of constituents.....	55
Comparison of fractionations obtained by different methods of distillation.....	56
Steam distillation with and without a dephlegmator.....	56
Direct distillation with and without a dephlegmator.....	57
Steam and direct distillation with dephlegmators.....	57
Steam and direct distillation with dephlegmators and direct distil- lation without a dephlegmator.....	57
Steam and direct distillation with dephlegmators.....	58
Conclusions.....	59
Alterations in composition during distillation.....	59
Changes in physical properties due to boiling at different constant temperatures.....	59
Crude wood turpentine.....	59
Refined wood turpentine.....	60
Conclusions.....	60

Changes in physical properties under conditions of fractional distillation . . . . .	61
Direct distillation of crude turpentine . . . . .	61
Steam distillation of crude turpentine . . . . .	61
Direct distillation of gum turpentine . . . . .	62
Conclusions . . . . .	62
Effect of alterations on interpretations of curves . . . . .	62
Turpentines containing no heavy oils . . . . .	62
Turpentines containing heavy oils . . . . .	63
Conclusions . . . . .	63
Choice of a Dephlegmator . . . . .	63
Refining . . . . .	64
Description of apparatus . . . . .	64
Boiling cap sections . . . . .	65
Reflux condenser sections . . . . .	65
Steam chamber sections . . . . .	65
Outlet sections . . . . .	65
Pressure regulators . . . . .	65
Separator . . . . .	66
Speed indicators . . . . .	66
General arrangement and operation of apparatus . . . . .	67
Refining of crude turpentine No. 1 . . . . .	68
Method of production . . . . .	68
Analysis and chemical treatment . . . . .	68
Distillation . . . . .	69
Products of distillation . . . . .	70
Heads . . . . .	70
Hearts . . . . .	70
Tails . . . . .	71
Refining of crude turpentine No. 2 . . . . .	71
Method of production . . . . .	71
Analysis . . . . .	71
Distillation . . . . .	71
Products . . . . .	72
Heads . . . . .	72
Hearts . . . . .	72
Tails . . . . .	72
Refining of crude turpentine No. 3 . . . . .	72
Method of production . . . . .	72
Analysis and chemical treatment . . . . .	73
Distillation . . . . .	74
Products . . . . .	74
Heads . . . . .	74
Hearts . . . . .	74
Tails . . . . .	74

Refining of crude turpentine No. 4 . . . . .	75
Method of production . . . . .	75
Analysis . . . . .	75
Distillation . . . . .	75
Products . . . . .	75
Heads . . . . .	75
Hearts . . . . .	76
Tails . . . . .	76
Products obtained by commercial refining method . . . . .	76
Refining of crude turpentine No. 5 . . . . .	76
Method of production . . . . .	76
Analysis . . . . .	77
Distillation . . . . .	77
Products . . . . .	77
Heads . . . . .	77
Hearts . . . . .	77
Tails . . . . .	78
Commercial scale refining . . . . .	78
Field work on crude turpentine No. 5 . . . . .	78
Summary of results of refining experiments . . . . .	80
Composition of wood turpentine . . . . .	80
The relations between composition and methods of production . . . . .	81
Comparison with composition of gum turpentine . . . . .	82
Heavy oils . . . . .	82
Dipentene . . . . .	83
Light oils . . . . .	83
Rosin oils . . . . .	84
Odor . . . . .	85
Effect of differences in composition on technical properties . . . . .	86
Volatility . . . . .	86
Solvent properties . . . . .	86
Drying properties . . . . .	86
Changes in composition after refining . . . . .	87
Composition of heavy oils in wood turpentine . . . . .	88
Specifications for wood turpentine . . . . .	89

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# WOOD TURPENTINES—THEIR ANALYSIS, REFINING, AND COMPOSITION

## INTRODUCTION

This investigation is a part of the general study by the Forest Service of the wood-using industries for the purpose of promoting the more economical utilization of the forest and its products. Crude wood turpentine is one of the important products obtained by most of the chemical industries using waste resinous wood as a raw material. The commercial turpentine prepared by the refining of such crude wood turpentine have been on the market for several years but there has been a general lack of authentic information on these products especially on the relations existing between the methods of production, the composition, and the properties; there was also no simple method available for the examination of these products by means of which the differences in their composition could be determined. A strong prejudice had also developed against any product sold under the name of wood turpentine, due partly to the large variation in the products from different plants and to the marked difference in odor between most of the wood turpentine and the commonly used "gum" turpentine, but aided also by the general lack of information on the subject.

These conditions have naturally resulted in a poor market for wood turpentine with a correspondingly slow development of the industry and incomplete utilization of the various kinds of waste wood available for the purpose. It was for the purpose of improving these conditions that this investigation was undertaken.

The following results have been obtained up to the present time:

1. A distillation method for the examination of turpentine has been developed from the results of which more complete and accurate conclusions can be drawn in regard to the composition of a turpentine than was possible from former methods of equal simplicity.

2. Five samples of crude wood turpentine produced by as many different commercial processes have been refined and methods of refining applicable to wood turpentines of a wide range in composition have been described.

3. It has been shown how the composition of wood turpentines is influenced by different methods of production, by refining and by storage and how wood turpentines compare with gum turpentines in composition.

The details of these results and the methods by which they were obtained are given in the following pages.

The next step in the investigation, the study of the relations between composition and industrial value, has been begun but since it will be sometime before the results are complete they will be reserved for a future publication.

## METHOD OF ANALYSIS

### *Need for a New Method*

There was necessary in this work a method for the examination of the crude turpentines and the volatile products obtained from them which would fulfill the following requirements:

1. Show quantitatively the proportions of the main constituents of the material examined, especially of those constituents which were to be separated in the refining process.
2. Show every possible difference in composition between the various refined turpentines.
3. Be fairly simple and rapid in operation.

No method was available which fulfilled these conditions. The usual methods for the examination of turpentines apply only to the refined product (usually only to gum turpentines) and are intended only for the detection of adulterations. The method described in Forest Service Circular 152<sup>1</sup> most nearly fulfills these conditions because, instead of determining the properties of the turpentine as a whole, the turpentine is first frac-

<sup>1</sup> "The Analysis of Turpentine by Fractional Distillation with Steam," by W. C. Geer.

tionated by distillation with steam and the properties of the fractions are determined; some idea of the proportion of the various constituents could, therefore, be obtained.

After an analysis by this method, however, the composition of the turpentine could be expressed only in terms of "constituents uniform in composition" and "heavy residue" without the possibility of distinguishing between the different kinds of turpentine or of obtaining indications of the actual chemical constituents present. It was found also (See pages 56 to 59) that the separation of the main constituents of the turpentine by this method of distillation was so incomplete—especially in cases where comparatively large amounts of "heavy residue" were present,—that the quantitative expression of the composition of the turpentine, even in such general terms as "constituents uniform in composition" and "heavy residue," was not accurate. It was necessary therefore, to have for use in this investigation another method for the examination of turpentines and the method described below was accordingly developed and adopted.

### *Description of Method*

This method is the same in general principles as that described in Circular 152 but is modified in several details so as to make it simpler, more accurate, and more rapid.

#### *Fractional Distillation*

Five hundred grams of the turpentine to be analyzed are weighed in a round bottomed flask of about 1,000 cubic centimeter capacity; the flask is connected with a condenser by a Hempel column of the shape and size shown in Figure 1 in the top of which is placed a thermometer with the bulb reaching to within one inch of the beads. The flask is heated on a sand bath or a piece of asbestos board and, in order to keep the liquid boiling smoothly without bumping, a small flat coil of copper or nicked wire is laid on the bottom of the flask. If the room temperature is very low a shield of asbestos board around the flask may also be desirable. The distillation is carried on at a

maximum rate of two drops a second<sup>1</sup> and the distillate is caught in weighed flasks of about 100 cubic centimeter capacity. Neither the size of the fractions, that is, the amount of distillate to be caught in each separate flask, nor the amount of undistilled residue to be left in the distilling flask can be definitely specified since the proper amounts may vary with different kinds of turpentines. In general, however, the fractions may well be larger (10 to 12 per cent) when the temperature of the distillation is changing slowly and regularly but should be smaller (4 to 5 per cent) when the temperature is changing rapidly. It is also usually unnecessary to continue the distillation after a temperature of 180°C., (corrected) is reached because this temperature seems to be reached just as almost all of the turpentine materials are distilled over and just before the heavy oils begin to come over in large quantities. This is especially true in the case of wood turpentines. In the case of gum turpentines and some wood turpentines, however, especially those with a small amount of heavy oil, the turpentine materials are all distilled over before this temperature is attained.

There are many details of manipulation which can not be completely specified in a method of this kind, which is to be applied to materials of widely variable character. Ordinary intelligence and a little experience are, however, sufficient to indicate the proper variations in detail which are desirable in the distillation of different materials.

### *Examination of Fractions*

The weight of each fraction is determined and the percentage weights of each fraction and of the total combined fractions (See Table I) are then computed. The maximum boiling point

<sup>1</sup> A slower distillation of course gives a better fractionation and the maximum rate mentioned should never be exceeded; there should, moreover, be no tendency to hasten the distillation in order to save time, because the work of determining the amount and properties of the fractions can be carried out at the same time as the distillation. Indeed, a moderately rapid and experienced worker with all the apparatus handy can make the necessary determinations and computations and can record and plot the results on six or seven fractions while nine or ten are being distilled.



of each fraction is read from the thermometer at the top of the column and the specific gravity and index of refraction of each fraction and of the residue left in the flask are determined.

*Boiling Point.*—The boiling temperatures as read should be corrected (1) for the prevailing barometric pressure using the factor  $0.056^{\circ}$  for every millimeter difference from the normal 760<sup>mm</sup> and (2) for the emergent stem of the thermometer according to the following formula:<sup>1</sup> To the observed value of the boiling point, T, should be added the factor  $0.000143(T-t)N$ , in which t is the temperature of the thermometer stem above the cork and N the length expressed in degrees of the mercury column above the cork.

*Specific Gravity.*—The specific gravity can be determined accurately enough by means of a Westphal balance making the determinations at room temperature and correcting to 15°C., by using the factor .00083 for every degree centigrade difference from this standard temperature. The correction for temperature is large enough so that especial care must be taken to make the temperature readings accurately. In order to make specific gravity determinations with the Westphal balance on as small a fraction as is often desirable, it is necessary to have a smaller cell than that usually furnished with the instrument. This can readily be made by properly shortening a test tube with a diameter only slightly greater than the bob of the balance and supporting it in a flat cork. In this way the gravity of a fraction of only 18 grams (3.6 per cent) can readily be determined on a balance with a bob having a displacement of 5<sup>cc</sup>.

*Index of Refraction.*—The index of refraction can be determined with sufficient accuracy by means of an Abbé refractometer taking the readings at room temperature and correcting by means of the factor .00047 for every degree difference from the standard temperature of 15° centigrade. It has been found that this factor .00047 is more nearly correct for the general run of turpentine than .00049 (as recommended in Circular No. 152) and that the use of different temperature correction factors for different values of the index of refraction is not necessary in order to obtain the degree of accuracy required for the work.

<sup>1</sup> Young's "Fractional Distillation;" p. 12.

### *Recording Data*

A typical data sheet showing the original and corrected values as first recorded is shown in Table I. For the purpose of making the interpretation of these results simpler and easier the final corrected values for the boiling point, specific gravity, and index of refraction of the different fractions are plotted against the total percentage weight of these fractions. The curves resulting from plotting the data given in Table I are shown in Figure 2.<sup>1</sup>

### *Interpretation of Distillation Curves*

In order to properly interpret these curves it is necessary to understand the behavior of a mixture of liquids on distillation, and a brief discussion of fractionation by distillation and of distillation curves will therefore be given followed by a discussion of the curves obtained by the distillation of two different turpentines.

### *Discussion of Theoretical Boiling Point Curves*

Let us assume a mixture of equal quantities of two volatile liquids A and B with boiling points 160° C. and 200° C., respectively. If on distilling this mixture a complete separation of the two components was obtained then the distillation curves formed by plotting the percentage of distillate against the boiling point would be represented by the vertical lines AX and BY (Figure 3); that is, all of substance A in pure condition would distill over first and then the pure substance B.

*Fractionation by Ordinary Distillation.*—Such a complete separation is, however, never obtained because the boiling point of one liquid is always affected by the presence of another volatile liquid. In this case, some of the higher boiling substance B would distill over with A long before the temperature of the distillation reaches 200°, the boiling point of B, and some of the lower boiling substance A would be left in the flask even after the temperature had risen above 160° C. When a mixture like the above is

<sup>1</sup> In all the figures showing distillation curves, unless otherwise indicated in the figure itself, the full circles represent boiling points, the open circles, specific gravities and the half-open circles, indices of refraction.

TABLE I.—TYPICAL DATA SHEET SHOWING RECORDS OF DISTILLATIONS

Fract. No.	Temperature			Weight			Percentage Weight		Specific Gravity			Index of Refraction				
	T	t	T-t n	Corrected Bar. 741.5 mm	Corrected Bar. 760 mm	Flask plus Distillate	Flask	Distillate	Single Fractions	Total Combined Fractions	Determined	Temperature °C.	Calculated for 15 °C.	Determined	Temperature °C.	Calculated for 15 °C.
1	156.5	49	108.56	157.4	158.5	79.6	32.1	47.5	9.5	9.5	.8596	21.5	.8650	1.4693	19.5	1.4714
2	157.0	50	107.57	157.9	159.0	94.1	39.0	55.1	11.0	20.5	.8597	21.5	.8651	1.4694	19.5	1.4715
3	157.3	50	107.57	158.2	159.3	80.3	25.3	55.0	11.0	31.5	.8599	21.5	.8653	1.4695	19.5	1.4716
4	157.7	51	107.57	158.6	159.7	97.6	36.6	61.0	12.2	43.7	.8601	21.5	.8655	1.4699	19.5	1.4720
5	158.0	50	108.58	158.9	160.0	83.1	28.3	54.8	11.0	54.7	.8605	21.2	.8656	1.4702	19.5	1.4723
6	158.8	50	109.58	159.7	160.8	96.7	32.5	64.2	12.8	67.5	.8609	21.2	.8660	1.4707	19.2	1.4727
7	159.7	51	109.59	160.6	161.7	77.4	27.3	50.1	10.0	77.5	.8615	21.0	.8665	1.4714	19.2	1.4734
8	162.4	51	111.62	163.4	164.5	96.2	43.5	52.7	10.5	88.0	.8625	21.0	.8675	1.4730	19.2	1.4750
9	167.3	52	115.67	168.4	169.5	61.0	27.1	33.9	6.8	94.8	.8639	21.0	.8689	1.4760	19.2	1.4780
Residue						150.6	125.5	25.1	5.0	99.8	.9408	20.0	.9450	1.4914	21.1	1.4943

distilled from an ordinary distilling flask the distillation curve would therefore be more like curve I in figure 3. This curve shows that the composition of the distillate gradually changes throughout the distillation from pure A to pure B, the first 25 per cent of the distillate being nearly pure A and the last 25 per cent being nearly pure B.

*Fractionation by Dephlegmation.*—In order to obtain better separations of A from B in a single distillation some kind of a still head or dephlegmator is used, (such as the Hempel column shown in Figure 1) in which the ascending vapors are partially condensed and flow downward in liquid form to the distilling flask. The descending liquid comes in contact with more ascending vapors and there is an interchange of constituents, some of the low boiling material in the liquid being vaporized and some of the high boiling material in the vapors being condensed, with the result that the vapors which finally leave the top of the dephlegmator contain a larger proportion of the lower boiling material than the vapors which enter the dephlegmator from the flask. That is, there is a more complete separation of the components when the dephlegmator is used. Under such conditions the distillation curve would be more like curve II in figure 3, which indicates about 45 per cent practically pure A, about 10 per cent of a rapidly varying mixture, and the rest practically pure B.

*Summary.*—This consideration of the boiling point curve of a mixture of two components may be summed up as follows:

(1) The more complete the separation the more accurately do the curves represent the composition of the mixture.

(2) The more vertical curves indicate a more uniform substance in the distillate.

(3) Curves more nearly horizontal indicate a distillate rapidly changing in composition.

#### *Distillation Curves of a Gum Turpentine*

The distillation curves for a turpentine are interpreted in a way similar to the theoretical curve in figure 3, but complications arise on account of the complexity of the mixture distilled and the incompleteness of the separation of some of the constituents.

Specific gravity and index of refraction are plotted, like the boiling point against percentage weight, and the three curves are considered together in interpreting the results of the distillation.

The curves in Figure 2 which give the results of the distillation of a gum turpentine, might be interpreted in the light of the previous discussion, as indicating a composition of about 95 per cent of some substance, "a," with boiling point  $158^{\circ}$  C., specific gravity .865, and index of refraction 1.4714 and about 5 per cent of some other material, "b," with values of all properties considerably higher (say specific gravity .95, index 1.489); the gradual increase in the values of all the physical properties from the first fraction up to 95 per cent might be thought to be due to a gradually increasing proportion of this high boiling and heavy material in the distillate (as was the case in the boiling point curves of Figure 3). But this interpretation is shown to be incorrect by the procedure described below which was carried through for an entirely different purpose (See page 62).

Figure 13 gives the result of a distillation of a part of the turpentine used in Figure 2, which had been redistilled several times in order to remove the high boiling and heavy material originally present. The curves show that this heavy material "b" has been entirely removed and yet the values for all the physical properties increased to some extent as the distillation progressed indicating that the distillate was not a pure substance. Evidently then the gradual increase of these values in Figure 2 was not (or at least not entirely) due to the presence of "b" in the first 95 per cent of the distillate, but instead there must be present another substance "c" with physical properties only slightly higher than those of "a," the boiling points of "a" and "c" being so close together that the substances are very incompletely separated by distillation.

This interpretation agrees with the results of recent investigations on the chemical constituents usually present in turpentine. According to Semmler<sup>1</sup> there may be present in American turpentine besides pinene<sup>2</sup> two other terpenes, camphene and

<sup>1</sup> "Die Aetherische Oele" Vol. II, pages 55 and 274.

<sup>2</sup> Boiling point,  $155^{\circ}$ - $156^{\circ}$  C., specific gravity .863; index of refraction 1.4678.

nopinene.<sup>1</sup> The physical properties of these two terpenes have not been accurately determined, but it is sufficient to know that they are all higher than those of pinene. The first 95 per cent of the distillate from this turpentine was probably composed of a mixture of pinene with either camphene and nopinene, or both, and the last 5 per cent was made up of materials with much higher physical properties, probably oxidation products of the terpenes.

In the distillation of turpentine by this method the separation between the terpenes and the high-boiling non-terpenes is sufficiently complete so that the physical properties of the first fractions are not appreciably influenced by the presence of materials with boiling points 30°—35° higher. The mixture of the terpenes—pinene, camphene and nopinene is, however, not sufficiently well separated to make it possible to estimate the proportions of the different constituents, and it will hereafter in this paper be designated as “pinene” unless for any reason it is necessary to mention the other constituents.

#### *Distillation Curves of a Wood Turpentine*

The curves obtained by the distillation of a wood turpentine (Figure 54) show this to be sufficiently different in composition from the gum turpentine just discussed that new points in the interpretation of the curves are introduced. The first 70–75 per cent of the distillate could well be, from the physical properties, a mixture of the same terpenes which are the main constituents of the turpentine shown in Figure 2, the slightly lower physical properties being accounted for by smaller proportions of either nopinene or camphene, or both. But between the points where 70 and 95 per cent distill the specific gravity of the distillate decreases while the boiling point and index of refraction increase. This indicates the presence of some substance with higher boiling point and higher index of refraction, but with lower gravity than “pinene.” There is a terpene—dipentene—whose physical properties correspond well with those required by this substance; it has a higher boiling point (175°C.), a lower specific gravity (.849 at 15° C.), and higher index of refraction (1.471 at 15° C.)

<sup>1</sup> The physical properties of both about the same at the following values: Boiling point, 160°–165°; specific gravity, .874; index of refraction, 1.4724.

than "pinene;" it is known to be one of the products of the action of high temperatures on pinene;<sup>1</sup> it has been identified as one of the constituents of wood turpentine produced in Finland and Russia;<sup>2</sup> and its presence in American "pine tar oil" has been indicated.<sup>3</sup> It is quite probable therefore that the substance whose presence is indicated by the marked decrease in specific gravity of the fractions as the boiling point approaches 175° C. is dipentene, and that it is formed from "pinene" by the high temperature employed in removing the turpentine from the wood.

*Chemical Identification of Dipentene.*—In order to make sure that dipentene was present in this turpentine, however, an identification by chemical means was carried out. By repeated fractional distillation, and final distillation over sodium, a considerable quantity of material was obtained with boiling points 172°–174.1° C., specific gravity .8527 at 15° C. and index of refraction 1.4771 at 15° C. Part of this material was treated with bromine in glacial acetic acid<sup>4</sup> and crystals were obtained which, after six crystallizations from ethyl acetate, melted at 125°–125.5° C., (dipentene tetrabromide 125°–126° C.) thus substantiating the conclusions regarding the presence of dipentene which were originally drawn from the physical properties. It seems very likely therefore that when a turpentine obtained from the long-leaf pine is distilled by the method described above, a decrease in specific gravity as the boiling temperature approaches 175° C. is a good indication of the presence of dipentene.

*Completeness of Separation of Constituents.*—The exact percentage of dipentene can not be determined from the curves in figure 54, since the separation between the "pinene" and the dipentene is not sufficiently sharp; there are small quantities of dipentene in the portion distilling between 70 per cent and 80 per cent as shown by the slight decrease in specific gravity, but it is only in the portion coming over after 80 per cent has been distilled that there are comparatively large quantities of dipentene

<sup>1</sup> Wallach, *Ann. Chem.* 227, 282.

<sup>2</sup> Asehan and Hjelt, *Chem. Ztg.* 18, 1566.

<sup>3</sup> Kremers, *Pharm. Rev.* 22, 150.

<sup>4</sup> Heusler-Pond, "Chemistry of the Terpenes," Pp. 73 and 95.

present (as shown by the decided changes in direction in the boiling point and index of refraction curves). The separation between the dipentene and the "heavy oils" is, however, quite complete, and the percentage of the latter can be determined with considerable accuracy. This turpentine contains then 95 per cent of terpenes (containing approximately 80 per cent "pinene" and 15 per cent dipentene) and 5 per cent of heavy, high boiling oils, probably non-terpenes.

Other points in the interpretation of distillation curves will be discussed as required in connection with the numerous analyses recorded on the following pages.

#### *Comparison of Fractionations Obtained by Different Methods of Distillation*

In order to show the advantages gained by the use of a dephlegmator, and by the use of direct distillation instead of steam distillation, the following distillations were carried out on the same turpentine: (1) Steam distillation without a dephlegmator, (2) direct distillation without a dephlegmator, (3) steam distillation with a Geer dephlegmator as described in Forest Service Circular No. 152, and (4) direct distillation through a five bulb Le Bel-Henninger dephlegmator. The last named will not be described because another form of dephlegmator was afterward adopted as most suitable for general work.

#### *Steam Distillation with and without a Dephlegmator*

In Figure 4 are plotted together on one sheet for better comparison the curves obtained by steam distillation both with and without a dephlegmator.<sup>1</sup> The curves showing the results obtained by the use of a dephlegmator indicate the better fractionation since they are more nearly vertical and have lower values over the first part of the distillation, and the breaks in the

<sup>1</sup> In the case of these distillations, and of all the rest of the analyses mentioned in this article, the original and corrected data will not be given, but only the curves obtained by plotting the corrected data; the curves are all that it is necessary to have in order to obtain the complete interpretation of the results, and there are so many distillations recorded in the following pages that the space required by the tabulated data would be prohibitive.



general direction are more marked than in the curves which give the results obtained by steam distillation without a dephlegmator.

#### *Direct Distillation with and without a Dephlegmator*

A still greater effect obtained by the use of a dephlegmator is indicated in Figure 5 where are plotted together the curves from two direct distillations, one with and one without a dephlegmator. Here the differences in the position and direction of the curves and therefore in the fractionation, are even more marked than in Figure 4.

#### *Steam and Direct Distillation with Dephlegmators*

Figure 6 gives a comparison of the fractionation obtained by steam distillation through a Geer dephlegmator with that by direct distillation through a Le Bel-Henninger dephlegmator. In the direct distillation curves there are all the evidences of better fractionation, i.e., lower values for the physical constants of the fractions over the first part of the distillation, more nearly vertical curves, and sharper breaks in the direction of the curves. On account of the better fractionation it is possible to judge the composition of the turpentine with a considerable degree of accuracy and it apparently contains very nearly 80 per cent of "pinene" the remainder being heavy oils with all the physical properties much higher. From the steam distillation curves, on the other hand, it would be impossible to make an accurate judgment of the proportion of "pinene" present in the turpentine, because the separations are so incomplete and the curves change direction so gradually. The distillate is practically pure "pinene" up to about 70 per cent, but for some distance beyond that point it is an indefinite mixture of "pinene" with heavier and higher boiling materials.

#### *Steam and Direct Distillation with Dephlegmators and Direct Distillation without a Dephlegmator*

Similar distillations were made on another kind of turpentine (refined turpentine No. 5) giving even more striking differences in the separations obtained. Figure 7 shows the results obtained by fractionating three samples of the same turpentine (1) by

steam distillation with a Geer dephlegmator (2) by direct distillation without a dephlegmator and (3) by direct distillation with a Le Bel-Henninger dephlegmator, the three sets of curves being plotted together on one sheet for easier comparison. The curves obtained by steam distillation with a dephlegmator, and by direct distillation without a dephlegmator show very similar characteristics; there are no rapid changes in direction until about 90 per cent is reached and then there is a rapid increase in all the physical constants; that is, these curves indicate about 90 per cent "pinene" and about 10 per cent of material with all physical constants higher. The curves obtained by direct distillation with a dephlegmator are, however, quite different; they indicate that there are three main constituents of this turpentine sufficiently different in boiling points and other properties so that approximate determinations can be made of the proportion of each, these proportions being about 80 per cent of "pinene," 15 per cent of dipentene, and 5 per cent of heavy residue. In the distillation by the first two methods the dipentene was not sufficiently well separated from the other constituents so that its presence was sharply indicated, the very slight and very gradual decrease in the specific gravity over the first 80 per cent of the distillation being the only sign of the presence of such a substance.

#### *Steam and Direct Distillation with Dephlegmators*

Another comparison of the results obtained by steam and direct distillation, both through a dephlegmator, is given in Figure 8, in this case on a still more complex turpentine. The curves obtained by the direct distillation with a Le Bel-Henninger dephlegmator indicate that this turpentine is composed of about 11 per cent "light oils" (with boiling points below those of "pinene"), about 32 per cent of "pinene," about 22 per cent of dipentene and 35 per cent of heavy oils. The separation between the "pinene" and the dipentene was not very sharply indicated (that is, the breaks in the direction of the curves are not very marked) but the amount of light oils, of turpentine oils ("pinene" and dipentene) and of heavy oils are quite accurately determined. In the steam distillation curves, however, no sharp separations of

the turpentine into its constituents are shown (that is, there are no sharp breaks in the curves). The presence of dipentene is not even indicated qualitatively, and the proportion of heavy oils (as in figure 6) can not be judged within 8 to 12 per cent.

### *Conclusions*

These examples of the results obtained in the fractionation of three different turpentines by different methods of distillation have shown very clearly that, so far as the completeness of the separations and the corresponding ease and accuracy of the interpretation of the results are concerned, direct distillation through a dephlegmator is the best distillation method for the analysis of turpentines.

### *Alterations in Composition during Distillation*

A possible objection to such a method is mentioned in Forest Service Circular 152<sup>1</sup>; viz., that the higher temperatures required would be likely to decompose some of the oil during the distillation so that the fractions would not represent the true composition of the original material. In those distillations described above in which the same turpentine was distilled by the two methods, there were no evidences of decomposition in any case except that the residues left in the distilling flask were usually darker in color when direct distillation had been used; the differences in the curves obtained by the two methods were of such a nature as would indicate only different fractionation.

### *Changes in Physical Properties due to Boiling at Different Constant Temperatures*

*Crude Wood Turpentine.*—In order to obtain some idea of the comparative effects of different methods of distillation on the physical properties of turpentines, two samples of the same turpentine (turpentine No. 4) were boiled under conditions similar to those of steam and direct distillation (that is, with and

<sup>1</sup> "The Analysis of Turpentine by Fractional Distillation with Steam," by William C. Geer.

without water being present) and the specific gravity and index of refraction were determined at regular intervals; in both cases a well cooled reflux condenser was used so that the loss was negligible. The effects of boiling under these two sets of conditions are shown graphically in Figure 9. By boiling in the presence of water at a temperature of about  $94^{\circ}$  C., the gravity of the turpentine was increased very slightly the first hour and after that decreased very slightly every hour until the boiling was stopped. By the boiling without the presence of water at a temperature of about  $162^{\circ}$  C., the gravity increased at the rate of .00045 per hour for the first two hours, and then at a much slower rate. The index of refraction was increased considerably by both methods of boiling during the first two hours and then more slowly.

*Refined Wood Turpentine.*—The results from a similar series of experiments on another turpentine (turpentine No. 5, the analysis of which is shown in Figure 7) are expressed graphically in Figure 10. Here the changes in the physical properties due to either method of boiling are less than were shown in Figure 9, being within the limit of the possible experimental error in some cases. But the same general tendency of the specific gravity to be slightly increased by the direct boiling and slightly decreased by the boiling with water is shown as in Figure 9. The index of refraction is, however, slightly decreased by the boiling with water instead of being increased, as in the previous case.

*Conclusions.*—The effect of the boiling on the physical properties of the turpentines is apparently not very great in either case, but for two reasons the results obtained are not conclusive: (1) The temperature to which the turpentines were subjected were only as high as would prevail at the very beginning of distillation; and therefore in the case of the direct distillation, probably do not come within  $40^{\circ}$  C. of the temperatures reached at the end of a regular fractional distillation; (2) Different components of the turpentine might have the physical properties changed in different directions and thus the changes in the properties of the turpentine as a whole would not show the actual changes in composition which had taken place.

*Changes in Physical Properties under Conditions of Fractional Distillation*

Another method for comparing the changes in composition due to steam distillation and direct distillation was carried out as described below.

*Direct Distillation of Crude Turpentine.*—Crude turpentine No. 4 was repeatedly redistilled by direct distillation through a Le Bel-Henninger dephlegmator, each time rejecting the heavy residue left in the flask and as much of the distillate as showed especially high physical properties; for instance, the first distillation was similar to the direct distillation shown in Figure 6, and the fractions up to 79.5 per cent formed the material for the next distillation, the residue and the last fraction of the distillate being rejected. The curves showing the course of the third and fourth distillations were practically identical and are both represented by the curves in Figure 11. All the heavy oils present in the original turpentine must have been removed by the first two distillations, otherwise the physical properties of the residue would have been higher in the third distillation than in the fourth. Since the original heavy oils had been completely removed, the higher physical properties of the residue in the third and fourth distillations must be due to the heavy oils formed during the course of the distillations. The difference in the values of the physical constants between the last fraction and the residue in Figure 11 is therefore an approximate measure of the change in composition due to the temperature of the distillation. The lack of any marked difference in properties between the first and second fractions indicates that there was no appreciable decomposition into substances with lower boiling points.

*Steam Distillation of Crude Turpentine.*—In order to obtain, for comparison, the change in composition due to distillation with steam, all the material represented by Figure 2, except the residue, was twice distilled by steam through a Geer dephlegmator. The curves for these two distillations were practically identical and are shown in Figure 12. Reasoning in the same way as above the difference in physical properties between the last fraction and the residue indicate the change in composition due to the dis-

tillation. This change is appreciable in the case of the steam distillation, but is somewhat less than in the direct distillation.

*Direct Distillation of Gum Turpentine.*—The same determination was made on a gum turpentine (the one whose analysis is shown in Figure 2). In this as in case of the wood turpentine the third and fourth distillations gave nearly identical curves which are shown in Figure 13. The amount of change in composition is also very nearly the same as in the case of the wood turpentine shown in Figure 11.

*Conclusions.*—It is evident then that under the conditions prevailing in the distillation shown in Figures 11 to 13, the amount of change in composition during analysis is very slight either in steam or direct distillation. This change apparently consists in the polymerization of a portion of the terpenes to substances with higher physical constants, and seems to take place mostly during the very last part of the distillation when the amount of oil in the distilling flask has become very small and when there is therefore a better chance for the sides of the flask to become superheated.

#### *Effect of Alterations on Interpretations of Curves*

*Turpentines Containing no Heavy Oils.*—When a turpentine containing no heavy oils is distilled by direct heat the undistilled residue left in the flask will contain a small amount of heavy oils owing to changes occurring during the distillation and the specific gravity and index of refraction of this residue will be higher than those of the last distilled fraction; the curves will therefore seemingly indicate that a small amount of heavy oils was present in the original turpentine, but from the curves of figures 11 and 13 the effect of the changes which occurred during the distillation can be determined, and the interpretation of the curves can be altered to correspond. For instance, in the distillation of 95 per cent of a turpentine containing no heavy oils, the production of heavy oils during the distillation will be sufficient to increase the gravity and index of the residue of 5 per cent by .0035 and .0040 respectively. Of course, if the residue is made smaller, say 2 per cent, then the apparent effect would be greater since there is a chance for more polymerization during the distillation

of that portion between 95 and 97 per cent, and the proportion of heavy oil to turpentine oil in the undistilled residue is increased (and hence the physical properties increased) as the distillation progresses. It is therefore necessary to leave about 5 per cent of oil undistilled in order to be able to correct accurately for the effect of polymerization.

*Turpentine Containing Heavy Oils.*—When, however, the turpentine to be distilled contains some heavy residue (as for instance in Figure 2) the conditions are somewhat different than in the above cases; the terpenes may all be distilled over and the residue left in the flask would then be all heavy oils; now these heavy oils might be changed by the heat more or less than the terpenes were in figures 11 to 13, but there is really no necessity for determining this change accurately because a small change in the physical properties does not affect the interpretation of the curves. For instance, if in Figure 2 the gravity of the residue had been .930 instead of .945, the composition of the turpentine as interpreted from the curves would still have been 95 per cent "pinene" and 5 per cent heavy residue; that is, a gravity of .93 is sufficiently higher than that of the terpenes so that the presence of a considerable amount of terpenes in the residue is excluded, and the only interpretation of the composition of the residue which it is possible to attempt is that it does not contain terpenes in considerable quantities.

*Conclusions.*—The change in composition of a turpentine during analysis by direct distillation is without effect on the interpretation of the results except in case there is no high boiling and heavy residue present in the original material, and in this case the approximate effect is known and the results can be corrected.

#### *Choice of a Dephlegmator*

The Le Bel-Henninger dephlegmator often mentioned in the foregoing has been used with good results in many turpentine analyses; it is efficient in fractionating power, and when properly constructed gives no trouble in filling up with liquid; the only objections to it are its cost and fragility. The simplest, least expensive and least fragile dephlegmator is of the Hempel column

type, and several different sizes of Hempel columns were tried to find if a practicable sized Hempel would give as good separations as the Le Bel-Henninger previously used. It was found that the Hempel column shown in Figure 1 gave slightly better separations than the five-bulb Le Bel-Henninger which has been used previously; a comparison between the results obtained by the use of these two dephlegmators is shown in Figure 14. The main difference between the curves obtained by the two types of dephlegmators is in the specific gravity in the vicinity of 90 per cent; the fractions obtained by distillation through the Hempel column have a lower gravity over this part of the curve, indicating a purer dipentene and therefore better fractionation; the sharper break in the curves at about 80 per cent also indicates better fractionation. On account of the simplicity and cheapness of the Hempel column as well as its better fractionation, it is recommended as the preferable dephlegmator for turpentine distillations. This type of dephlegmator has been used in making many of the distillations recorded in the following pages, and has given very satisfactory results.

## REFINING

The refining was done on five samples of crude wood turpentine collected from commercial plants using widely varying processes. A brief description of each of these processes will be given with the discussion of the work done on the samples. The apparatus used in the refining, and the method of conducting the distillations will be described first since the same arrangement of apparatus and the same general method was used in the refining of all the samples, and the description will therefore apply to all.

### *Description of Apparatus*

The refining still was of the continuous type with two phases, giving two distilled products and one undistilled residue. It was designed by the makers especially for this work since stills of this type for the refining of turpentine had not previously been used or manufactured in this country.



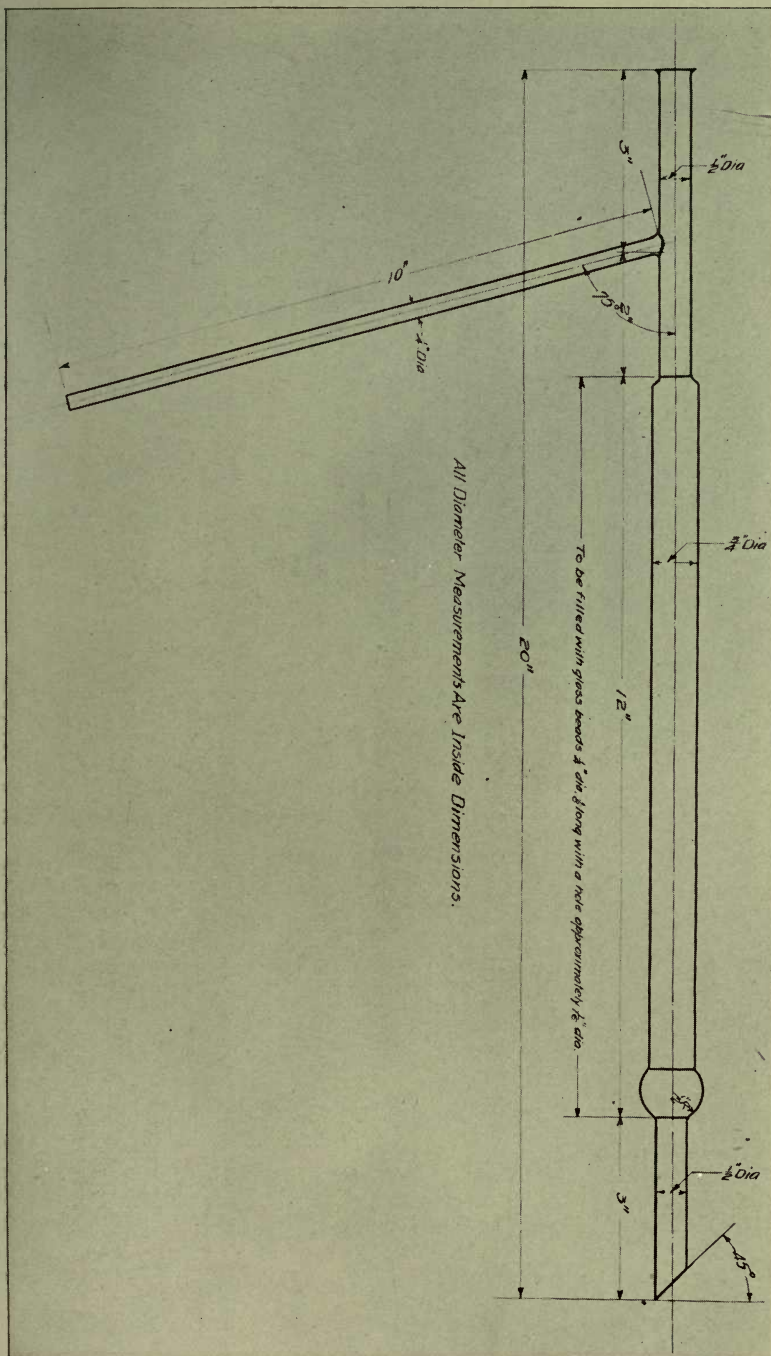


Fig. 1.  
Hempel Column.

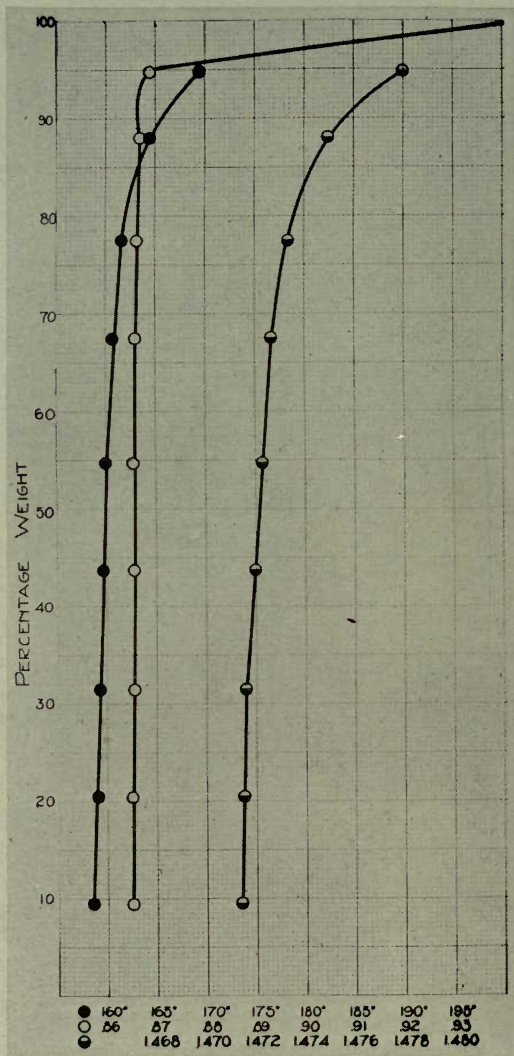


Fig. 2.

Typical curves showing boiling points, specific gravities, and indices of refraction of a gum turpentine.

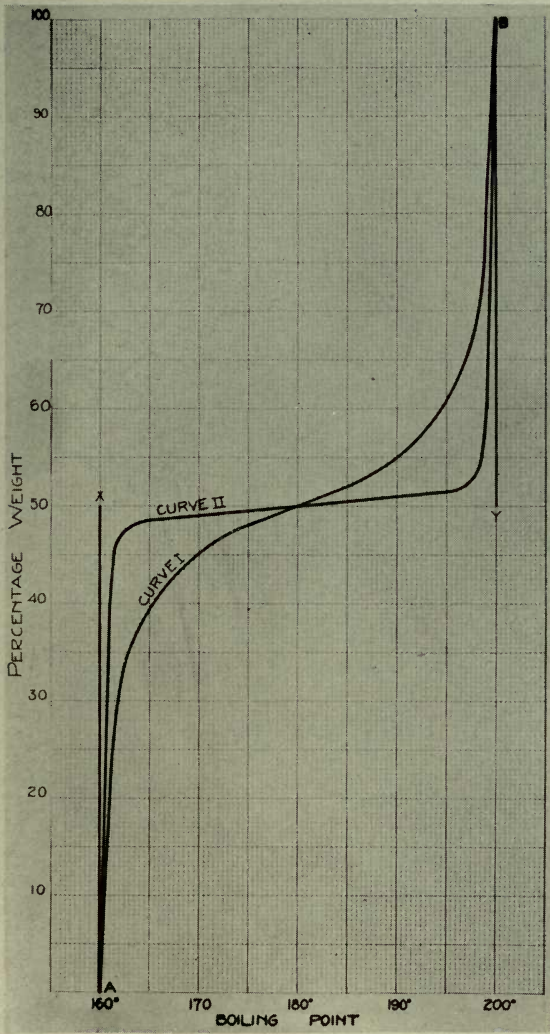


Fig. 3.  
Curves illustrating theory of fractional distillation.

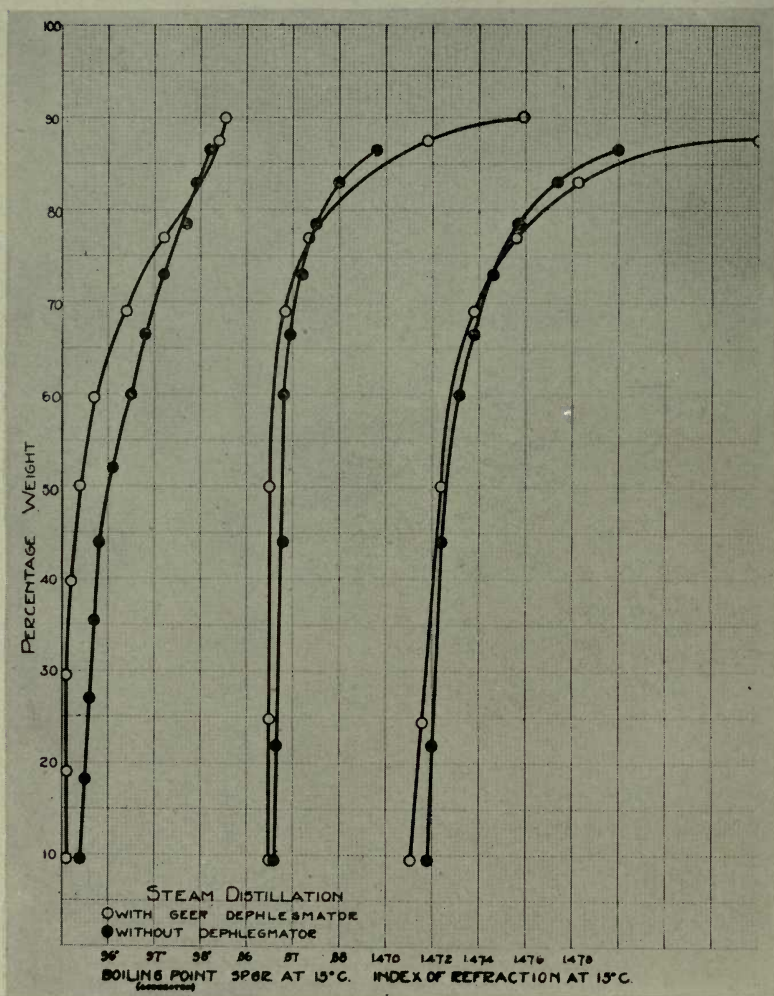


Fig. 4.

Comparison of fractionation obtained in steam distillation with a Geer dephlegmator and without a dephlegmator.

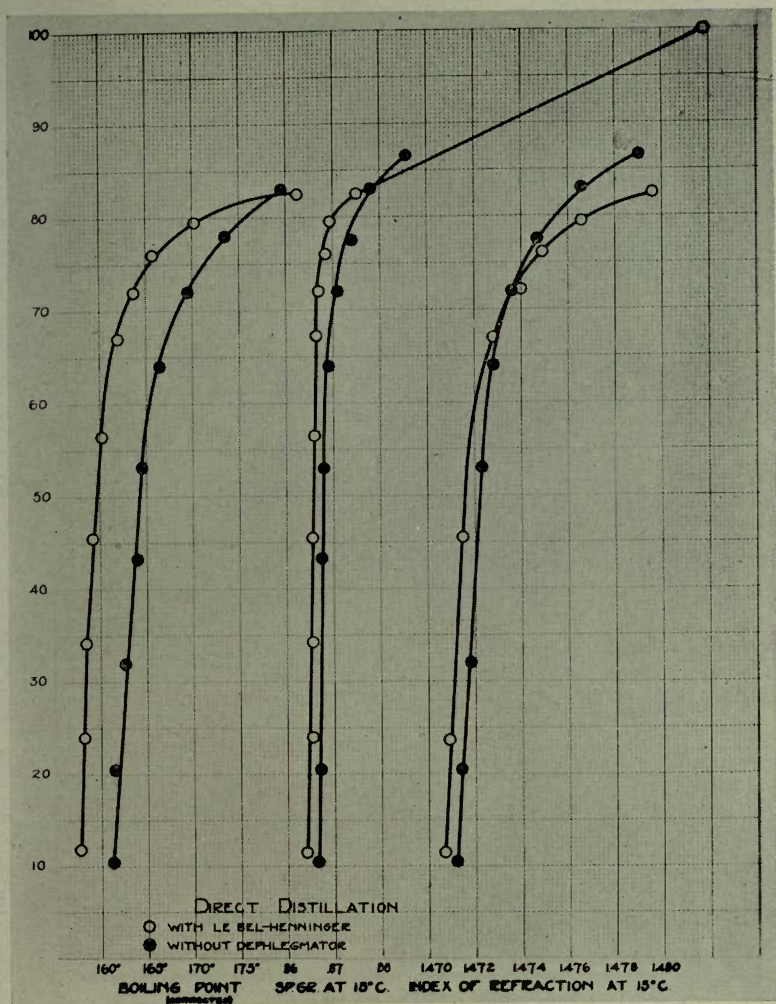


Fig. 5.

Comparison of fractionation obtained in direct distillation with a Le Bel-Henninger column and without a dephlegmator.

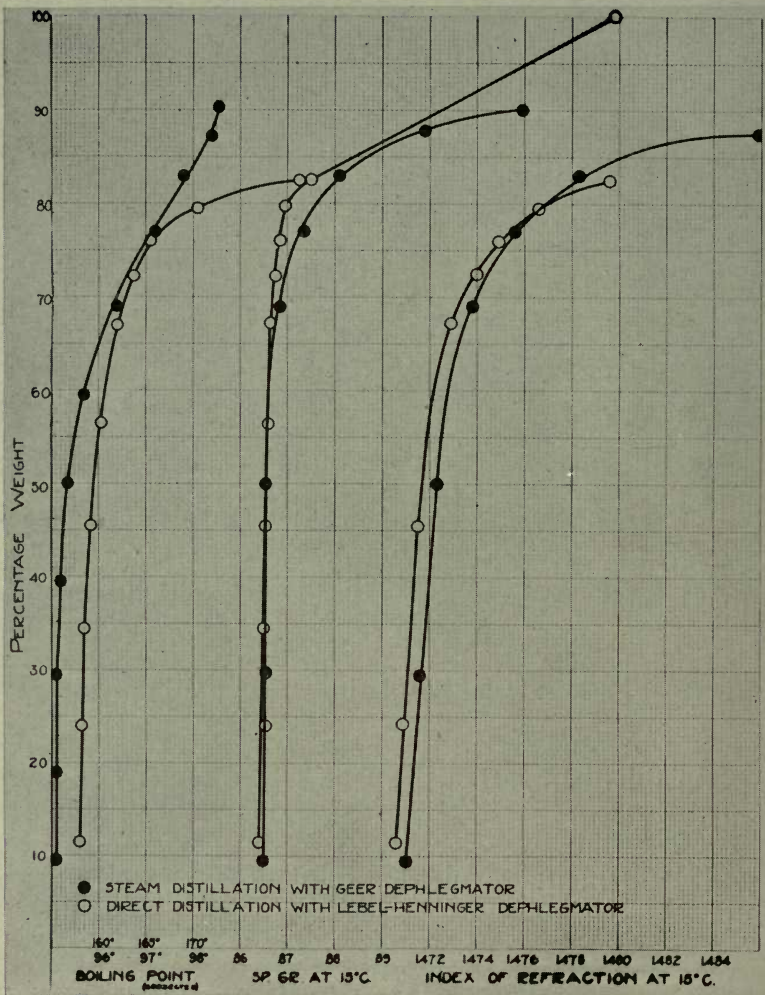


Fig. 6.

Comparison of fractionation obtained by steam distillation with a Geer dephlegmator and direct distillation with a Le Bel-Henninger dephlegmator.

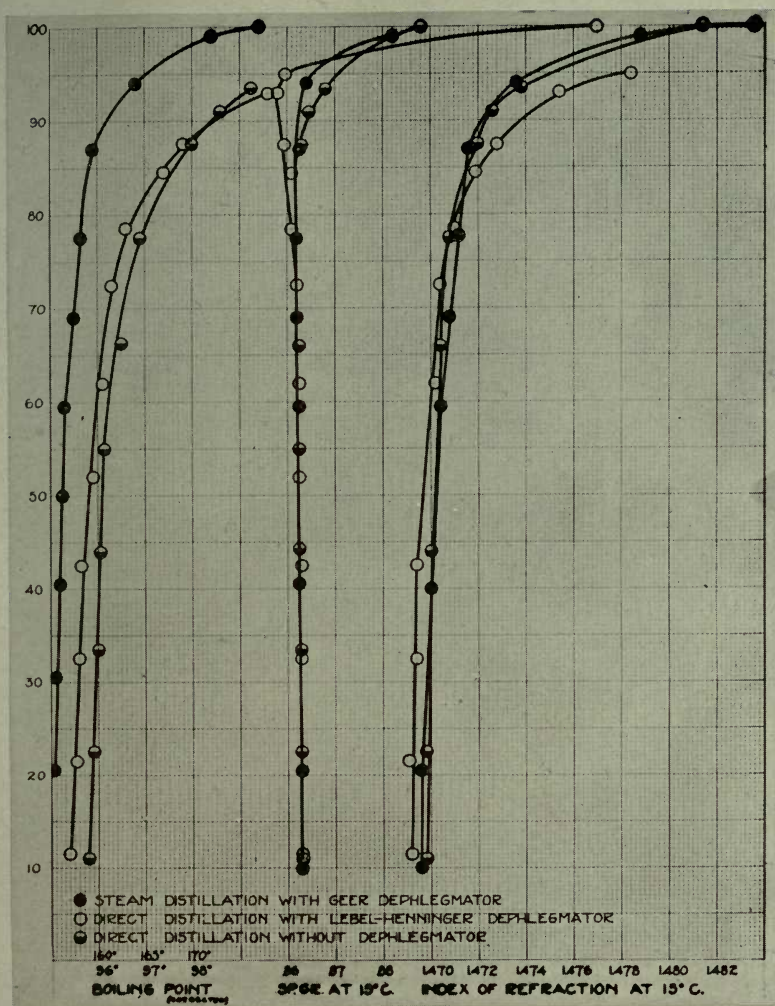


Fig. 7.

Comparison of fractionation obtained by (1) steam distillation with a Geer dephlegmator, (2) direct distillation with a Le Bel-Henninger dephlegmator, and (3) direct distillation without a dephlegmator.

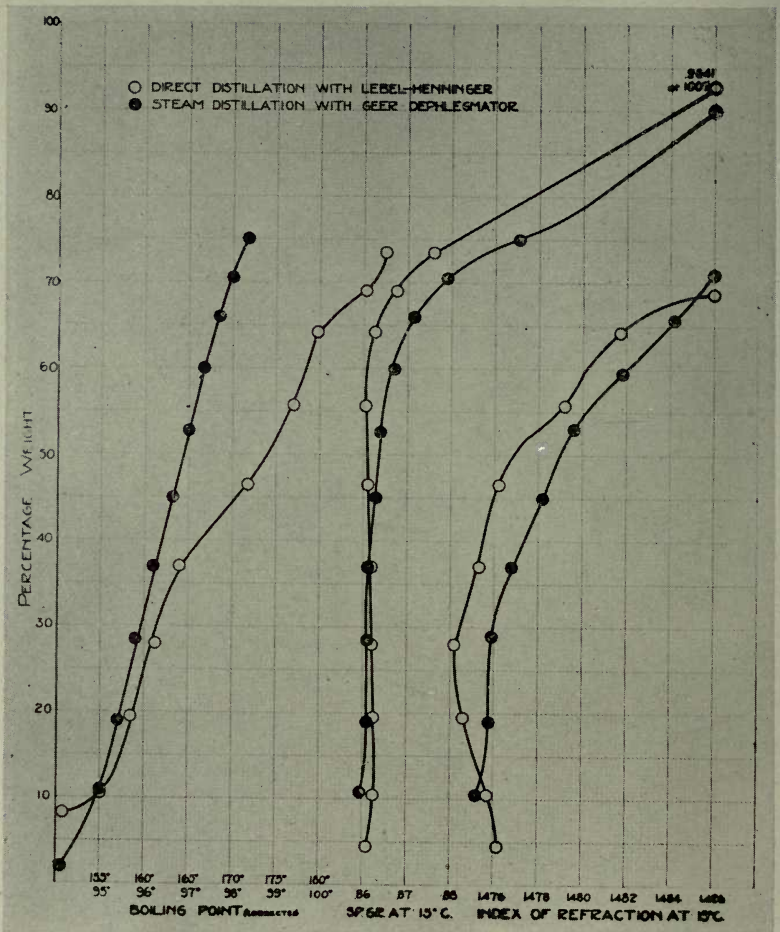


Fig. 8.

Comparison of fractionation obtained by direct distillation with a Le Bel-Henninger dephlegmator and steam distillation with a Geer dephlegmator.



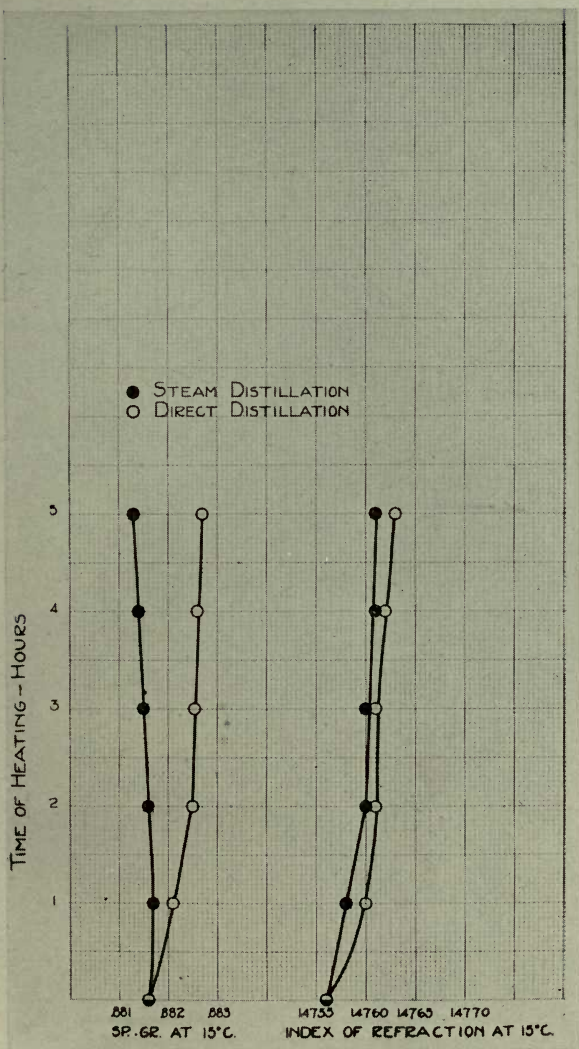


Fig. 9.

Effect of boiling in the presence of water (steam distillation) and of boiling without water (direct distillation) on the specific gravity and index of refraction of crude wood turpentine.

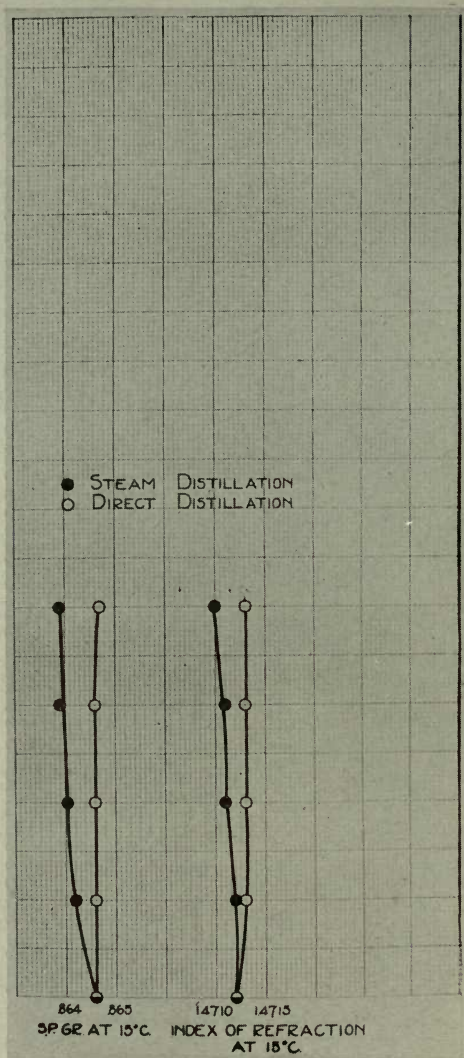


Fig. 10.

Effect of boiling in the presence of water (steam distillation) and of boiling without water (direct distillation) on the specific gravity and index of refraction of refined wood turpentine.

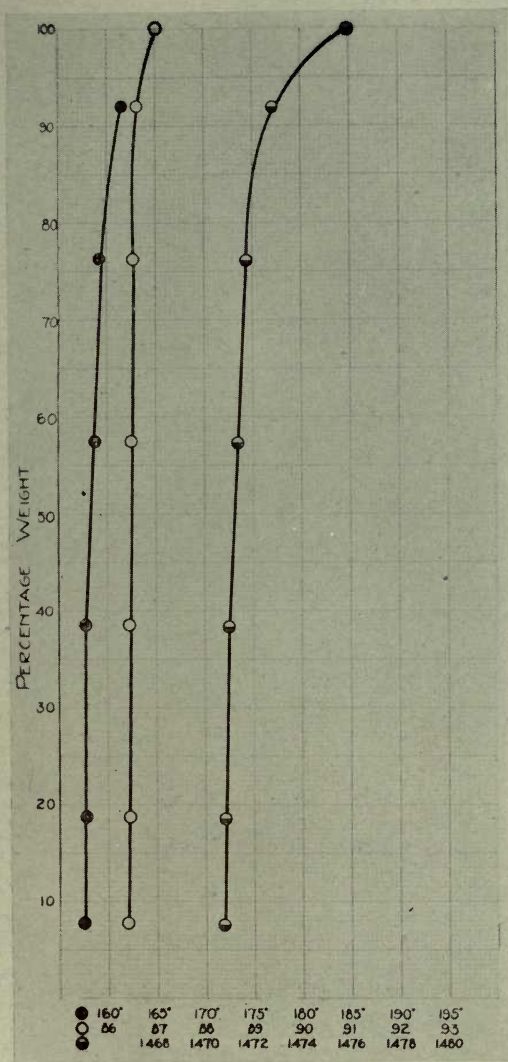


Fig. 11.

Alteration in physical properties of a crude wood turpentine due to direct distillation.

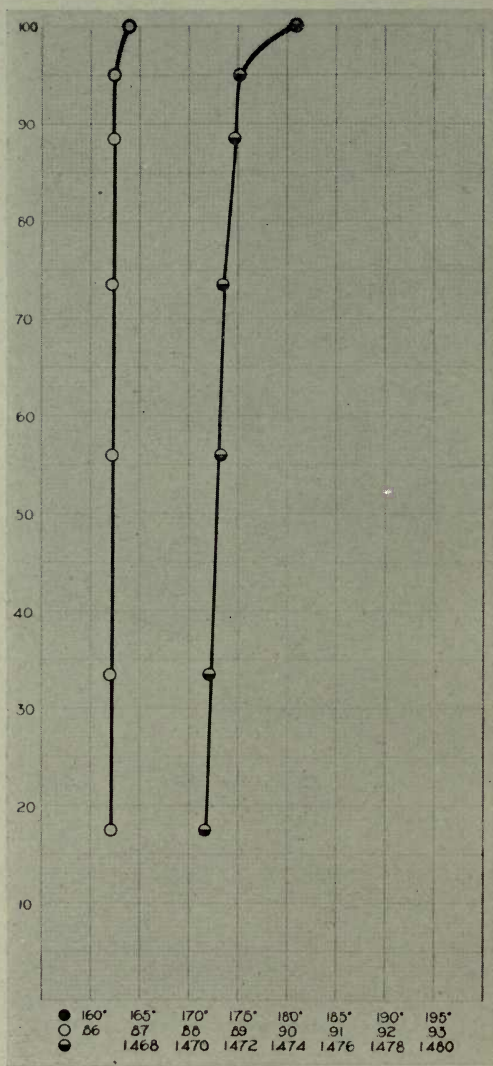


Fig. 12.

Alteration in physical properties of a crude wood turpentine due to steam distillation.

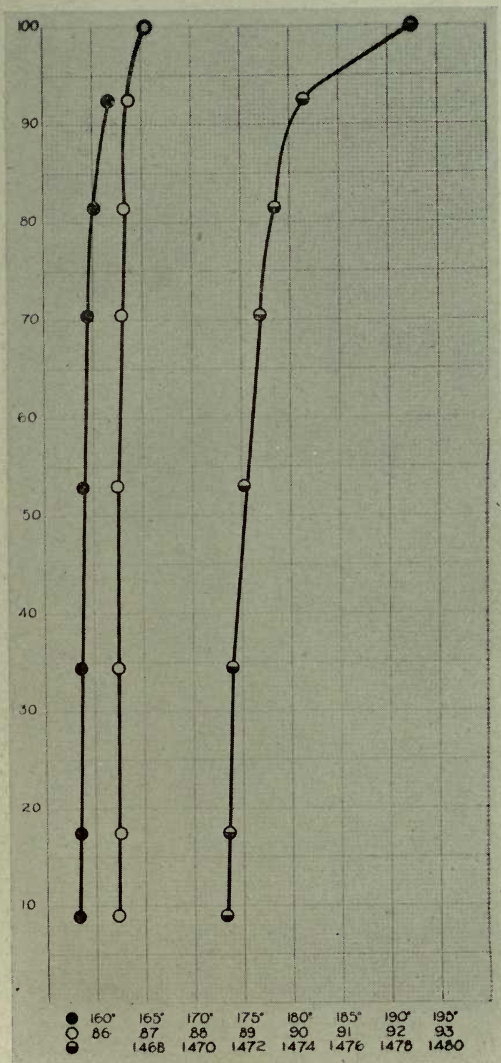


Fig. 13.

Alteration in physical properties of a gum turpentine due to direct distillation.

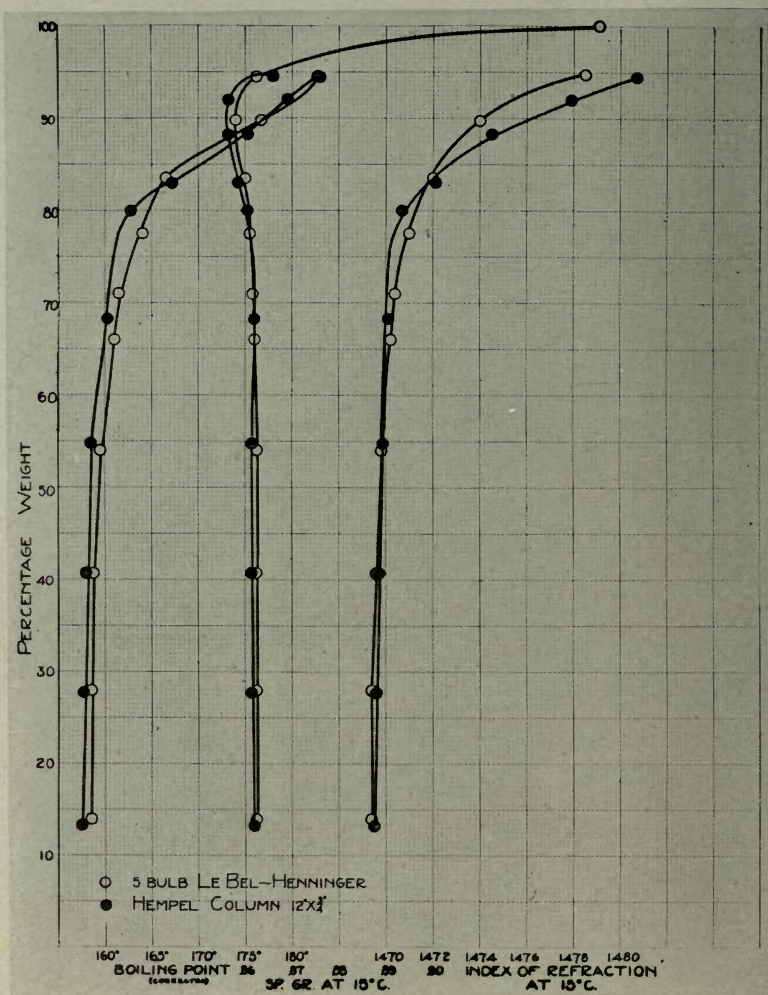


Fig. 14.

Comparison of fractionation with Le Bel-Henninger and Hempel column dephlegmators.

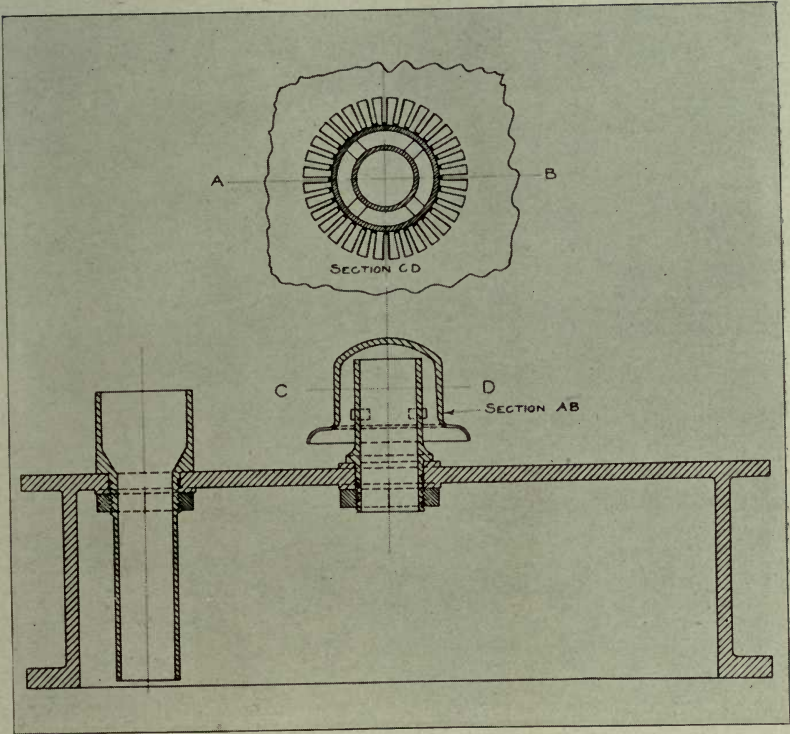


Fig. 15.  
Boiling cap sections.

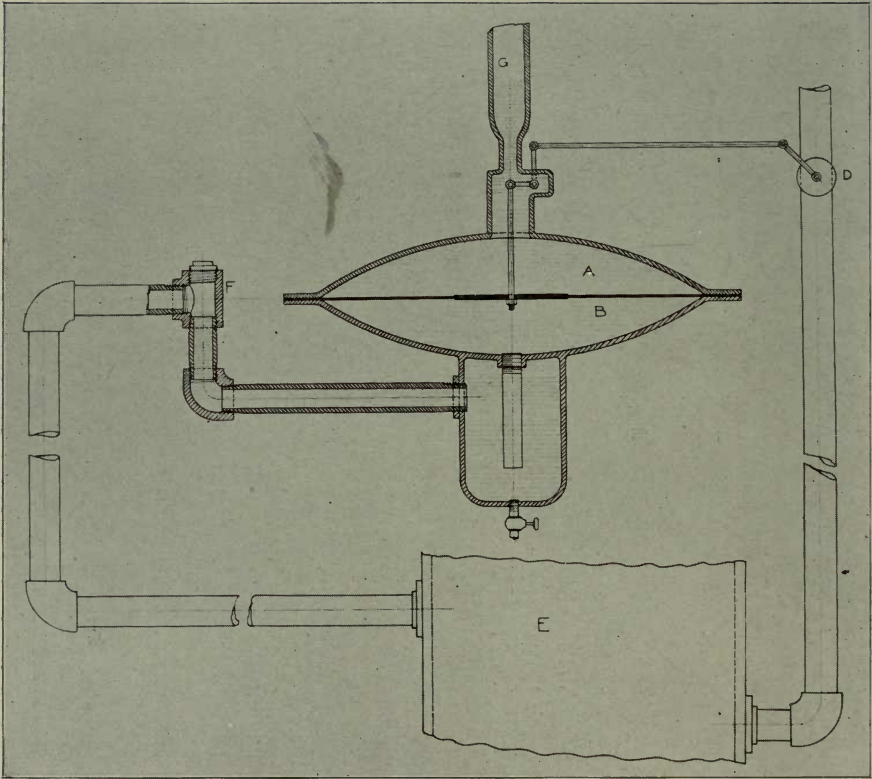


Fig. 16.  
Pressure regulator.



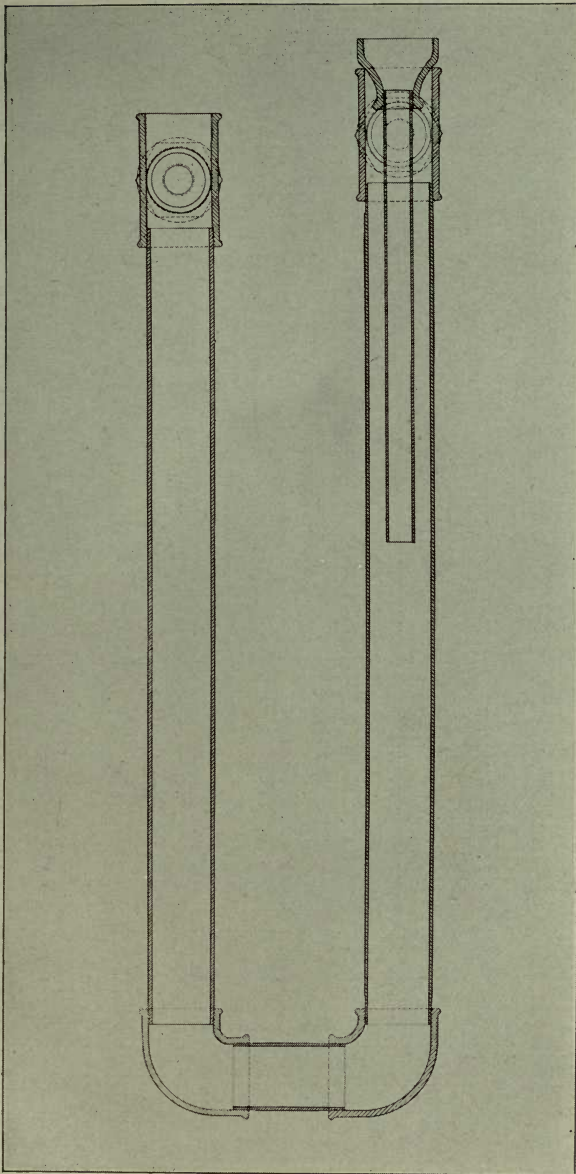


Fig. 17.  
Separator.

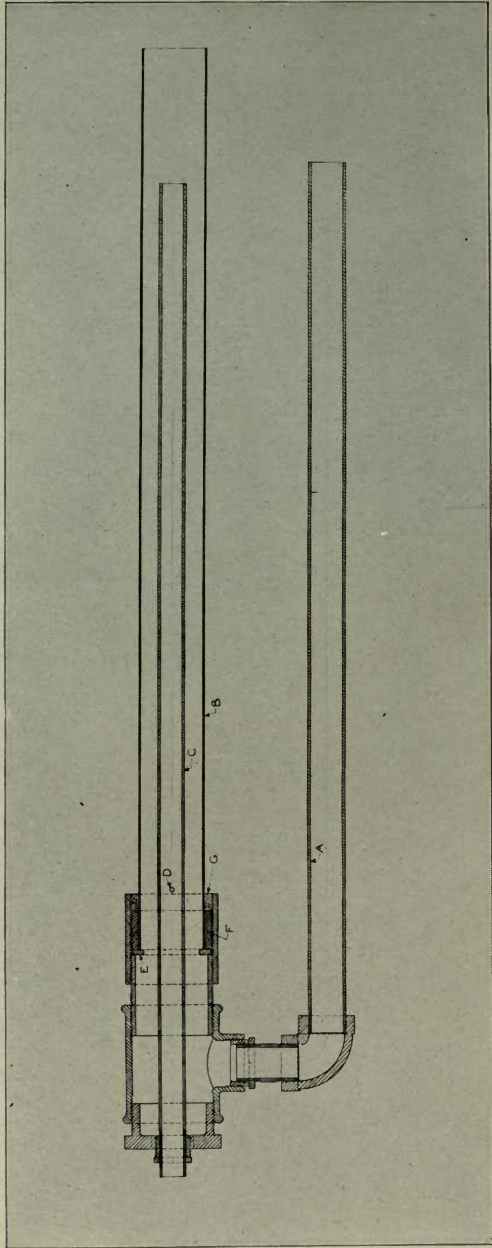


Fig. 18.  
Speed Indicator.

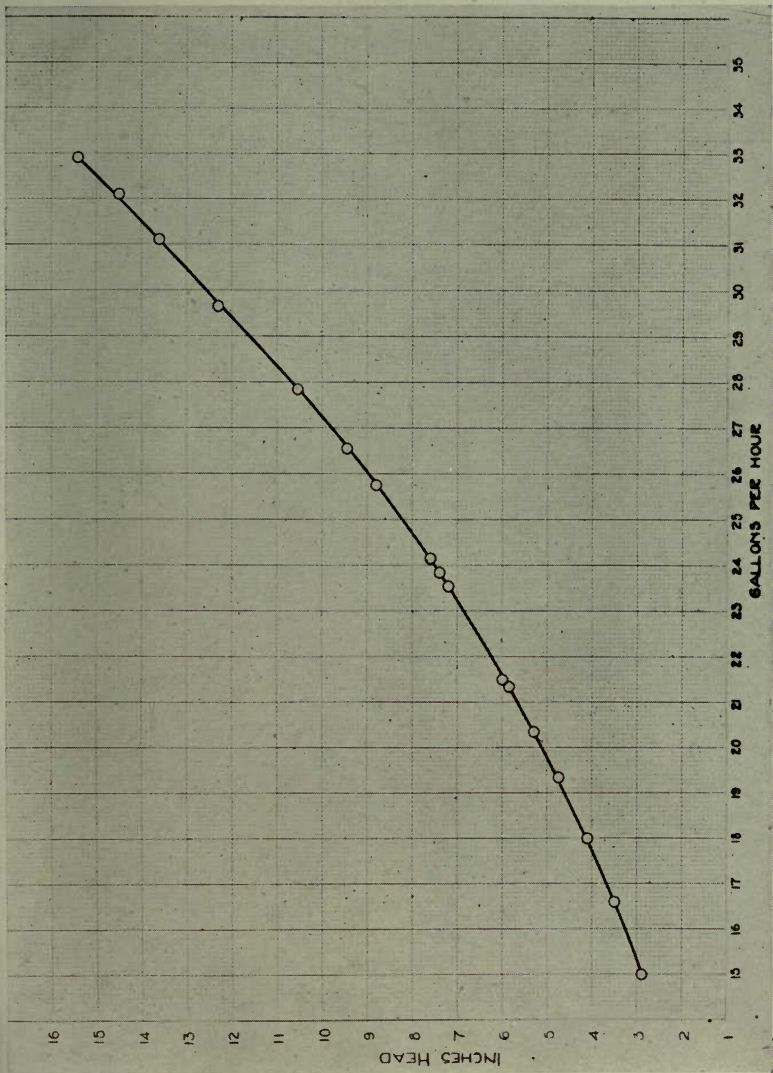


Fig. 19.

Calibration curve for crude turpentine "speed indicator."

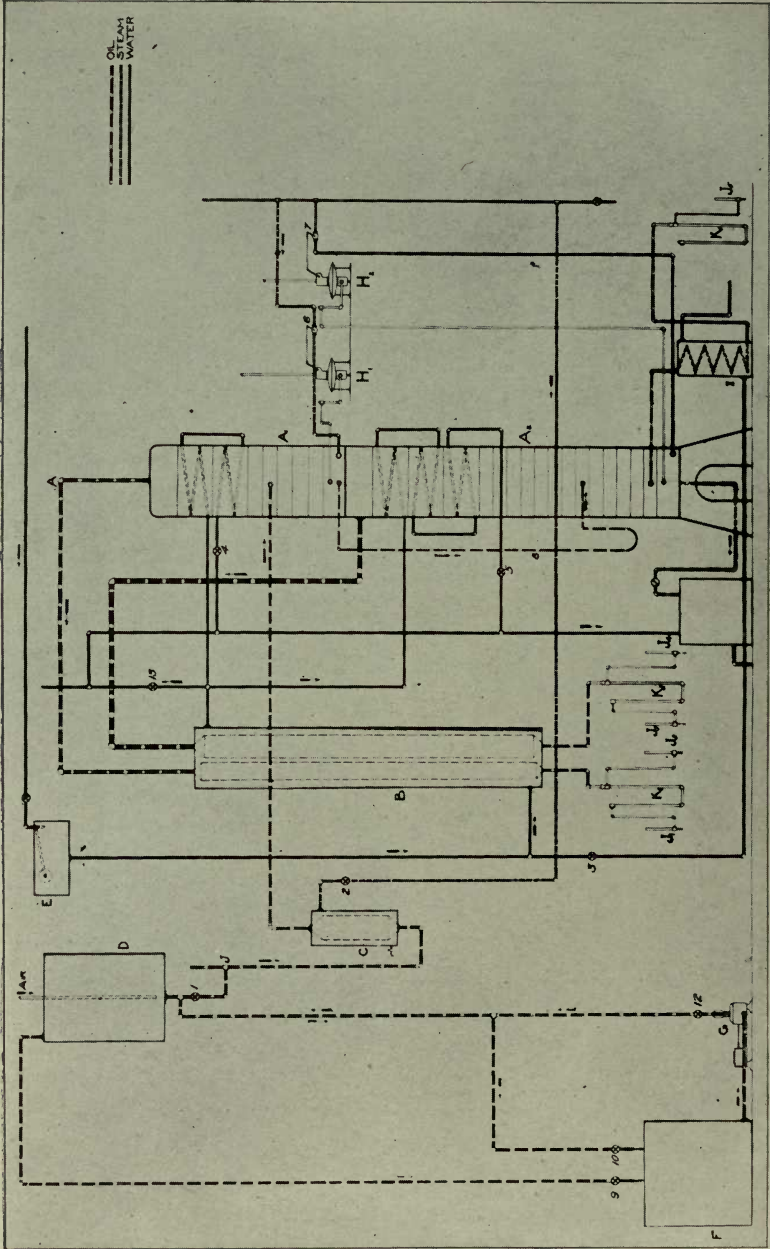


Fig. 20.  
General arrangement of apparatus for refining crude turpentine.

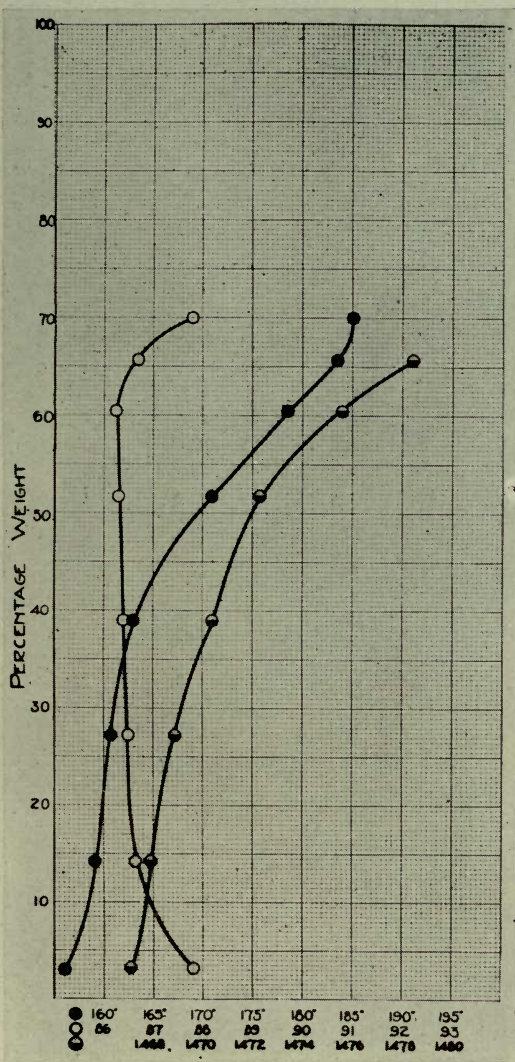


Fig. 21.

Boiling point, specific gravity and index of refraction curves for crude turpentine No. 1, untreated.

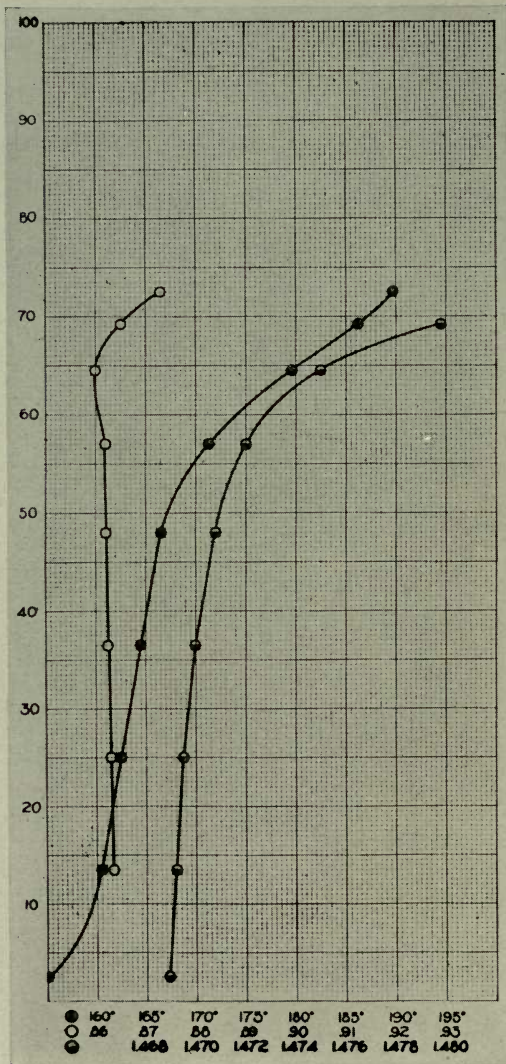


Fig. 22.

Boiling point, specific gravity and index of refraction curves for crude turpentine No. 2, after treatment with caustic soda solution.

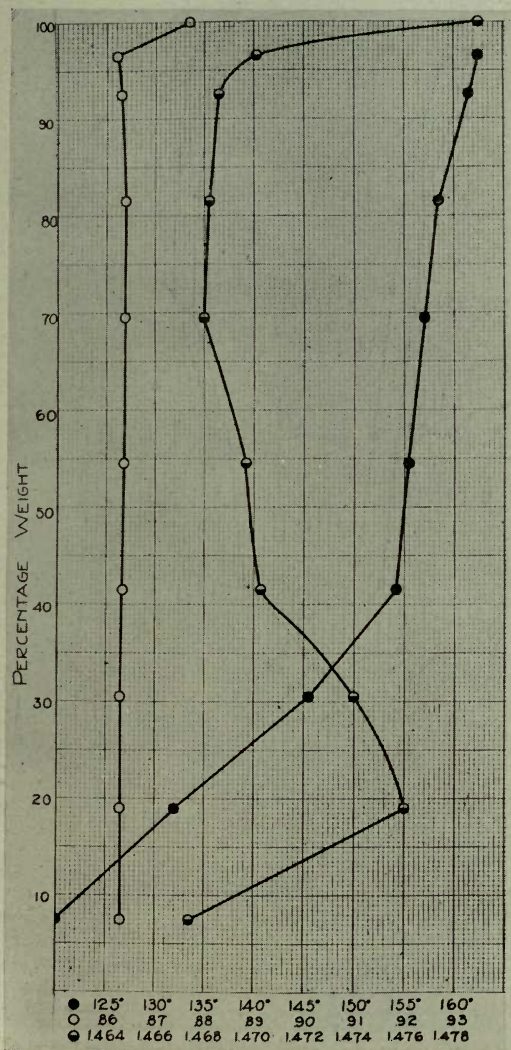


Fig. 23.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 1.

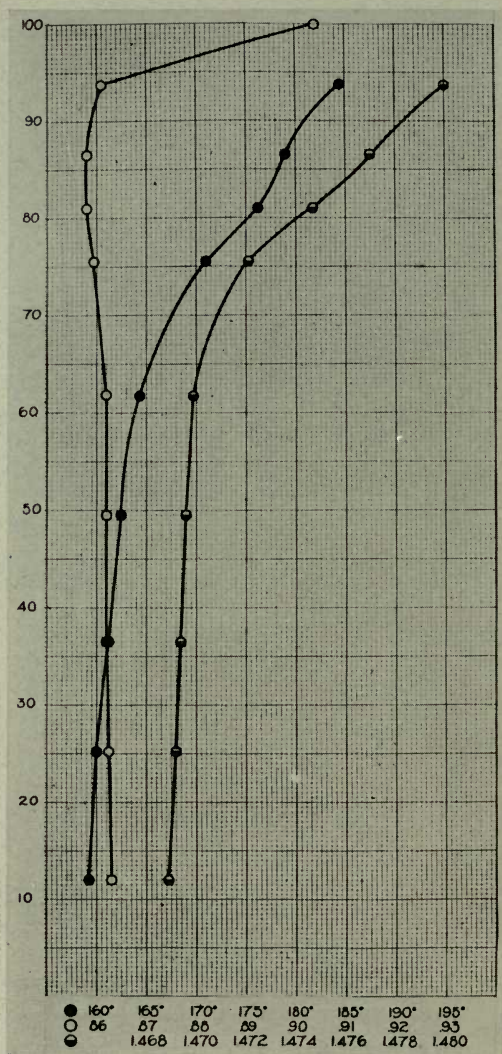


Fig. 24.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 1.



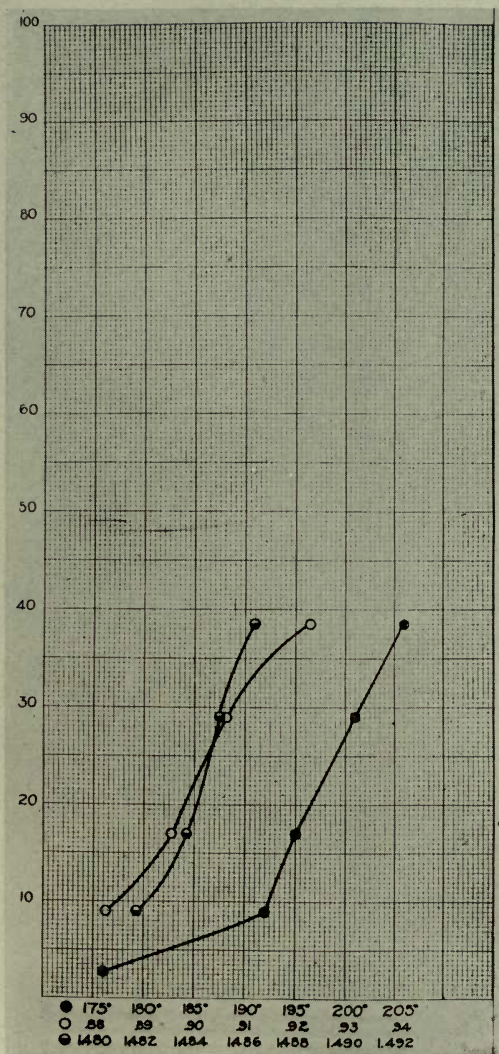


Fig. 25.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 1.

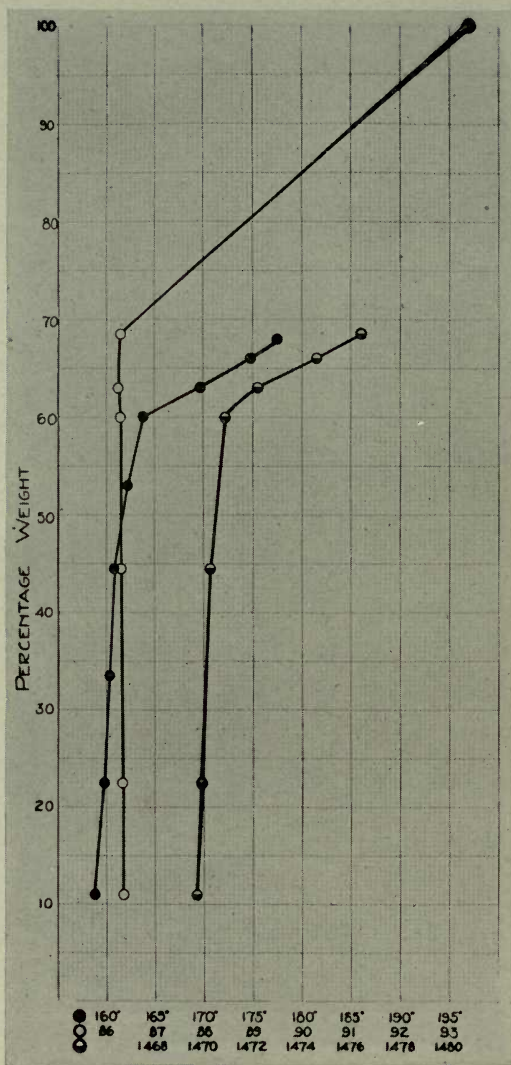


Fig. 26.

Boiling point, specific gravity and index of refraction of crude turpentine No. 2.

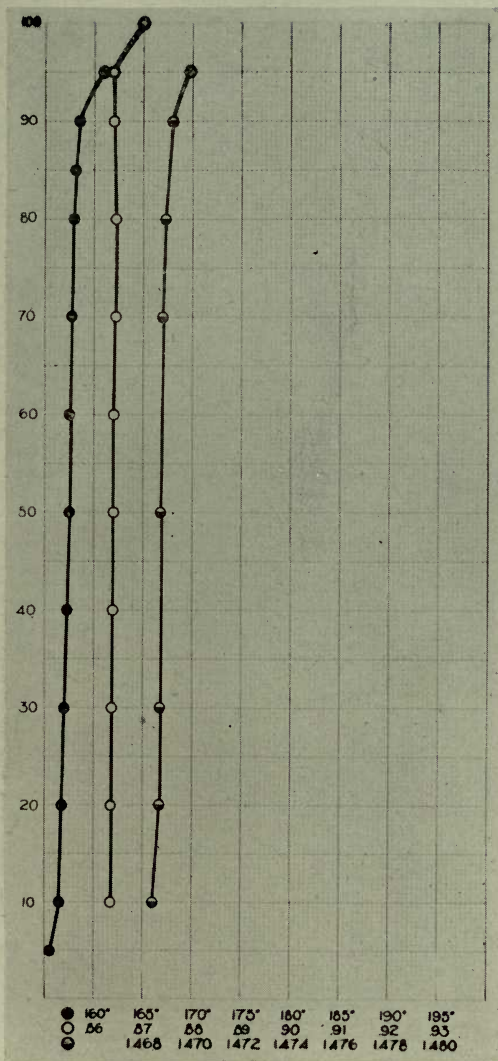


Fig. 27.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 2.

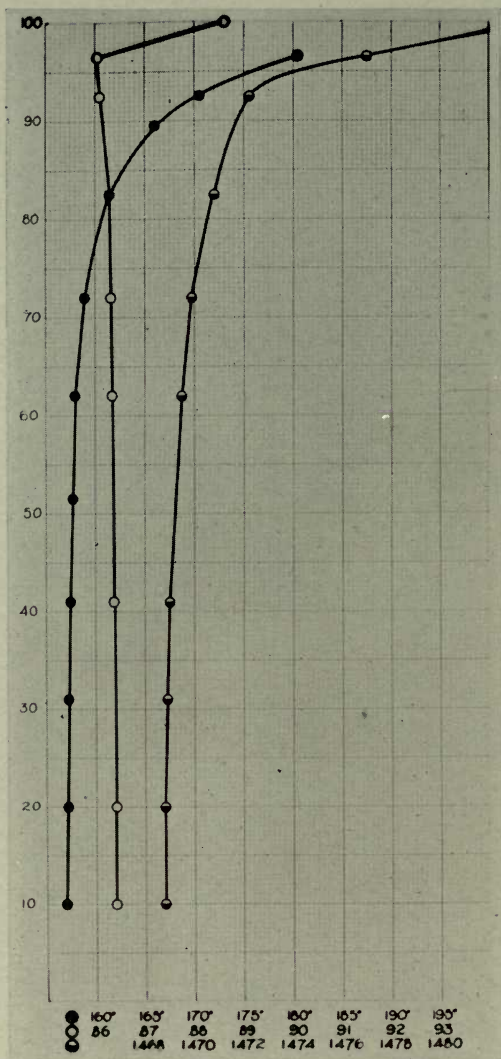


Fig. 28.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 2.

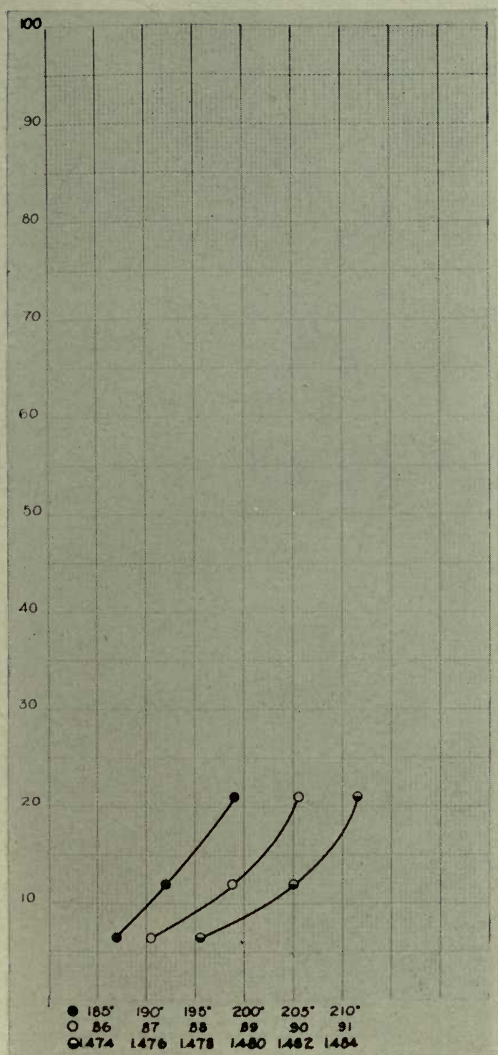


Fig. 29.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 2.

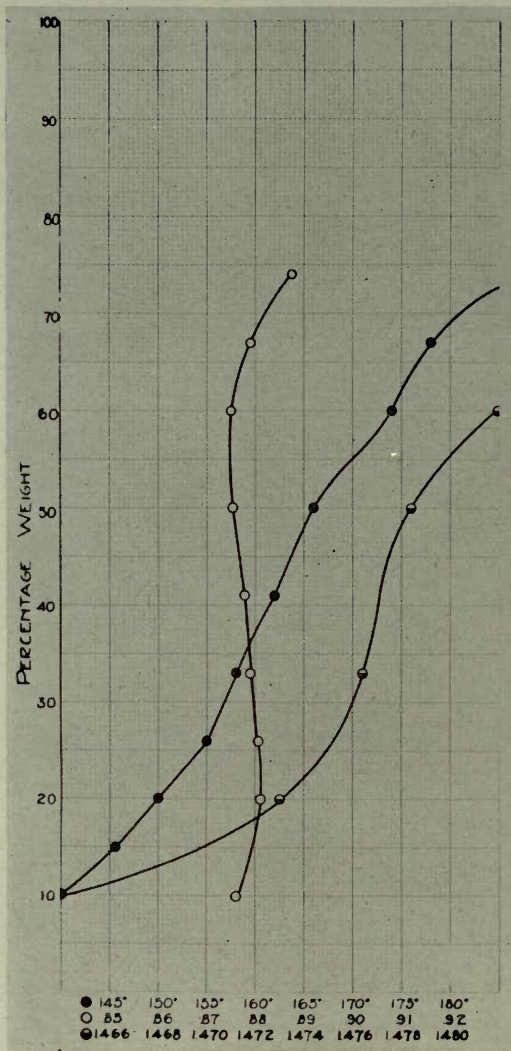


Fig. 30.

Boiling point, specific gravity and index of refraction of crude turpentine No. 3, untreated.

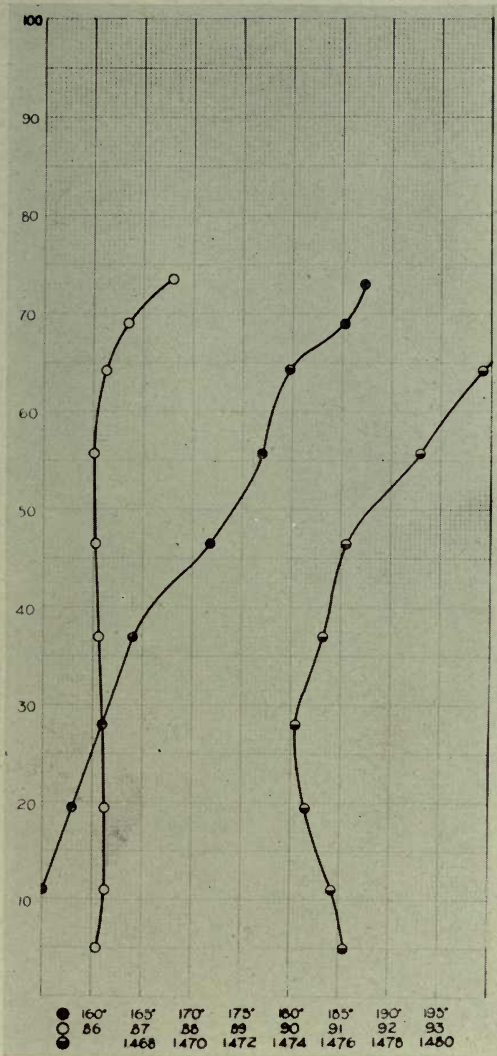


Fig. 31.

Boiling point, specific gravity and index of refraction of crude turpentine No. 3, after treatment with caustic soda solution.

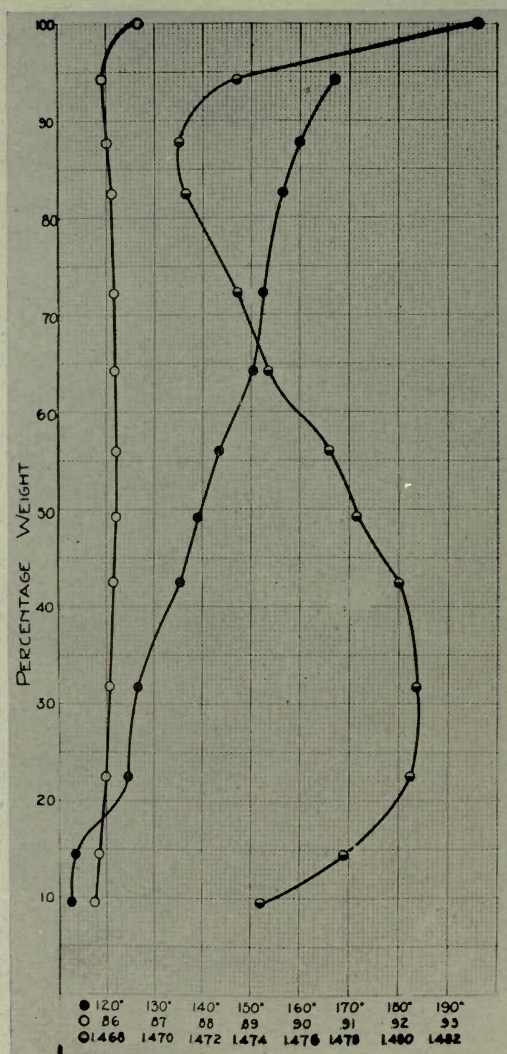


Fig. 32.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 3.



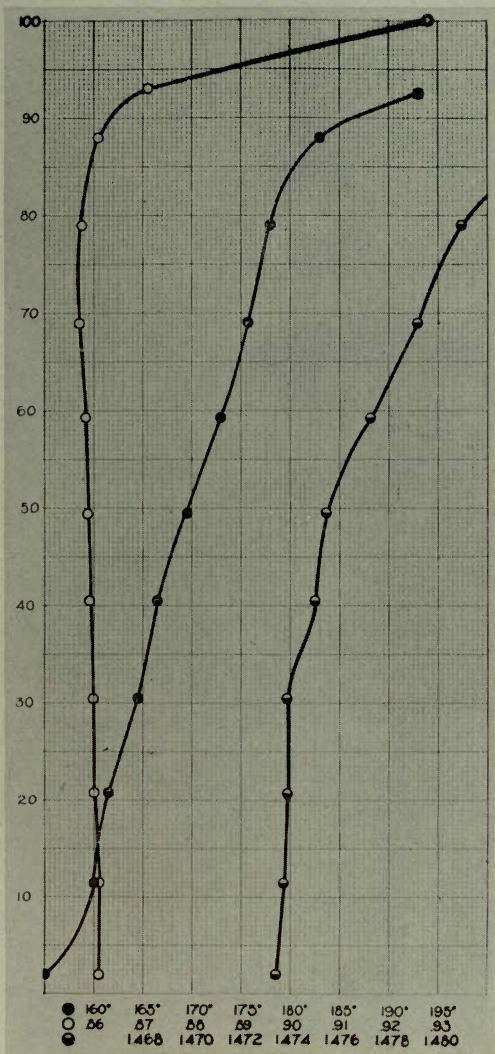


Fig. 33.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 3.

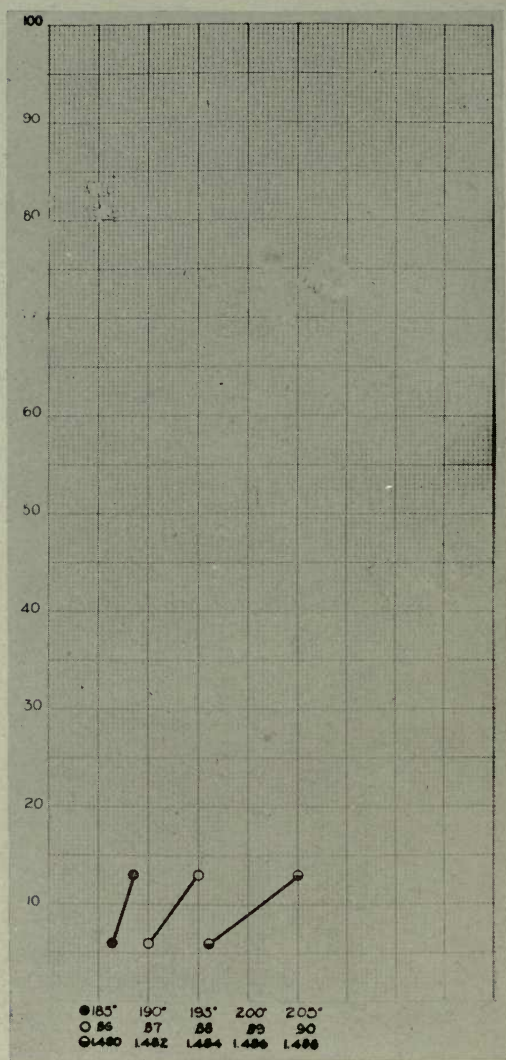


Fig. 34.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 3.

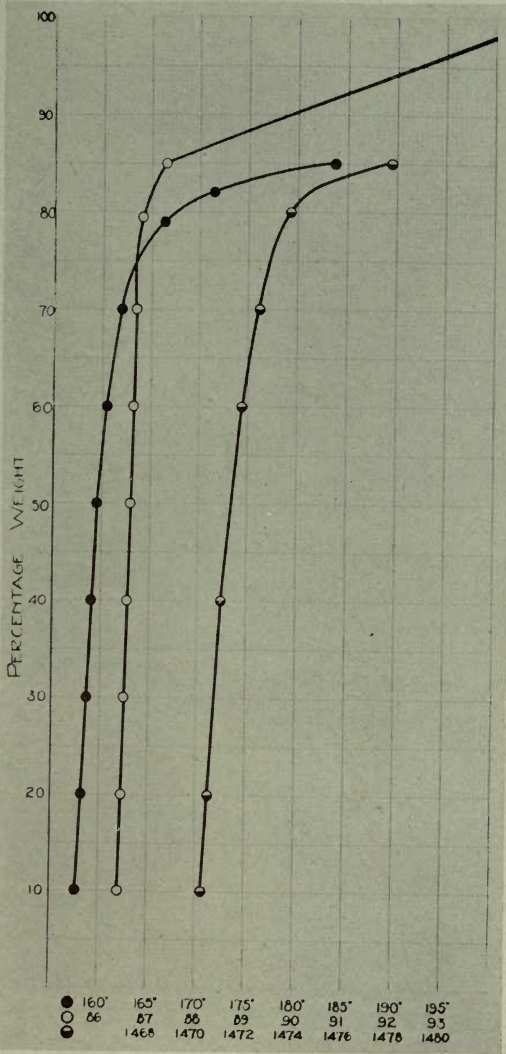


Fig. 35.

Boiling point, specific gravity and index of refraction of crude turpentine No. 4.

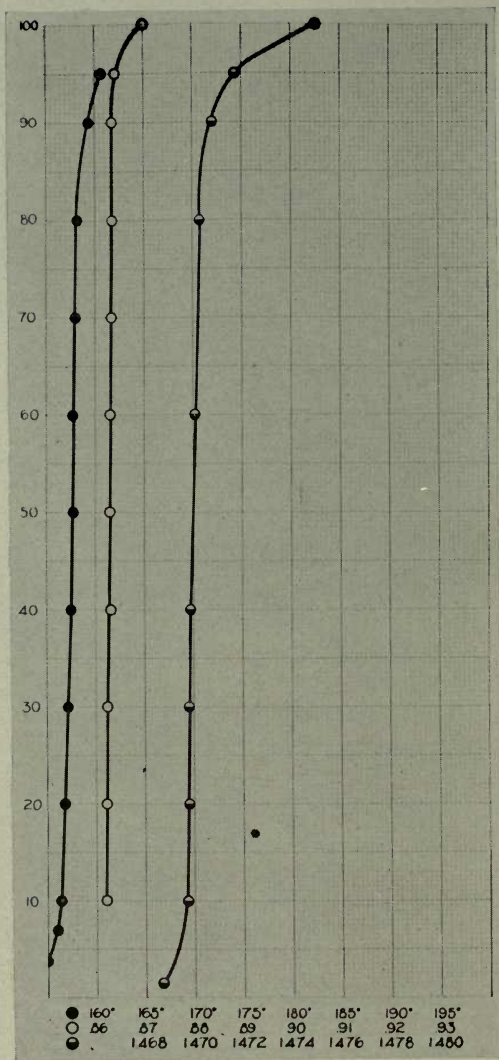


Fig. 36.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 4.

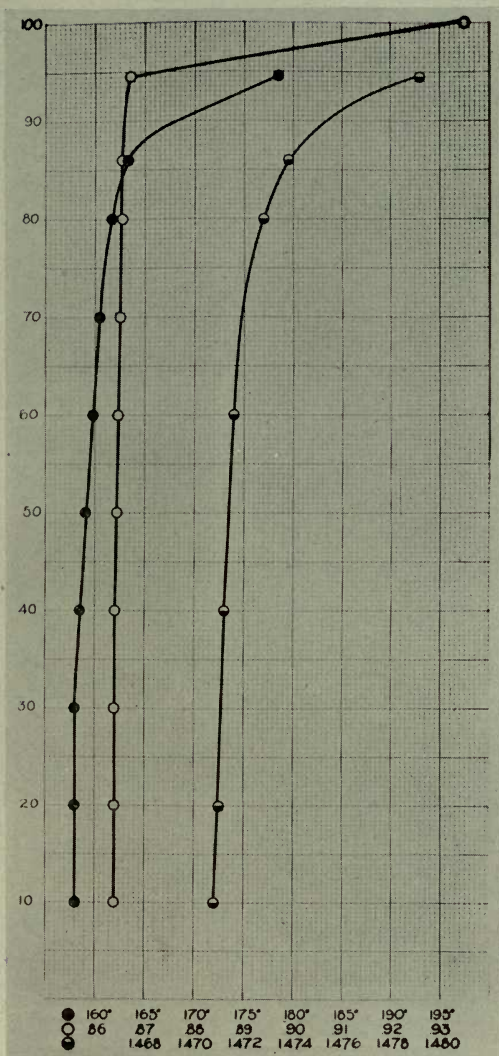


Fig. 37.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 4.

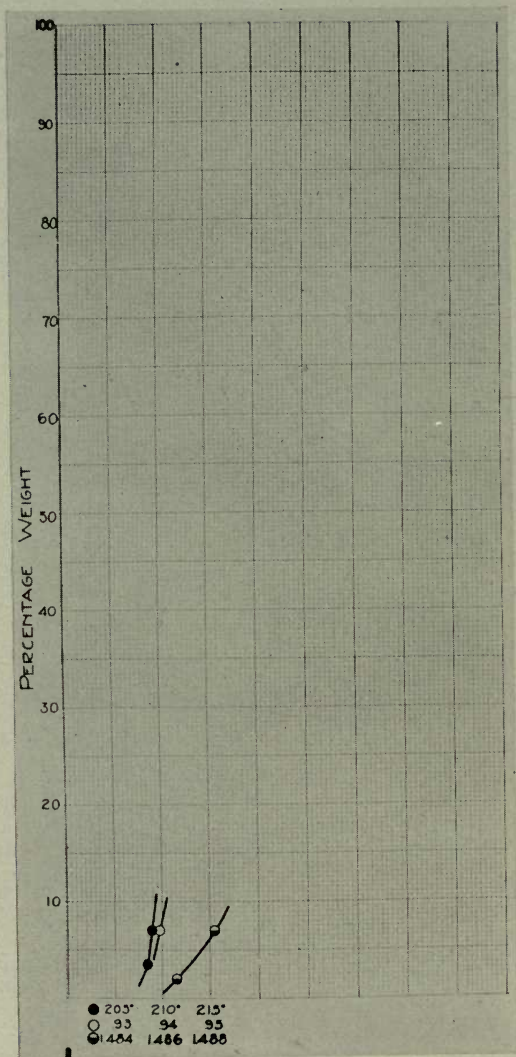


Fig. 38.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 4.

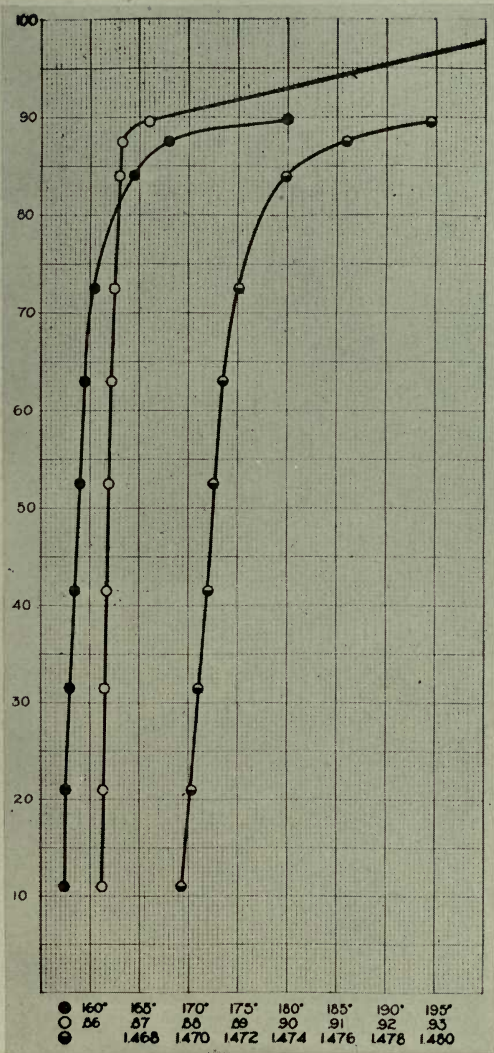


Fig 39.

Boiling point, specific gravity and index of refraction of a commercial wood turpentine refined (Crude No. 4) in an ordinary pot still.

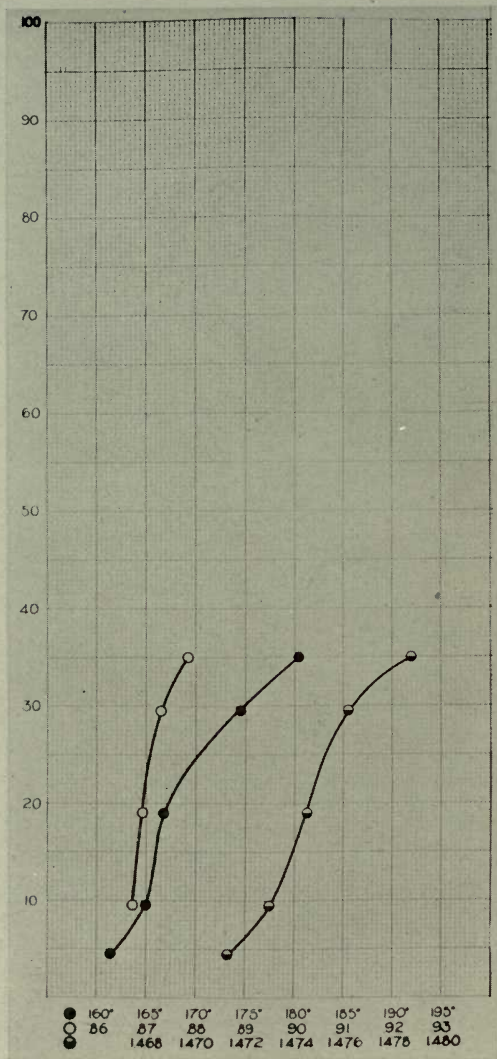


Fig. 40.

Boiling point, specific gravity and index of refraction of commercial pine oil refined in an ordinary pot still.



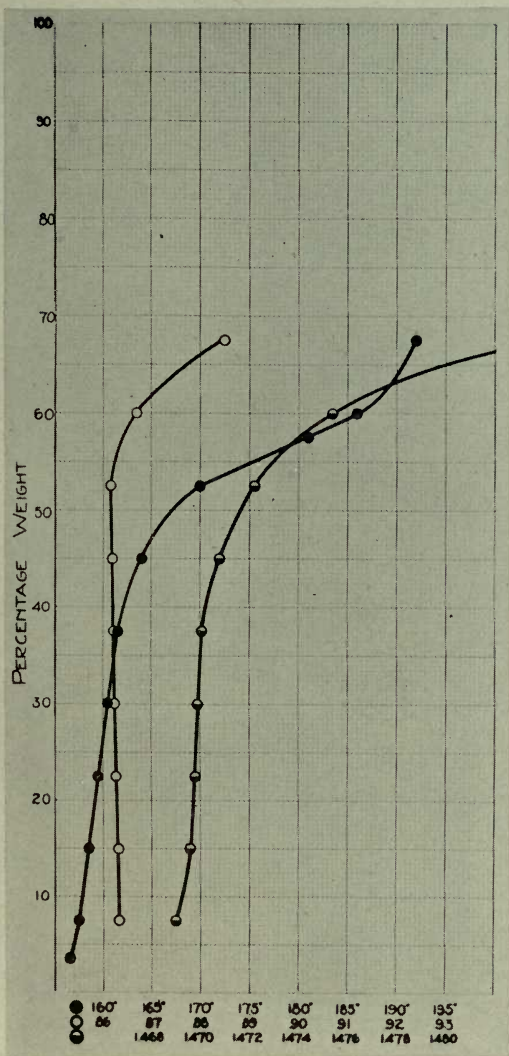


Fig. 41.

Boiling point, specific gravity and index of refraction of crude turpentine No. 5.

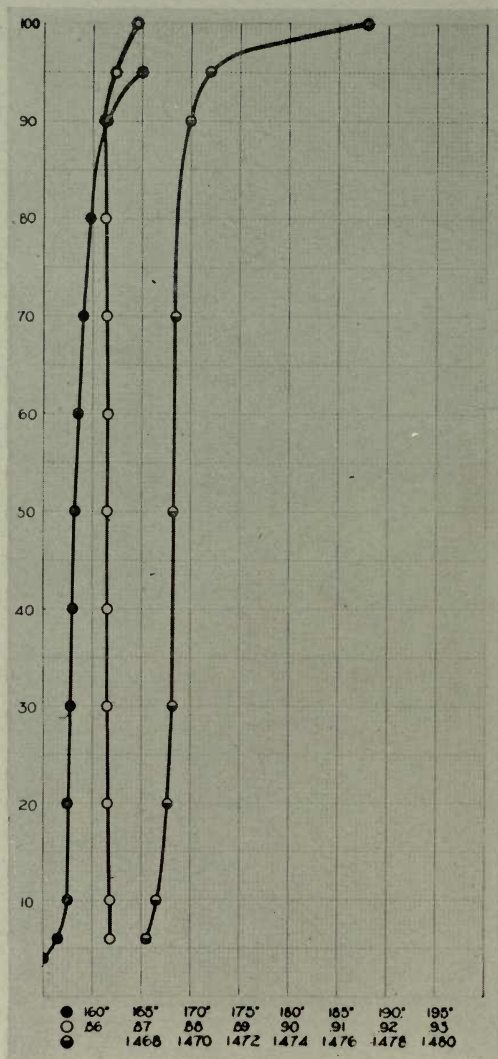


Fig. 42.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 5.

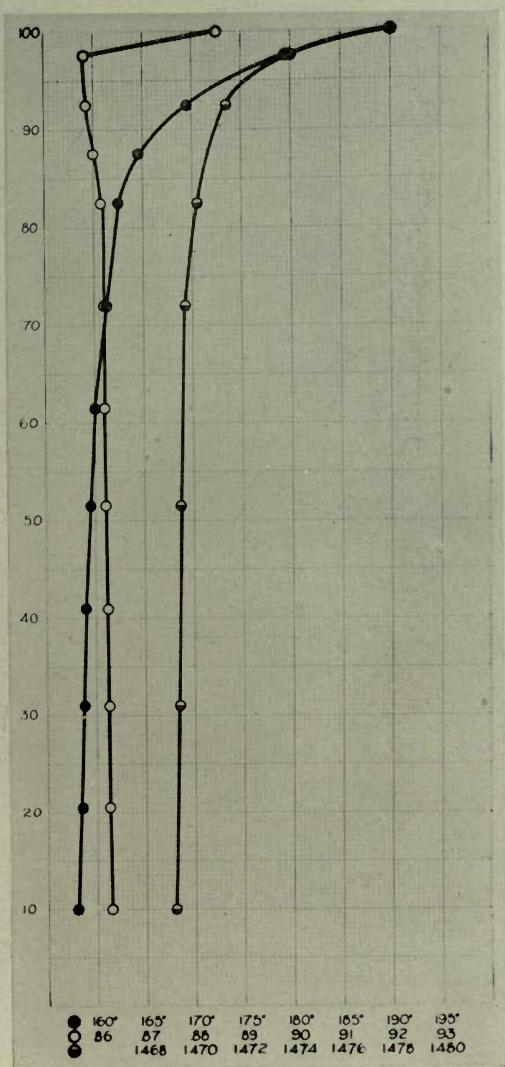


Fig. 43.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 5.

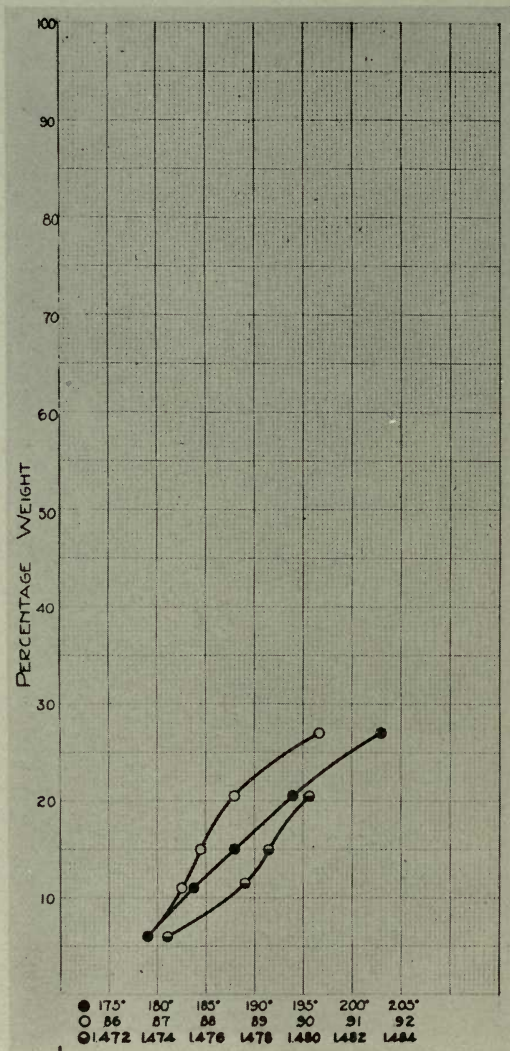


Fig. 44.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 5.

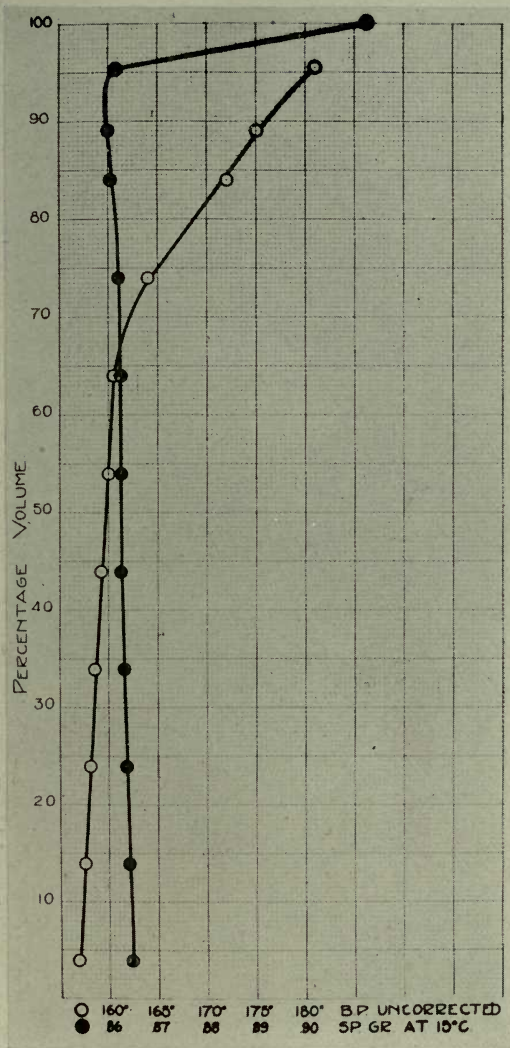


Fig. 45.

Boiling point and specific gravity of turpentine obtained in commercial refining of crude turpentine No. 5.

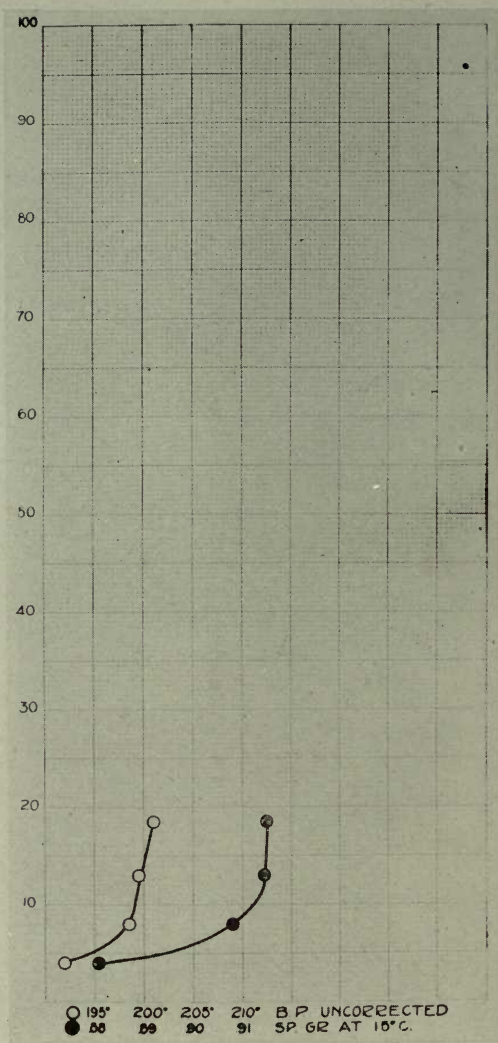


Fig. 46.

Boiling point and specific gravity of pine oil obtained in commercial refining of crude turpentine No. 5.

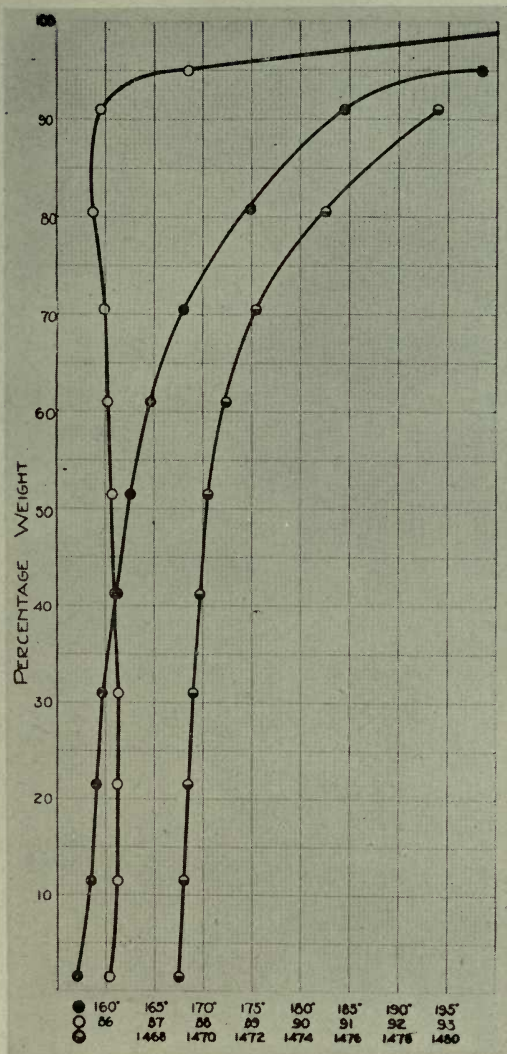


Fig. 47.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 1 analyzed after six months.

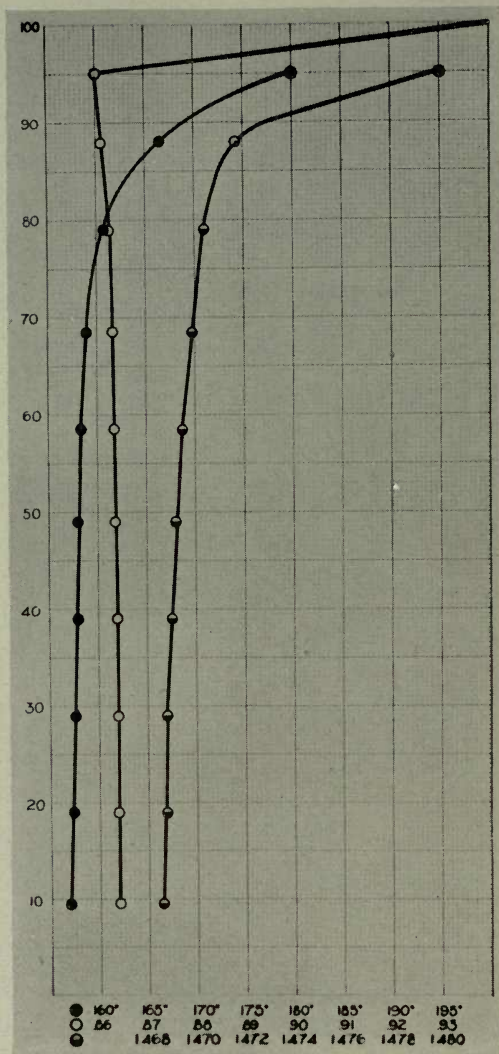


Fig. 48.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 2 analyzed after nine months.



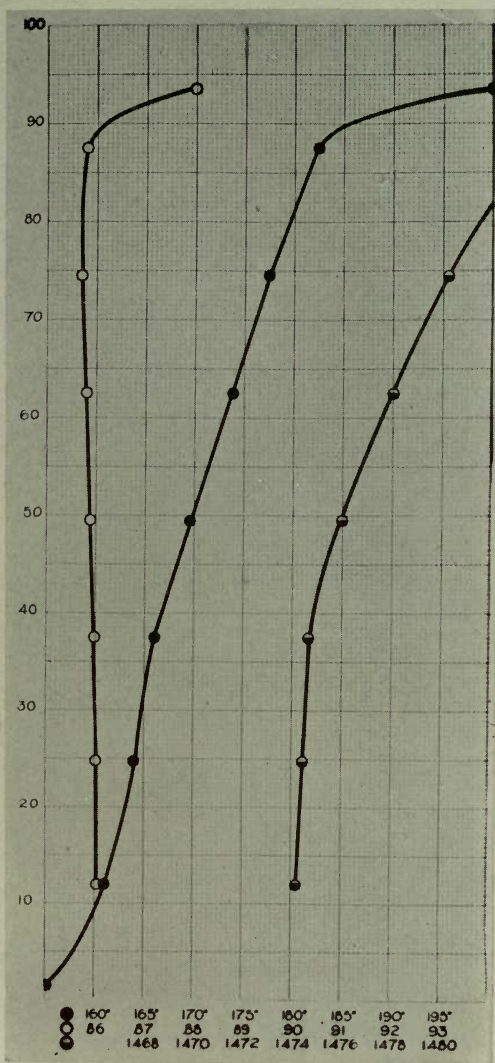


Fig. 49.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 3 analyzed after nine months.

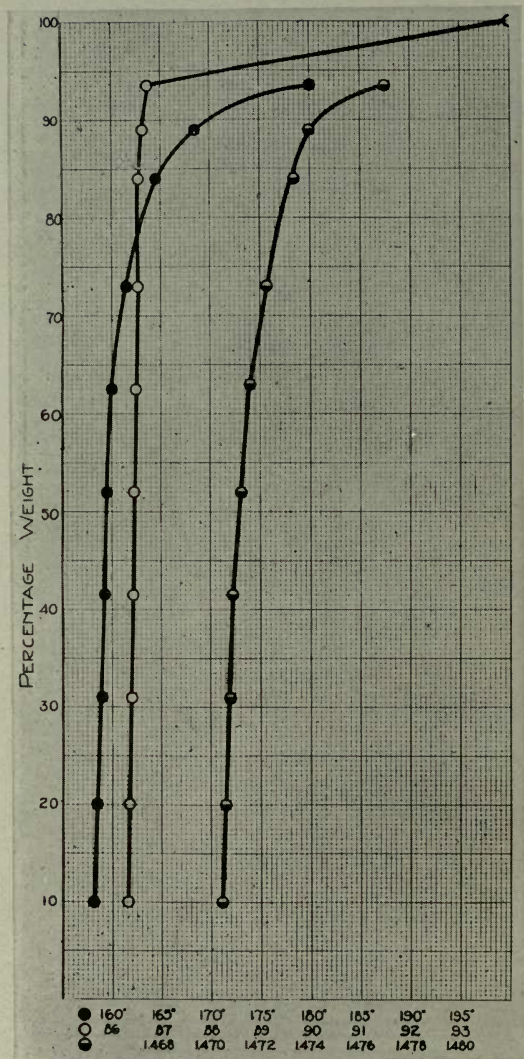


Fig. 50.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 4 analyzed after nine months.

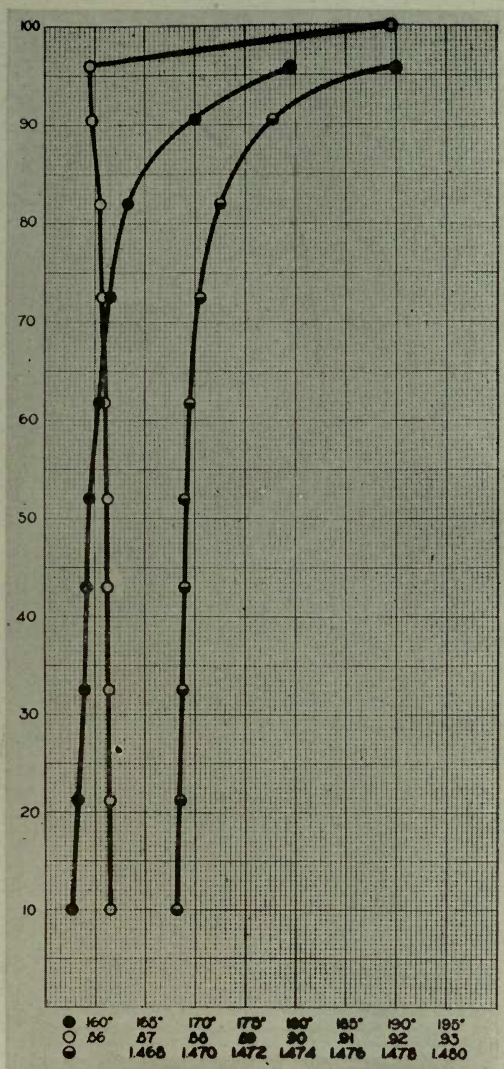


Fig. 51.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 4 analyzed after three months.

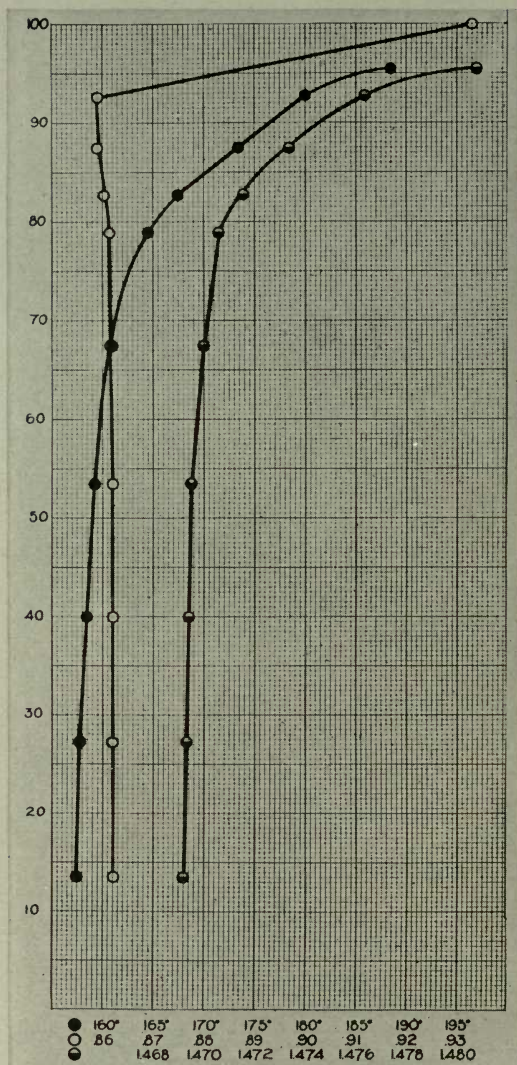


Fig. 52.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 5 analyzed after six months.

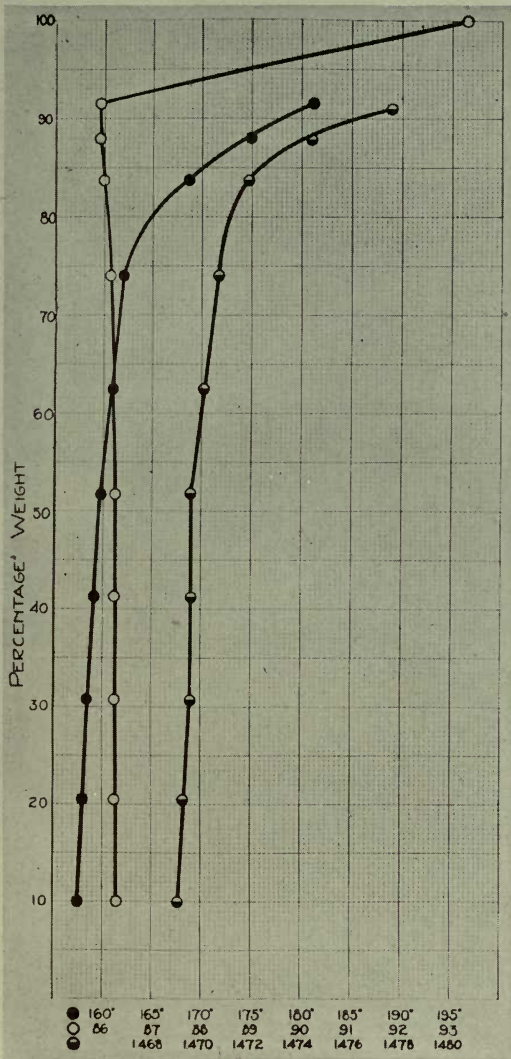


Fig. 53.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 5 analyzed after ten months.

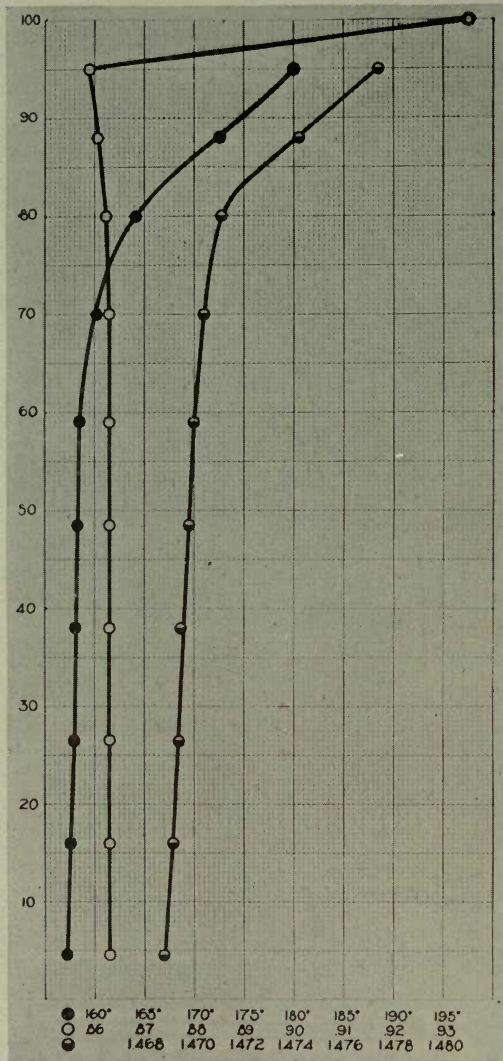
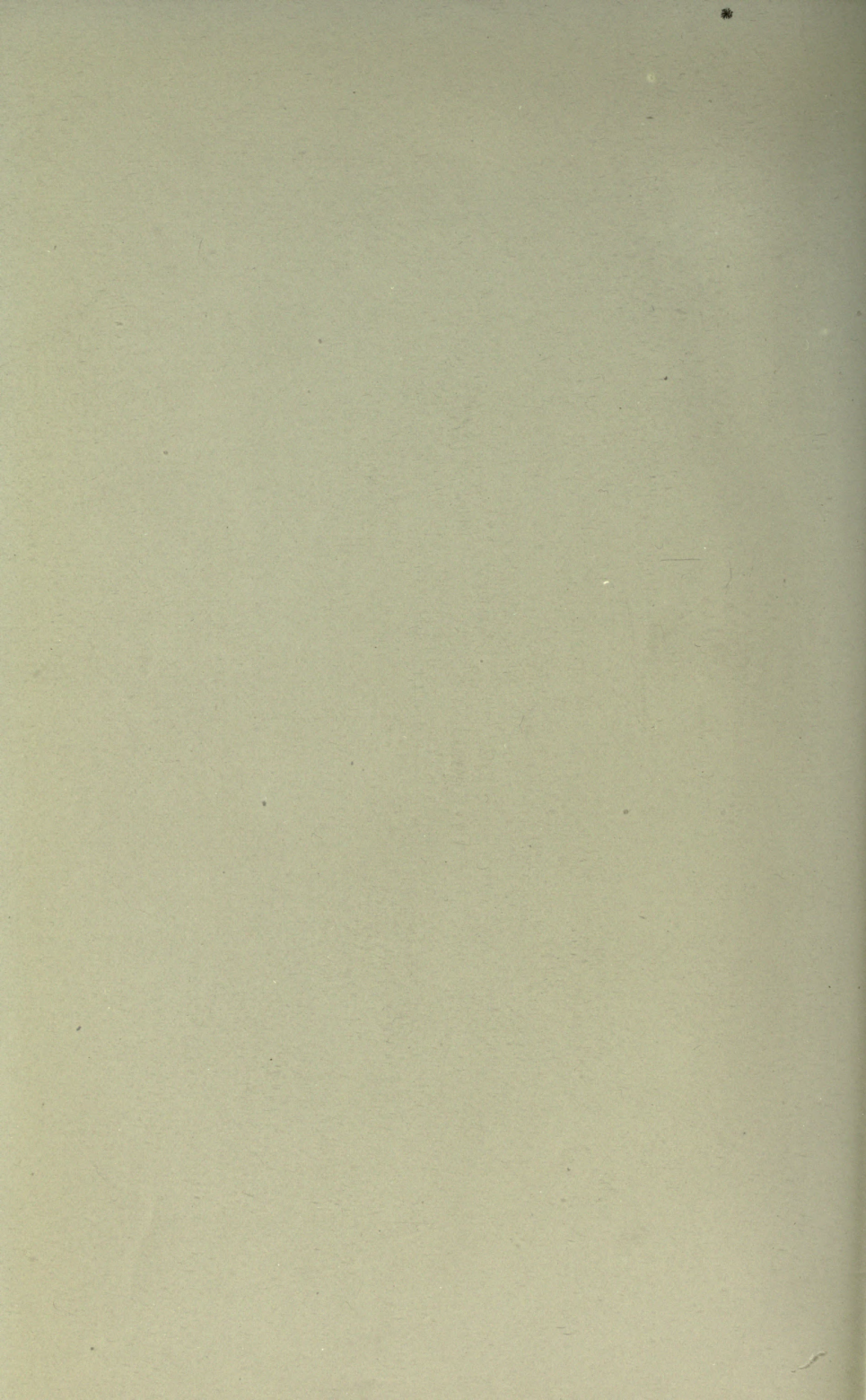


Fig. 54.

Boiling point, specific gravity and index of refraction of turpentine obtained from crude No. 5 after redistillation.







### *Boiling Cap Sections*

The boiling cap section, shown diagrammatically in Figure 15, is the typical and important division of the column, the other kinds of sections being modifications of this typical section. Each section is 14 inches by 12 inches inside diameter, and is supplied with eight boiling caps and two return pipes. The liquid level on each section is kept even with the top of the return pipes, and the vapors from the section below are made to pass through this liquid by means of the boiling caps; the rim of each cap is slotted so that the vapor passes through the liquid in small bubbles, and good contact between the ascending vapor and the descending liquid is thus obtained.

### *Reflux Condenser Sections*

The reflux condenser sections are really a combination of a boiling cap section with a reflux condenser; that is, they are similar to Figure 15 except that below the return pipes there is a chamber filled with copper tubes around which the vapors must pass and through which water is kept flowing.

### *Steam Chamber Sections*

The steam chamber sections are like the boiling cap sections except that they are higher and are furnished with two steam inlets near the bottom, and an opening near the top for connection with the pressure regulators.

### *Outlet Sections*

The vapor outlet sections are simply chambers for covering the top of the last boiling cap or reflux section, and are provided with a suitable opening for conveying the vapors to the condenser.

### *Pressure Regulators*

A sketch of the pressure regulator is given in Figure 16. It consists essentially of two chambers A and B separated by the rubber diaphragm C. Any motion of the diaphragm such as might be caused by a change of pressure in either chamber, is communicated by the system of levers to the steam valve D.

For instance, if there is an increase of pressure in the steam chamber E, there is a corresponding increase of pressure on the bottom of the diaphragm and the diaphragm moves upward, closing the valve D until the pressure is again normal in E.

### *Separators*

The separator, Figure 17, is the same in principle as the ordinary automatic oil and water separator used in practice, but it is made much more compact in order that only a small amount of oil can be retained in it at one time. This apparatus can be made entirely from ordinary iron pipe and pipe fittings. A separator like that shown in the drawing with a total length of 3 feet and with the main tube made of 2 1/2-inch iron pipe was sufficient for the separation of 20 to 23 gallons of refined turpentine from about the same amount of water per hour.

### *Speed Indicators*

The speed indicator,<sup>1</sup> Figure 18, is based on the principle that there is a definite relation between the rate of flow of a liquid through a small aperture, and the pressure of the liquid at the aperture. The liquid, as for instance the refined turpentine, enters the indicator from the separator through A. The only outlet for the liquid is the tube C which may be entered from the top or through the aperture D; this aperture is made small enough so that, with the normal flow of the liquid, it is necessary for the liquid level to rise some distance in the tube B in order that the pressure may be sufficient to make the liquid flow through D at the same rate it enters through A. The height of the liquid level in B is a measure of the rate of flow through D, and the relationship between these factors is obtained by calibration; that is, by measuring the rate of flow from C, while the liquid

<sup>1</sup> This apparatus can be made almost entirely from ordinary iron pipe and pipe fittings. The pipe C should, however, be of brass so that the aperture D may not be changed in size by rusting and of course the tube B must be of glass. The method of fastening the glass tube into the iron parts is shown in the drawing; E is a support of tin plate or other thin, easily shaped, metal soldered to the nipple in order to support the tube B and the packing F; C is a thin layer of litharge and glycerin cement which makes the joint oil or water tight.

level is maintained at constant measured distances above D. The calibration curve for the crude turpentine indicator is shown in Figure 19.

The other parts of the apparatus were of standard design and require no special explanation.

### *General Arrangement and Operation of Apparatus*

A diagram of the general arrangement of the apparatus is given in Figure 20. The fractionating column A is divided into the two separate columns  $A_1$  and  $A_2$  at the place marked by the heavy line.  $A_1$  and  $A_2$  are made up of the different kinds of sections already described, as follows:  $A_1$  from the bottom upward, one steam chamber section, five boiling cap sections, two reflux condenser sections and one outlet section.  $A_2$  is similarly made up of one steam chamber section, thirteen boiling cap sections, three reflux condenser sections and one outlet section.

The tank for crude oil F is connected through the pump G with the reservoir D; the overflow pipe from D, through valve 9, furnishes an air outlet for D while it is being filled and serves the purpose also of notifying when D is full; the return pipe through valve 10 also makes it possible to draw out any material from D directly into the tank F. The reservoir D is simply a 110 gallon steel drum arranged on the principle of a Mariotte's bottle in order to keep the flow of crude turpentine through valve 1 constant, whatever the level of crude turpentine in D. The reservoir D having been filled, and valve 10 closed, valve 1 is opened until the crude is running at the required speed as registered on the speed indicator J, say 25 gallons per hour. The crude then flows through the feed heater C, where it is heated by steam from valve 2 to a temperature of about 95°C., and enters the upper column  $A_1$  at the fourth boiling cap section as indicated. The steam supply is now adjusted by the pressure regulator  $H_1$ , and the water in the reflux sections by valve 4 so that the distillate leaving the top of column  $A_1$  is running at the required speed as indicated on the speed indicator  $J_2$ . The speed required is determined from the analysis of the crude turpentines; for instance, if 5 per cent of low boiling material which it is desired to remove from the refined turpentine is present in the crude, then

it is only necessary to adjust the speed of the first distillate to 5 per cent of the speed of the crude.

The portion of the crude not distilled in column  $A_1$  flows from the bottom section through the trapped pipe 8 into the column  $A_2$  at the sixth boiling cap section. Here the distillation process is repeated as in the top column, the water and steam supplies being adjusted by valve 5 and the regulator  $H_2$ , respectively, so that the distillate leaves the top of  $A_2$  at the required rate.

The undistilled residue or "tails" runs out in liquid form from the first boiling cap section, is cooled in the tails cooler I, separated from the water, and the speed measured in the indicator  $J_3$ . The speed of the tails is not directly controlled, but is dependent upon the speeds of the other products, being equal to the speed of the crude, minus the sum of the speeds of the two distillates.

A constant head for the water supply is maintained by means of the float valve in the reservoir E so that when the valves 4, 5, and 13 are once adjusted, the flow of water through the condenser B, and therefore through the refluxes of  $A_1$  and  $A_2$  will be constant. The pressure regulators  $H_1$  and  $H_2$  are used to maintain a constant pressure of steam in the bottom section of the columns  $A_1$  and  $A_2$ , respectively, and therefore the speed of the distillates, once properly adjusted, should remain constant. There were in most cases, however, small variations in the speed of the different products during the course of the distillation.

### *Refining of Crude Turpentine No. 1*

#### *Method of Production*

This crude turpentine was obtained from a plant using the destructive distillation process; during the first part of the distillation, however, the retorts are heated slowly, so that, while the crude turpentine is being distilled from the wood, the temperature is kept as low as is readily possible.

#### *Analysis and Chemical Treatment*

The analysis of the crude is given in Figure 21. The odor of the first four fractions was very disagreeable, and the color was a dark yellow; these properties, in connection with the high grav-

ity, indicated the impossibility of obtaining by distillation alone any refined turpentine of good quality from this part of the crude, although the boiling points were mostly within the range of a good turpentine. On account of the probability that the contaminating material could be removed by treatment with alkali, the original crude turpentine was agitated with a warm caustic soda solution until there was no further action.

The analysis of the treated crude is shown in Figure 22. The gravity of the first few fractions was decreased and the index of refraction was increased by the treatment; the color and odor of all the fractions were also improved. The first fraction of the treated crude, however, had a more disagreeable odor and more color than the other fractions; the second fraction had these undesirable qualities, but to a lesser degree; the rest of the fractions were practically colorless and had only slight traces of the strong odor of the first fraction. The fact that the portion of the distillate having the undesirable properties had also boiling points lower than the rest of the material, made it seem possible that the undesirable portion could be separated by distillation, with a consequent improvement in the properties of the refined turpentine.

The heavy oils began to come over in quantity at about 70 per cent and the distillate beyond this point was practically free from terpenes.

### *Distillation*

It was decided therefore to separate this crude turpentine by the refining process into two distilled products and a residue, as follows: (1) "Light oils" or "heads" with boiling points below those of turpentine, 5 per cent; (2) refined turpentine or "hearts," 65 per cent; and (3) "heavy oils" or "tails" with boiling points and gravity above those of turpentine, 30 per cent. In order to secure such a separation in the refining still it was necessary to regulate the flow of the different products to the following speeds (the crude turpentine running at 25 gallons per hour):

For heads 5 per cent of 25 or 1.25 gallons per hour.

For hearts 65 per cent of 25 or 16.25 gallons per hour.

For tails 30 per cent of 25 or 7.5 gallons per hour.

In the distillation of this turpentine and all others as well, the first runnings of the distillates were caught separately until the adjustment was completed, because the composition of the products would be at first very variable. The analyses shown hereafter represent the composition of the products obtained after the still was properly adjusted and running smoothly. For instance, this run on Turpentine No. 1 occupied about four and one-half hours, but the products shown in the analyses were obtained during a little less than four hours of this time.

### *Products of Distillation*

The analyses of the products obtained from the distillation of Crude Turpentine No. 1 are shown in Figures 23, 24 and 25.

*Heads.*—The heads, Figure 23, are seen to be very variable in composition, about the first 70 per cent having higher indices of refraction and lower boiling points than the first fraction of the hearts; this portion of the distillate also had a darker color and more disagreeable odor than the fractions above 70 per cent. That portion above 70 per cent could well be included in the hearts without affecting the properties of the latter but it is probably not possible to separate completely as small an amount of heads as were present in the crude, 2.5 to 3.0 per cent, without removing some of the hearts at the same time.<sup>1</sup>

*Hearts.*—The analysis of the hearts is shown in Figure 24; there is apparently no material in the hearts with boiling points below 158°C., and the color and odor of the first fractions were not markedly different from those of the next few fractions; that is, the separation of the heads from the hearts was complete. This separation of the low boiling constituents improved both the color and odor of the refined turpentine, making it almost colorless and leaving only a faint trace of the "destructive distillation" odor. There was a small amount, about 6 per cent, of heavy material in the hearts, showing an incomplete separation from the tails.

<sup>1</sup> The heads, on account of the method of their production could not contain any heavy oils and the higher physical properties of the residue in this analysis (and in the analyses of all the other heads) must be due to polymerization during the distillation (See page 62.).

*Tails.*—The tails were analyzed (Figure 25) only to determine how good a separation was obtained between the tails and the hearts. All the properties of the first fraction (9 per cent) of the tails were higher than any fraction of the hearts, except, of course, the residue. But since the composition of the distillate was changing rapidly at this point (the curves all slanting decidedly) it is probable that a small amount of this first fraction was composed of material with properties the same as some portion of the hearts; perhaps 3 to 4 per cent of the tails were composed of materials which should have been in the hearts.

### *Refining of Crude Turpentine No. 2*

#### *Method of Production*

This crude turpentine was produced at a plant using "light-wood" as a raw material. The process of distillation was the steam process and was different from the usual steam process only in the small size of the chips and in the steam pressure used, which was about 50 pounds.

#### *Analysis*

The analysis of this crude is shown in Figure 26. There were no evidences in this crude of low boiling material similar to that in Crude Turpentine No. 1, but the odor of the first fraction was quite different from the second, and it was decided to separate a small amount of heads in order to find if the odor of the hearts was improved. This crude turpentine is seen to contain about 60 per cent "pinene," 8 per cent dipentene and 32 per cent heavy oils. It was decided to attempt to obtain about 4 per cent of heads, which would leave about 64 per cent of turpentine material to be separated as hearts.

#### *Distillation*

The crude was run into the still at a speed varying from 24.8 gallons per hour to 25 gallons per hour; the heads were kept as close as possible to 1 gallon per hour (varying from 0.5 to 1.5 gallons per hour) and the hearts varied from 15.7–16.1 gallons per hour. Except for the rather large variation in the heads, the distillation seemed to run smoothly.

### *Products*

The analyses of the products are given in figures 27, 28 and 29.

*Heads.*—Although the difference in odor between the heads and the hearts was quite noticeable, they did not show any great difference in other properties; the odor of the first 10 per cent of the heads was also somewhat different from the rest of the fractions. The amount of material present in these heads with properties different from the main part of the turpentine (hearts) is therefore very small in proportion to the original crude, so small that it is impracticable and really unnecessary to separate it.

*Hearts.*—The hearts contain only about 3.5 per cent of heavy material, and the gravity of this portion is only slightly greater than that of the main part of the hearts, the gravities being 0.885 and 0.863 respectively, which shows a very satisfactory separation of hearts and tails.

*Tails.*—The tails, however, contain a small amount of material which might have been included in the hearts. The properties of the first fraction of the tails (7 per cent) are higher than any portion of the hearts except the residue, but the difficulty of completely separating in one distillation a small amount of turpentine material, from a large proportion of higher boiling material like the "pine oil," and the fact that the properties of the distillate were changing rapidly when this fraction was taken both indicate that there was a considerable proportion of turpentine material present in this first fraction of the tails. Perhaps 5 per cent of these tails were composed of turpentine materials. This is, however, a fairly satisfactory separation, only 5 per cent of 32 per cent, or 1.6 per cent of the original crude, not being properly separated.

### *Refining of Crude Turpentine No. 3*

#### *Method of Production*

This turpentine was obtained from a destructive distillation plant using "lightwood" as a raw material; the distillation process is very similar to that employed by the hardwood retort plants in the North, the horizontal cylindrical retorts holding



about one cord of wood and the complete distillation taking only twenty-four hours. The total distillate is condensed and collected together and the pyroigneous acid removed from the crude oil by settling. The crude oil thus obtained is distilled with steam until nearly all the volatile oil is removed. The crude turpentine used in the refining experiments was a sample of the distillate obtained from the crude oil as above.

### *Analysis and Chemical Treatment*

The analysis of the crude is shown in Figure 30. It can be seen from the curves that this crude is a very complex mixture since none of the properties remain at all constant over any considerable portion of the distillation; a large part boils below the usual boiling point of turpentine, and the specific gravity over the complete range of the distillation is higher than any portion (except the residue) of a refined turpentine should be. All the fractions were also colored and had very disagreeable odors. It was seen therefore that no separation by distillation alone could give any amount of distillate with properties suitable for a refined turpentine, and that a chemical treatment was necessary before refining by distillation. The crude was therefore agitated with caustic soda solution at 55° C. until there was no more action, which is shown by treating a small amount with additional caustic soda at the same temperature without any change in color of the caustic solution resulting.

The analysis of the crude treated in this manner is given in Figure 31. The proportion of material boiling below 155° C. was decreased considerably, the specific gravity of all the fractions was decreased, and the color and odor of all the fractions improved. The index of refraction curve was, however, somewhat irregular, and all the fractions still retained some disagreeable odor. That portion of the distillate between about 11 per cent and 64 per cent was more suitable for a refined turpentine than that above or below and it was therefore decided to separate the treated crude into 11 per cent heads, 53 per cent hearts, and 36 per cent tails.

### *Distillation*

The crude was run into the still at a speed of 25 gallons per hour and the speeds of the heads and hearts were maintained as nearly as possible at 11 per cent of 25 or 2.75 gallons per hour and 53 per cent of 25 or 10.75 gallons per hour respectively. During this distillation great difficulty was experienced in regulating the speed of the products and the effects of this are seen in the composition of the products.

### *Products*

The analyses of the products are shown in figures 32, 33 and 34.

*Heads.*—The heads, Figure 32, contained about 80 per cent of material of complex composition with widely varying boiling points and indices of refraction; the color of this portion was also darker and the odor much more disagreeable than the last 20 per cent. The properties of this last 20 per cent were such that it could well be included in the hearts, that is, the separation of heads from hearts was not complete.

*Hearts.*—As far as the specific gravity and index of refraction of the first fraction of the hearts, Figure 33, are concerned, it would seem that the separation of the heads from the hearts was complete, but the boiling point, the odor and color of this first fraction indicated that a small amount of heads material was present in the hearts. This incomplete separation between the heads and hearts was probably largely due to the variation in the speed of the heads; this speed varied from 3.1 to 2.3 gallons per hour and while the heads were running at 3.1 gallons per hour, some hearts material would be distilled over with the heads, and when the speed dropped to 2.3 gallons per hour some heads material would escape in the returns from column A<sub>1</sub> to column A<sub>2</sub> and thus get into the hearts. The hearts also contained probably more heavy material with boiling points above 180°C. than is desirable in a well refined turpentine.

*Tails.*—The tails, Figure 34, contain about 5–6 per cent of hearts material showing an incomplete separation of hearts from tails.

*Refining of Crude Turpentine No. 4**Method of Production*

The turpentine plant from which this sample of crude was obtained is operated in connection with a sawmill cutting almost exclusively longleaf pine. The raw material for the distillation consists of all the sawdust normally produced in the mill, together with the waste slabs, edgings, trimmings, etc., the large-sized material being "hogged" before it is conveyed to the turpentine plant. The steam distillation process is used, the maximum pressure in the retorts being 10 pounds.

*Analysis*

The analysis of this crude turpentine is given in Figure 35. This crude is of simple composition in comparison with Nos. 1, 2 and 3, being composed of about 84 per cent of turpentine and 16 per cent pine oil, with no evidences of the presence of any dipentene, or of any heads, except that the odor of the first fraction was somewhat different from the next few fractions.

It was desired to obtain one refined steam distilled turpentine containing comparatively large amounts of pine oil in order that the technical properties of two turpentines similar in composition, except for the proportion of pine oil present, might be compared. It was decided therefore to separate this crude into about 2 per cent heads, 88 per cent hearts, and 10 per cent tails and thus obtain a refined turpentine with more heavy oils than No. 2, the other steam distilled turpentine refined.

*Distillation*

The crude turpentine was run into the still at the rate of 24.8 gallons per hour. The speed of the heads varied from 0.2 to 1.0 gallons per hour with an average of about 0.5 gallons per hour, and the hearts varied from 20 to 23 gallons per hour with an average of about 21.7 gallons per hour.

*Products*

*Heads.*—The analysis of the heads from this run, Figure 36, showed that only a very small amount of material different from

the main portion of the turpentine is present. The first fraction of 1.5 per cent had a slightly lower index of refraction than any of the rest of the fractions, and the odor of the first 10 per cent of the distillate was quite different from the rest of the distillate. As in the case of Crude Turpentine No. 2, however, the amount of this material is so small, and its properties are so slightly different from the rest of the turpentine, that it is unnecessary to attempt to separate it.

*Hearts.*—The analysis of the hearts, Figure 37, showed about 6.5 per cent of pine oil present, as was to be expected from the manner of regulating the distillation.

*Tails.*—The tails, Figure 38, were apparently entirely free from hearts material, the very high values for the physical properties of the first fraction of 6.5 per cent, indicating that only a very small proportion of this fraction could possibly be made up of turpentine material. The separation in this case is therefore very satisfactory, the hearts containing probably no more heavy material than is allowable in a good grade of turpentine, and the tails being practically free from turpentine.

#### *Products Obtained by Commercial Refining Method*

In order to obtain a comparison between the efficiency (as regards completeness of separation) of the column still used in this investigation and that of the ordinary pot still used in practice, samples of the turpentine and pine oil, refined at the plant where this crude turpentine was produced, were obtained and analyzed. The samples were both from the same charge of crude and were refined by a single distillation with steam. The turpentine, Figure 39, is seen to contain about 12 per cent of heavy oils while the pine oil, Figure 40, contains about 30 per cent of turpentine, showing that a very incomplete separation was obtained.

#### *Refining of Crude Turpentine No. 5*

##### *Method of Production*

This crude turpentine was produced from "lightwood" by means of the bath process of distillation. The "lightwood" in cordwood form is loaded on cars and run into the large horizontal

cylindrical retorts, then the hot bath material, pine tar pitch, is circulated through the retort, the "extractor" and the furnaces in the order given. In the furnaces the temperature of the bath material is kept up to the maximum of 195° C. In the extractor live steam is blown through the bath to remove the volatile oils which are carried by the bath from the retort. These volatile oils constitute the crude turpentine used in the refining experiments.

### *Analysis*

The analysis of this crude turpentine is given in Figure 41. There was no evidence of any heads material in this crude except a slightly different odor in the first fraction; and apparently about 57 to 58 per cent could be obtained which would contain a very small amount of heavy oils. It was decided therefore to attempt to separate the crude into the smallest possible amount—2 per cent—of heads, 55 per cent of hearts and the rest tails.

### *Distillation*

The crude was run into the still at the rate of 25 gallons per hour, and the steam and water were adjusted to give as nearly as possible 0.5 gallons per hour of heads, and 13.75 gallons per hour of hearts; these adjustments were maintained within the usual limits of variation.

### *Products*

*Heads.*—The analysis of the heads thus obtained is given in Figure 42. From the boiling point and index of refraction curves it is apparent that the first 10 per cent of the distillate contains a small amount of material with properties somewhat different from the rest of the distillate, and this was further indicated by the odor of the first fractions. As was the case with Turpentine No. 2 and No. 4, however, it is probable that there is so little of this material present that it is not only impracticable but unnecessary to attempt its separation.

*Hearts.*—The hearts, Figure 43, are seen to be almost free from heavy oils, only about 2 per cent of material with a gravity of .890 being present, and the low gravity and index of the residue indicating that even this 2 per cent is largely composed of sub-

stances similar to the last few fractions of the distillate. A very nearly complete separation of hearts free from tails was therefore accomplished in this run.

*Tails.*—The tails, however, are seen (Figure 44) to contain probably 15 per cent of hearts material, so that the separation of tails free from hearts was not complete.

### *Commercial Scale Refining*

The refining done on the five crude turpentines described above was intended not only as experiments in refining, but also as a study of the composition of crude wood turpentines and the products obtainable from them, and especially as a means of obtaining samples of wood turpentine with known compositions and methods of production, so that these samples might be used in tests to determine the industrial value of wood turpentines of different composition. The best conditions for the different distillations were not studied, the arrangement of the still was not changed throughout the experiments, and only in two cases were the distillations repeated in order to secure better results. It must not be considered therefore, that the best possible results were obtained, or that the most suitable arrangement of the column was used in all cases. The composition of the crude turpentines Nos. 2, 4 and 5, for instance, was such that the separation of constituents with boiling points below those of refined turpentine was not necessary, and instead the production of a refined turpentine and a refined pine oil would have been preferable, but the arrangement of the column was not suitable for the production of these last products, and therefore in no case was a refined pine oil produced.

It will be interesting in this connection to give a brief statement of some of the results obtained in another piece of work in which more nearly commercial conditions prevailed and in which the column was arranged for the production of a refined pine oil as well as a turpentine.

### *Field Work on Crude Turpentine No. 5*

In this work the still was set up at the plant where the crude turpentine No. 5 was produced. The general arrangement of

the still was the same as in the previous work except that the crude reservoir was modified so that continuous long runs could be made and the grouping of the sections was changed so that the upper column,  $A_1$ , contained 13 boiling cap sections and three reflux condenser sections while the lower column,  $A_2$ , contained only five boiling cap sections and two reflux condenser sections. The refined turpentine was distilled from  $A_1$  and the refined pine oil from  $A_2$ . (See Figure 20) The analyses of the products obtained from one run shown in figures 45 and 46 give a good idea of the separations obtained under these conditions; the turpentine contained about 4 per cent pine oil, and the pine oil contained about 2 per cent turpentine.<sup>1</sup> This seemed to be about the limit of the completeness of separation possible, since with larger proportions of pine oil in the turpentine, the amount of turpentine in the pine oil decreased, and vice versa.

Another point of interest obtained in this piece of work was on the test for determining the proper control of the distillation; the control of the still by the specific gravity of the products rather than by the speed of the products was found to be very easy. In this case where the specific gravities of the two constituents to be separated were so different, (say, 863 and 945) such a method of control was very delicate, but in a case like the distillation of crude turpentine No. 3 where two products (heads and hearts) with gravities very nearly the same are to be separated this method would not be applicable.

<sup>1</sup> It will be noticed that figures 45, and 46 are different in many ways from the distillation curves shown previously; index of refraction curves are not given, the boiling point values are uncorrected, and the percentages are by volume and not by weight. These represent the results from such analyses as can be obtained with apparatus which is readily transportable and which can be set up and used without many of the conveniences of the ordinary chemical laboratory. Two 50 c.c. cylinders graduated to 1 c.c. and one 500 c.c. measuring flask can take the place of the more delicate balance in determining the percentages of distillate, and for rough field work the refractometer and barometer can be dispensed with; otherwise the method is the same as previously described. For many purposes a simpler method of this kind is entirely sufficient but for close, careful work the refinements mentioned in the description of the method on pages 66-68 are necessary.

### *Summary of Results of Refining Experiments*

The crude turpentines described above are sharply divided into two groups according to their composition, and the methods used in their production. The methods necessary for their proper refining naturally follow the same grouping, which is as follows:

Group 1. Includes crude turpentines Nos. 2, 4, and 5 which were produced at temperatures below 200° Centigrade.

Group 2. Includes crude turpentines Nos. 1 and 3 which were produced at temperatures above 200° Centigrade.

The following conclusions have been reached for the refining of crude wood turpentines like those of Group 1:

1. A fractional distillation without chemical treatment is sufficient for the production of good grades of turpentine and pine oil.

2. The separation of light oils with boiling points lower than those of the turpentine, is unnecessary.

3. Better separation of the turpentine from the pine oil or, in other words, a greater purity of the final products is obtained with a column still than with an ordinary pot still.

In the refining of crude wood turpentine like those of Group 2, the following conclusions apply:

1. A chemical treatment is required before a distillation can produce a good grade of refined turpentine.

2. The color and odor of the refined turpentine obtained from the chemically-treated crudes by distillation are much improved by the separation of the "light oils" with boiling points lower than those of the turpentine.

3. Although no data are given here to show the results obtained in an attempt to separate the "light oils" by distillation in an ordinary pot still yet it is probable such a separation could not be made successfully.

### COMPOSITION OF WOOD TURPENTINES

Nearly all the experimental work done in connection with this investigation has already been recorded in the previous pages and this division will consist mainly in correlating and discussing some of the data already given, together with information along the same line from other sources.



*The Relations Between Composition and Methods of Production*

If the crude turpentines are arranged according to the maximum temperatures of their production, the order would be Nos. 4, 2, 5, 1 and 3 (See description of methods of production under each crude turpentine.) The proportion of dipentene in the refined turpentines prepared from these crudes increases in the same order as the maximum temperatures of production (See Figs. Nos. 37, 38, 43, 14 and 33). The comparison of the maximum temperatures with the proportion of dipentene in the *crude* turpentines would have been perhaps more proper, but the analyses of the crude turpentine do not in all cases indicate the proportion of dipentene present, as for instance, in Crude Turpentine Nos. 1 and 3, Figures 21 and 30.

As would be expected also there is a relation between the maximum temperatures and the amount of "light oils" (with boiling points below 157° C.); in Crude Turpentines Nos. 1 and 3 produced at (unknown higher temperatures, light oils are present).

A similar relation also holds between the maximum temperatures of production and the amount of products removable by treatment with caustic soda. These relations between composition and temperature of production are given in tabulated form below:

Table 2. Relations between composition and temperature of production for crude wood turpentines

Crude Turpentine No.	Maximum Temperature of Production	Dipentene in Refined Turpentine	Light Oils Boiling Point Below 157° C. insoluble in NaOH	Oils, Soluble in NaOH
4	116° C.	Practically none <sup>1</sup>	None	None
2	148° "	About 10%	"	"
5	195° "	" 15%	"	"
1	High	" 25%	About 3%	Some
3	Higher	" 40%	" 11%	More

<sup>1</sup> For a more probable reason than difference in temperature for the smaller amount of dipentene in Turpentine No. 4 see page 83.

*Comparison with Composition of Gum Turpentine*

Before this comparison can be made it will be necessary to add a few words on the composition of gum turpentine to supplement Figure 2. A study of the variation in composition of gum turpentine now in progress in the Forest Products Laboratory indicates that the volatile oil freshly distilled from the oleoresin obtained by chipping live trees of longleaf pine, contains only very small amounts of heavy oils (with gravity above .875). Therefore the 5 per cent of heavy oils shown in Figure 2 are probably due to a partial oxidation of the terpenes in the original freshly distilled oil. Except for the presence of these heavy oils, Figure 2 may be considered as representing the composition of a typical gum turpentine; the only difference between this and other gum turpentine would be in the range of the values for the physical properties of the fractions; in some cases the range of values would be slightly lower; in others, slightly higher.

*Heavy Oils*

The volatile oil obtained by the distillation of pitchy wood from the long leaf pine contains, however, considerable quantities of heavy oils (See analyses of the crude turpentine.) and the presence of these in refined wood turpentine is, therefore, very probable because complete separations of heavy oil from turpentine can not be made even with an efficient column still. Even less perfect separations can be made with the pot stills commonly used, and there is a natural tendency on the part of the refiner to increase the proportion of refined turpentine which can be obtained from the crude turpentine by increasing the proportion of heavy oils in the refined product.

The usual presence of heavy oils in wood turpentine and their usual absence in gum turpentine is then the first difference between these two classes of turpentine. Even in an old gum turpentine which does contain heavy oils (like Fig. 2) it is probable that the composition of these heavy oils is different from those in wood turpentine (See section on Heavy Oils, page 88).

### *Dipentene*

The presence of dipentene in many wood turpentines and its absence in gum turpentines is another possible difference. The refined turpentines obtained from four of the five samples of crude turpentine described contained dipentene and it is probable that most wood turpentines will contain appreciable amounts of this substance. In some seventy-five samples of gum turpentine which have been examined in the Forest Products Laboratory no dipentene has been detected by the method of analysis used. It appears that the presence of dipentene in wood turpentine is not entirely due to the temperature to which the turpentine is subjected, because most gum turpentines have been subjected to temperatures of at least 150° C. during their distillation, and yet crude turpentine No. 2 which was produced at 50 pounds steam pressure (148° C.) contained considerable quantities of dipentene. Dipentene was also found in the volatile oil distilled from lightwood by steam at atmospheric pressure.<sup>1</sup> The influence of temperature is indicated by the increased amounts of dipentene in wood turpentines produced at high temperatures. The dipentene in wood turpentine may then come from two sources, (1) from the dipentene present in the volatile oil as contained in the wood and (2) from the transformation of some of the "pinene" into dipentene by the high temperatures used in the distillation.<sup>2</sup>

### *Light Oils*

The presence of "light oils" in the wood turpentines produced at higher temperatures is another possible difference. It is possible to refine a crude turpentine containing light oils so that the refined turpentine shall be free from light oils (as in the case of crude No. 1) but the separation is difficult and can not readily be made without some kind of a fractionating column. If light

<sup>1</sup> Distillation experiments at Forest Products Laboratory, the report on which has not yet been published.

<sup>2</sup> The absence of noticeable amounts of dipentene in Turpentine No. 4 may be explained from its source—green sawmill waste; that is, old, dead, lightwood or stumps may contain dipentene while green freshly cut timber, may not. It is expected that these debatable points will be settled by some work now under way in this laboratory.

oils are present in the crude turpentine small amounts are liable to be found in the refined turpentine.

### *Rosin Oils*

The fourth possible difference between wood and gum turpentines is difficult to describe since it does not greatly affect the physical properties expressed in the distillation curves. For instance, in the analysis of refined turpentine No. 3 (Figure 33) it was quite noticeable that the odor and color of all the fractions were different from the similar fractions of other turpentines. Except for the small amount of "light oils" present (See p. 87) the peculiar odor and color apparently did not tend to concentrate either in the first or last fractions, but were distributed rather evenly throughout the distillate. These properties were therefore probably due to the presence of some materials other than terpenes, with boiling point, gravity, and index of refraction not much different from the terpenes, the only very strong indications shown in the distillation curves of the presence of materials other than terpenes being in the high index of refraction of the first 30 per cent. From the method of production of this turpentine these other materials can only be high temperature decomposition products of wood fiber or of rosin. Decomposition products of wood fiber could not be present in very appreciable proportion because it is known that the oils from this source insoluble in caustic soda, with boiling points  $155^{\circ}$  to  $180^{\circ}$  and gravity in the vicinity of .85 to .87, are extremely small in amount. It is known, however, that from the destructive distillation of rosin yellow oils answering these requirements can be obtained; the odor of these rosin oils (rosin spirits, rosin naphtha) is very similar to the fractions of this destructively distilled wood turpentine and it is very probable that the peculiar characteristic odor and color of destructive wood turpentines are due largely to the presence of "rosin spirits."

These comparisons of composition have shown that most wood turpentines will be sufficiently different in composition from gum turpentines so that the method of analysis used in these investigations will readily distinguish between them; a wood turpentine produced from green timber at such low temperatures that no

dipentene is formed and so refined that no heavy oils are present is, however, very similar to a gum turpentine. That is, the terpenes present in the wood from a freshly-cut longleaf pine tree are very similar to the terpenes in the oleoresin obtained by chipping the live longleaf pine tree. The boiling point, the specific gravity, and the index of refraction curves from the two turpentines are not very different, but in general these properties seem to be slightly lower in the fractions from the wood turpentines (Compare Figures 2 and 37.). This difference is, however, not great enough to provide a sure means of distinguishing between the two kinds of turpentines since a gum turpentine with especially low values for the physical properties might be almost the same as a wood turpentine with especially high values. It is probable, therefore, that the same constituents are present in each but that more of the higher boiling and higher gravity terpenes are generally present in the gum turpentines.

#### *Odor*

There is a considerable difference in odor between the gum turpentines and the wood turpentines even between these which are nearest alike in composition, but in most cases this difference in odor is not due to differences in the main constituents present. For instance, in the refined turpentine from No. 4 it is very probable that the main constituents are the same as in the gum turpentine shown in Figure 2, and yet there was a decided difference in the odor of these two turpentines. Even the presence of dipentene does not entirely account for the difference in odor between wood and gum turpentines, it being noticeable that refined turpentines No. 2 and No. 5, both of which contained considerable quantities of dipentene, resembled gum turpentine in odor more than the products from No. 4 which was more nearly like gum turpentine in composition. It seems likely, therefore, that the distinctive odor of many wood turpentines is due to some material which occurs in so small a quantity that its presence is not readily indicated in any other manner than by the odor. The odor of a wood turpentine like No. 3 is probably due to the presence of rosin spirits, as mentioned on page 84.

*Effect of Differences in Composition on Technical Properties*

Since the reports on the industrial values are not included in this bulletin, it may be necessary to correct the impression in regard to the value of wood turpentine which has perhaps been given by the above discussion. The chief valuable properties of turpentine are usually considered to be its volatility, its solvent power, and its "drying" properties.

*Volatility.*—The volatility of wood turpentines would probably not be greatly affected by the differences in composition mentioned above, this property being measured approximately by the range of boiling points of the various constituents. Large quantities of heavy oils would of course decrease the volatility, but it is doubtful whether the effect of small quantities up to 10 per cent would be noticeable in practice.

*Solvent Properties.*—It is very probable that the solvent properties of dipentene are quite similar to those of "pinene" since these terpenes are so much alike in other respects; the solvent properties of the other materials which do not occur in gum turpentines but which may be present in wood turpentine are probably sufficiently similar so that the small proportion of these which may be present does not appreciably effect the solvent properties of the mixture.

*Drying Properties.*—In drying properties dipentene is apparently equal to "pinene" since it has been found that the time required for drying a mixture of dipentene and linseed oil is the same as for drying a similar mixture of "pinene" and linseed oil.<sup>1</sup> In the case of the drying properties also it is possible that small amounts of rosin spirits, light oils or even heavy oils would not greatly affect the value of the turpentine. Until further data are available on the relation between the composition and industrial value of turpentines, the differences in composition between wood and gum turpentine should not be considered as necessary indications of corresponding differences in value.

<sup>1</sup> Unpublished Mss. on "Terpenes as Oxygen Conveyors," by Edward Kremers.

*Changes in Composition after Refining*

The analyses of the refined turpentines given above in the description of the refining work were made within a few days after the refining. These samples were all kept for considerable periods afterward, some being stored in glass carboys and others in wooden barrels or iron drums, and analyses were made from time to time in order to determine if any changes in composition had taken place. Since the methods of storage were not the same in all cases the results are not accurately comparable either with each other, or with ordinary commercial conditions of storage, but they do indicate, however, the kind of changes and the possible amount of such changes which may take place during storage.

Refined Turpentine No. 1, the original analysis of which is shown in Figure 24, was analyzed again after six months. (See Figure 47.) The only change which had taken place in this time was an increase in the amount of heavy residue from about 6 to 10 per cent; the odor and color had not been appreciably affected.

Refined turpentine No. 2 (original analysis Figure 28) was analyzed again after nine months (See Figure 48.); during this period the heavy residue had increased from 3.5 per cent with a gravity of .885 to 5.5 per cent with a gravity of .94. Otherwise the sample seemed to be unchanged, still being colorless and with no appreciable change in odor.

Refined turpentine No. 3 (original analysis Figure 33) was analyzed after a period of nine months (See Figure 49.); no indications of change in composition were observed.

Refined turpentine No. 4 (See Figure 37.) was analyzed after a nine months' period (See Figure 50.); no apparent change in composition had taken place meanwhile.

Refined turpentine No. 5 (See Figure 43.) was analyzed again after three months (Figure 51); during this short time the amount of heavy residue had increased from 2 per cent with gravity of .885 to 4 per cent with gravity of .92. Other analyses were made six and ten months (figures 52 and 53, respectively) after the original analyses; the amount of heavy residue increased gradually with the time. At the time of the last analysis a considerable yellow color had developed in this sample, perhaps from the

natural process of "aging" or more likely by contamination from an incompletely cleaned iron drum in which it was stored during a part of the time. In order to remove this color and also part of the heavy residue the sample was redistilled with steam in a small laboratory still without a fractionating column; the composition of the redistilled turpentine is shown in Figure 54.

#### *Composition of Heavy Oils in Wood Turpentine*

The presence of considerable quantities of heavy oils in the crude wood turpentine produced by steam distillation (See Analyses of crude turpentine Nos. 2 and 4, figures 26 and 35) indicates that some heavy oils occur in the wood as such and are not formed during the distillation process. Experimental work on the steam distillation of longleaf pine has further confirmed these indications since it was found that the proportion of heavy oil in the crude turpentine did not seem to be directly influenced by the temperatures of the distillation.

In the usual commercial refining practice these heavy oils are distilled over after the turpentine and are marketed without further treatment as "pine oil." It was probably a sample of this "pine oil" which was examined by Schimmel and Company,<sup>1</sup> who identified the following bodies:

$\alpha$ -pinene,  $\beta$ -pinene (nopinene), camphene,  $\iota$ -limonene, dipentene, cineol, fenchyl alcohol, camphor, borneol, methyl chavicol, and  $\alpha$ -terpineol. The first six of these, on account of their low boiling points (all below 177° C.) are to be considered as normal constituents of the refined turpentine<sup>2</sup> which, however, occurred

<sup>1</sup> Semi annual Reports April, 1910, page 100.

<sup>2</sup> With the exception of limonene and cineol, these low boiling constituents have been indicated as probable constituents of wood turpentine by the distillation curves previously shown (See p. 15 especially).

On account of the similarity between the two substances limonene could not be distinguished from dipentene by its effect on the distillation curves. Therefore limonene might have been present in any of the wood turpentine which contained dipentene. Cineol, however, has a considerably higher gravity (.930) and a lower index of refraction (1.458) than dipentene and a boiling point (176°-177° C.) which is near enough to that of dipentene so that the two would occur in the same fractions. It is probable therefore that very large quantities of cineol could not have been present in those turpentine whose distillation curves show a decreasing gravity and increasing index of refraction between 170° and 180°.



in the "pine oil" on account of incomplete separation in the refining.

The last five constituents have boiling points above 200° C. and may be considered as normal constituents of "pine oil" although, of course, small amounts of these substances may be present in the refined wood turpentine. (See page 82.)

Since none of these five substances are known to be produced by the rapid oxidation of "pinene" or of the other terpenes in turpentine it is probable that the composition of the heavy oils in a wood turpentine (due to incomplete separation in refining) is not the same as those in a gum turpentine (produced by atmospheric oxidation). (See page 82.)

The heavy oils in destructively distilled wood turpentines probably consist of these same materials together with some decomposition products of the rosin (rosin oils).

#### *Specifications for Wood Turpentines*

It is seen from the above comparisons that specifications for gum turpentine based on the physical properties would not be applicable to all classes of wood turpentine. The presence of dipentene especially would make such specifications inapplicable because dipentene has a lower specific gravity and at the same time a higher boiling point than the terpenes in a gum turpentine. It might also be desirable to have one set of specifications which could include wood turpentines containing small amounts of low boiling material (like No. 3 shown in Figure 33) and such turpentines would certainly be excluded by any specifications based on the properties of gum turpentine.

It is apparent that in the preparation of specifications for turpentine these possible variations in composition must be taken into account and it is probable that some method of examination must be used which will differentiate (1) between high boiling points due to dipentene and high boiling points due to heavy oils; (2) between low gravity due to dipentene and low gravity due to adulterations and (3) between low boiling points due to incomplete separation of light oils and low boiling points due to the addition of substances not normally present in crude

wood turpentines. Such specifications can not be definitely recommended at the present time because there is not sufficient information available on the technical value of wood turpentines of different composition but meanwhile the method of analysis previously described will be of value in determining the composition of wood turpentines and the various distillation curves shown in this bulletin will furnish for comparison a good idea of the variation possible in authentic wood turpentines.

## APPENDIX

### *Practical Tests on Wood Turpentines*

Samples of each of the five wood turpentines, the refining of which is discussed in this bulletin, were submitted to the Paint Manufacturers' Association and to several manufacturers of paints and varnishes for testing. In these tests the sample turpentines were given the same numbers as the crude from which they were distilled. The sample numbers and the numbers of the corresponding text figures, which show the composition of the turpentines at the time they were sent out for test, are as follows:

Turpentine	Figure showing composition
No.	No.
1	47
2	48
3	49
4	50
5	54

The reports of the tests are given in full as submitted by the various coöperators. It is not the purpose to make a detailed analysis of the reports for the purpose of drawing conclusions in regard to the use of these turpentines in the paint and varnish industries. This can best be done by those thoroughly familiar with the requirements of these industries. However, the following significant facts are apparent.

1. The lack of concordance between the reports shows the futility of attempting to establish a general relation between the composition and industrial value of turpentines without

standard methods for determining the industrial value. The (individual) reports probably indicate very accurately the relative industrial values of the different turpentines so far as the particular company making the report is concerned, but no general relation is established.

2. Aside from the odor the wood turpentines do not seem to vary much from each other or from gum turpentine; at least the differences between the several turpentines as indicated in any one report are not greater than the differences reported for the same sample by different manufacturers.

3. Although the odor is the property most emphasized in the reports there is no unanimity of opinion on the relative odors of the different samples and in most cases the objection is that the odor is different from gum turpentines rather than that it is inherently objectionable.

The reports follow:

#### REPORT I

“Referring to the samples of turpentine which you sent us October 24th, we have completed the preliminary investigation, and in carrying through the tests, which were made comparatively, we have added to the five samples submitted by you, a sample of regular standard gum turpentine, marked “A” and a sample of our standard wood turpentine which we are regularly using, marked “B.” We found the specific gravities to be as follows:

A	.8680
#4	.8680
B	.8650
#3	.8650
#1	.8650
#2	.8635
#5	.8625

<i>Flash Point:</i>	A and B	(not taken)
	#3	113 Degrees Fahr.
	#1	109.4 “ “
	#5	105 “ “
	#4	103.6 “ “
	#2	101.8 “ “

*Staining Power:* (on white paper, least staining power ranked first)

#5 1st  
 A 2nd  
 #3 3rd  
 B 4th  
 #2 5th  
 #1 6th  
 #4 6th

*Evaporation:* (on white paper, shortest time ranked first)

#5 1st  
 A 2nd  
 #2 2nd  
 B 4th  
 #3 4th  
 #1 4th  
 #4 7th

*Odor:*

#5 and A-equal  
 #1-2-4 and B-equal  
 #3-objectionable odor and color.

“When used for varnish reducing, and carefully watched, we were unable to note any perceptible difference, either in setting or in completed drying after 24 hours. What we considered the most delicate test in practical use was in using them for thinning quick drying black, and the results here were as follows (the time given is in minutes and represents the time when the black had dried sufficiently hard to be varnished over without rubbing up)

A	50 minutes
B-1-2-5	90 minutes
#3 and 4	105 minutes

“After six days the quick drying black which had been thinned with these various turpentine was examined, and we found that a sample thinned with A showed little or no tendency to thicken up; #5 thickened slightly; and the balance had all thickened quite a little but showed practically no differences.

"In a general way I would say that it is our judgment that for the general purposes for which material of this kind is used, odor is the most important feature, inasmuch as unfortunate odor has been the greatest objection to a large use of this class of material in the past, and at the present time it is the main cause of the prejudice against it.

"From the standpoint of working qualities there is as you will note quite a decided action in slowing up the drying. I am not aware as to just what causes this, and of course for many purposes it would not be serious. There are many uses however for quick drying color where the time requirements are so imperative that none of these materials could be used. We do not understand why the same measure of influence on the drying does not show up in connection with varnishes, but as a matter of fact it does not.

"We should say that your sample #5 is decidedly better in general characteristics than any wood turpentine we have ever seen. In every point excepting the drying in quick drying black it shows up entirely equal to straight turpentine.

"#1-2-4 are satisfactory as wood turpentines, and would be usable for all purposes for which high grade wood turpentine is at the present time usable.

"The sample tested under "B" represents wood turpentine of which we have used a considerable quantity, and with which we have had practically no trouble excepting from the standpoint of odor.

"It is impossible at the present time to substitute wood turpentine for a pure spirits, in many places, on account of the stronger odor, and from this standpoint your sample #5 looks particularly interesting."<sup>1</sup>

<sup>1</sup>The large variation in the drying properties found by the quick drying black test indicated that this test offered a fairly simple method of determining the effect of the removal of the heavy oils on the drying properties. Small samples of each of the five turpentines were redistilled so as to prepare samples containing no heavy oils and these special samples were submitted for the drying test. It was reported that the time of drying of all the samples had been brought closer together and closer to that of gum turpentine.

## REPORT II

"Sample was taken from each can and compared in laboratory with pure gum spirits. The only objection raised being the decidedly objectionable odor in the #3 as well as the objectionable odor and slow evaporating in #5.

"The samples were then tested as a thinner or solvent in an ordinary House Paint and the same results obtained, the man applying the goods objected to the odor of both #3 and #5.

"I then melted a batch of varnish and divided it into six equal parts thinning five of these with the five samples of Wood Turpentine and the sixth part with pure gum spirits<sup>1</sup> so that the body or base of all are identical.

"After filtering and settling these six varnishes were submitted to practical tests by our head tester who reports as follows:

Working with Brush,	Good.
Drying	{ #3 and #6 best. #1, #2, and #4 fair. #5 slow.

"Color all up to standard, odor #3 and #5 strong odor, #3 most objectionable, #1, #2, and #4 fair, #6 sweet.

"In having this test made we took great care both in making and testing the varnish. The man who tested did not know that he was not testing a regular run of six batches of one of our standard varnishes which shows conclusively that he was doing his duty in an unbiassed manner and as you will note his report on odor corresponds with both laboratory report and test made by painter."

## REPORT III

"Material or Subject—Wood Turpentine Nos. 2, 3, 4, and 5. From—United States Dept. of Agriculture—Forest Products Lab.

Remarks—For a comparative test with Pure Gum Turpentine as to suitability for varnish making.

<sup>1</sup> Reported as No. 6.

	#2	#3	#4	#5	Gum Turps.
<i>I. Chemical Tests</i>					
Specific Gravity...	0.864	0.868	0.870	0.866	0.865
Residue on Evap...	0.64%	2.60%	0.79%	0.67%	about 0.60%
Iodine Absorption..	371.6%	298.7%	388.5%	392.9%	429%
<i>Distillation Test:</i>					
Boiling Point.....	154°C	155°C	150°C	153°C	154°C
-165°C.....	86%	40%	87%	91%	95%
165°-175°C.....	9%	44%	8%	6%	5%
Over 175°C.....	5%	16%	5%	3%	....
	100%	100%	100%	100%	100%
Color.....	W. W.	Pale Straw	W. W.	Very pale Straw	
Odor.....	Best Mild	Rank Penetra- ting	Third Greasy	Second Good but strong	

II. Varnish-making tests: Solvent power was tested by mixing 10 parts of each sample (also of Gum Turps.) with 1 part of a hard gum varnish. The pure turpentine precipitated the gum within  $\frac{1}{2}$  hour: #2 followed very shortly, then #5 (after about 6 hours). #4 held the varnish in solution, showing only a slight separation at the surface-edges after a week: #3 held the varnish in solution perfectly for more than two months.

“Other qualities were tested by reducing equal weights of the gum and oil from an agricultural varnish taken from the same batch, with equal volumes of the samples as well as with pure turpentine, in such a way as to have all conditions as nearly as possible the same. The varnishes so made were not filtered, but were allowed to settle and age for three months. The percentage of volatile matter was then determined and the varnish was submitted to the usual tests of body, flowing, drying, brushing, etc.

“The percentages of volatile matter were: For (I) varnish made with Gum Turps., 53.50; (II) #2 54.87; (III) #3 52.35; (IV) #4 53.32; (V) #5 54.10. The gum turp. varnish was the same in “body” as IV (as shown by the rate of rise of the air bubble in a

narrow test tube of the varnish); II and V were both slightly lighter in body, as would be expected from the higher percentage of volatile matter; but on the other hand III was still thinner, tho showing less volatile. This fact is doubtless due to the much greater solvent power of Turpentine #3, which results in a much less viscous solution.

"Varnish IV showed the poorest flowing qualities; V was slightly better, I and II (in order) still better, and III much the best. The drying test shows that the varnishes with lighter body dry faster and harder, tho II in drying faster than III, shows an exception. The relative order is II first, III, V, IV, I. From a consideration of factors involved, it is evident that if all were brought to the same body, II, V, and IV would dry at about the same rate, followed by III and I.

"In brushing qualities Varnish I was ranked first, V next, III next, followed by IV and II. This ranking denotes the comparative ease with which a smooth, glossy film of proper thickness can be obtained upon a filled board.

"The results of the tests may then be summarized as follows:

"The samples are all stronger solvents than Gum Turpentine, #3 being the strongest, #2 and #5 only slightly better than the Gum Spirits. If odor could be disregarded, #3 would probably be in all respects the best substitute for Gum Spirits and would be an improvement on it in some ways; but #3 is too disagreeable in smell to be used, except in small proportions. The choice therefore lies between #2 and #5, with the majority of points in favor of the latter."

## REPORT IV

### PAINT MANUFACTURERS' ASSOCIATION

*"Varnish Tests Made with Wood Turpentines Submitted by U. S. Forest Products Laboratory"*

"Two grades of varnish were made up from each of the wood turpentines—rubbing varnish, and spar varnish. The formulas used throughout in making up these varnishes are as follows:



RUBBING VARNISH				SPAR VARNISH			
By measure		By weight		By measure		By weight	
Gums....	21.4	Gums ....	27.97	Gums ....	16.4	Gums ....	20.17
Oils .....	19.4	Oils .....	18.62	Oils .....	42.3	Oils .....	41.5
Turps....	59.2	Turps ....	53.26	Turpentine	41.3	Turpentine	38.2
	—	Driers ....	.15		—	Driers ....	.13
Total ..	100.0		—	Total ...	100.0		—
		Total	100.00			Total	100.00

"In the manufacture of the varnishes it was noted that Nos. 2 and 4 had the best odor, while Nos. 1, 3, and 5 under heat gave off strong odors, somewhat irritating to the eyes. By heating up the various turpentines alone to 100° and observing the odor, the same result was obtained.

"The varnishes which were manufactured from these turpentines were applied to oak panels six inches wide, twelve inches high, and one inch thick. After the panels had been properly coated, they were subjected to a series of tests, and the data obtained from these tests is also recorded in the charts on the following pages.

#### *"Paint Tests with Wood Turpentines"*

"After the varnish test had been finished, the various turpentines were used to thin one standard paint formula, and this paint formula was applied to a series of panels to be placed on the Southern Test Fence. The formula selected for the test consisted of 45 parts corroded white lead, 45 parts zinc oxide, 5 parts of asbestine, and 5 parts of whitening. This paint was divided into portions and thinned respectively with the five turpentines submitted for test. The paint formula itself was made up in condition resembling a ready mixed paint, as found upon the market, but containing nothing in the vehicle portion except linseed oil and drier. This formula was thinned in the proportion of one pint of turpentine to a gallon of paint for the priming coat, and  $\frac{1}{2}$  pint turpentine and  $\frac{1}{2}$  gallon linseed oil for the second coat. The third coat was used without reduction. During the application of these paints the painter noted that No. 3 had a very objectionable odor, while Nos. 1, 2 and 4 had a very good odor, No. 2 probably being the best. In working and flattening

## EXTERIOR VARNISH

No. Panel No. No. of Coats Odor	1 I	2 II	3 III	4 IV	5 V
Action on eyes	Three Fair; resembles gum turpentine but not quite as nutty	Three Excellent odor; as good as pure gum turpentine	Three Extremely bad odor. Resembles pyroligneous acid and acetone	Three Fair; resembles turpentine	Three Fair
Ease of Application	None Slight ethereal odor	None Dries quickly	Extremely irritating	Very slight	None Easy
General Working Character	Easy Good	Pulls when dry	Easy	Easy	Easy
Color Density <sup>1</sup>	A	B	Easier than I or II	D	C
Period of Tackiness	A coat—3 hr. 30 min. B " 6 hr. 10 min. C " 6 hr. 00 min.	3 hr. 30 min. 6 hr. 10 min. 5 hr. 45 min.	2 hr. 50 min. 6 hr. 5 min. 5 hr. 35 min.	2 hr. 55 min. 5 hr. 35 min. 5 hr. 10 min.	2 hr. 55 min. 5 hr. 30 min. 5 hr. 15 min.
Period of Hard Drying	Allowed 2 days between application of first and second coats 4 days allowed between second and third coats	11 seconds	7.6 seconds (3 trials)	10.7 seconds (7 trials)	11 seconds (4 trials)
Body (Rise of a bubble 2.5 cm. long in a tube .8 cm. dia. and 28 cm. long)	10 seconds (Average of 3 trials)	11 seconds (4 trials)	7.6 seconds (3 trials)	10.7 seconds (7 trials)	11 seconds (4 trials)

1A, B, C, and D indicate degrees of darkness, A being darkest and D lightest.

## RUBBING VARNISH

	1 VI	2 VII	3 VIII	4 IX	5 X
No. Panel No.	Three	Three	Three	Three	Three
No. of Coats	VI	VII	VIII	IX	X
Odor	Fair; resembles gun turpentine but not quite as nutty	Excellent odor; as good as pure gum turpentine	Extremely bad odor. Resembles pyroigneous acid and acetone	Fair resembles turpentine	Fair
Action on Eyes	Slight ethereal odor	None	Extremely irritating	Very slight	None
Ease of Application	Easy	Works easily at first but dries quickly and pulls on rubbing	Very easy. Does not dry readily under brush	Harder to rub than VIII but easier than VII	Same as No. 2
General Working Character	Good	Good	Good	Good	Good
Color Density <sup>1</sup>	A	C	D	A	B
Period of Tackiness	A coat—1 hr. 35 min. B " 1 hr. 30 min. C " 2 hr. 30 min.	1 hr. 35 min. 1 hr. 25 min. 2 hr. 25 min.	1 hr. 20 min. 1 hr. 25 min. 2 hr. 20 min.	1 hr. 30 min. 1 hr. 30 min. 2 hr. 15 min.	1 hr. 20 min. 1 hr. 30 min. 2 hr. 10 min.
Period of Hard Drying	Allowed 2 days before applying second coat Allowed 4 days before applying third coat	9.8 seconds (5 trials)	6.7 seconds (5 trials)	9.8 seconds (7 trials)	9.0 seconds (8 trials)
Body (Bubble 2.5 cm. long rises in tube .8 cm. diameter and 28 cm. long)					

Temperature of laboratory during application of varnish A coat, 90.5° F. B coat, 93.2° F. C coat, 86° F. 1 A, B, C, and D indicate degrees of darkness, A being darkest and D lightest.

properties, Nos. 1, 2, 4 and 5 gave the best results, and fully as good results as with the use of pure gum spirits. . . .

"The evaporative values of these turpentine are satisfactory in every case, No. 3 evaporating more rapidly than the others, and none of them leaving any stain."

NOTE:—The panels painted with these test paints were exposed in September, 1910 (see Bulletin 30, Paint Manufacturers' Association), and the report of an inspection made in Feb., 1912, includes the following paragraph:

"The panels which were painted with pigment Formula 31 ground in pure linseed oil and reduced with various wood turpentine as thinners, indicated that the highest types of these materials were well suited to replace pure gum spirits of turpentine as a thinner for paints to be exposed out-of-doors. Wood Turpentine No. 2 gave the whitest surface, while Wood Turpentine No. 5 gave the darkest."

#### REPORT V

"#2, this is the best sample both in regard to odor and color and other qualities; it compares satisfactorily with Gum Spirits.

"#4 and #5, these rank about the same from our point of view, being somewhat inferior to #2. #4 is lighter in color but #5 has less objectionable odor.

"#1, this is next in quality to #4 and #5.

"#3, this is the least desirable of the lot, having very disagreeable odor and very dark in color. It also forms considerable residue when distilled with steam.

"From a commercial point of view, we believe that #2 could be used to a considerable extent in the Paint and Varnish Industries in place of Gum Spirits, but the odor of all the others would prevent their use except in a very small way."

## THE PAST, PRESENT, AND FUTURE OF THE NAVAL STORES INDUSTRY

BY CHAS. H. HERTY

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The limited use of the oleoresinous exudate of pine trees dates back many centuries, but the real beginning of an industry on a large scale is closely associated with the discovery of the vast pine forests which extend along the southeastern and southern coasts of the United States from North Carolina to Texas.

These forests lie chiefly in the coastal plain and in the slightly hilly country between the Piedmont plateau and the coastal plain, a strip varying in width from one hundred to two hundred miles and characterized by a sandy soil, covered for the most part with "wire grass," this furnishing a beautiful carpet of green in spring and summer, but making a serious fire risk in winter. The longleaf pine readily sheds its lower limbs, especially in close stands, so that the forests are remarkably open and free from that undergrowth, which, in the northwest, leads to such destructive forest fires.

The early settlers in eastern North Carolina began the exploitation of their forests of longleaf pine for the purpose of providing tar and pitch for use in the construction of wooden ships, and gradually extended their operations to the collection of crude turpentine which was shipped to northern cities or England for distillation. The forests covered the entire territory and, as clearings for farms were needed, destructive methods of operation were welcomed and encouraged.

At the same time limited operations were being conducted upon the maritime pine in southwestern France between Bordeaux and Bayonne. To receive the crude turpentine the French made use of a hole dug in the sand at the base of the tree. The oleoresin flowing from the wound on the trunk above was col-

lected in these holes. Necessarily by this method much of the material was wasted and rendered impure.

#### AMERICAN METHOD OF COLLECTION

In North Carolina the method of collection was improved, or thought to be improved, by cutting a large opening, the "box," in the base of the tree. Into this box the crude turpentine flowed and was collected at regular intervals. The conservative character of the men engaged in this industry led to the continuance of this wasteful and destructive method of "boxing" until the very recent past.

Briefly, the method of operating so long in use in the United States is as follows: In the winter the laborers are engaged in cutting "boxes." Each box is then "cornered," a wide chip being removed from each half of the box to provide a surface suitable for directing the flow of crude turpentine to the box. Meanwhile, other laborers are employed in clearing all combustible material from around each tree, "raking." Ground fires are then started to consume the dead wire grass, chips, etc. With the opening of Spring "chipping" begins. This consists in scarifying each week the trunk of the tree above the "cornered" surface by means of a "hack," a U shaped steel tool set in a wooden handle. Attached to this handle is a heavy iron weight to give momentum to the free arm swing used in chipping. After four or five weeks the "boxes" average a good filling and the crude turpentine, "dip," is then transferred to buckets by flat, iron paddles, and from the buckets it is collected in barrels conveniently placed in the woods. In the Fall, at the end of the chipping season, the hardened oleoresin, which has gradually collected during the chipping season on the scarified surface of the tree, is removed by scraping, giving thus the name "scrape" to this product, which is sold as "Gum Thus," or distilled. In the following Winter the trees are again raked and the grass fired, and in the Spring chipping is resumed at the point on the trunk of each tree where it ceased the previous year. This cycle is usually continued from three to four years, although in early days it was often continued ten or twelve years, the scarified surface extending high on the trunks. Necessarily

the yield from such high chipping was largely decreased, owing to the increased distance of flow to the receptacle.

In the early days of the North Carolina industry, no effort was made to distill the product, but gradually it became clear that it would be better to separate the crude turpentine into spirits of turpentine and rosin by distillation in the woods. For this purpose iron stills were used at first, but results were unsatisfactory until the introduction of copper stills, which were less liable to crack and could be heated with greater uniformity and better control.

The industry now began to grow rapidly and before many years it was found that the supply of available timber in North Carolina was rapidly decreasing. This led many of the operators to transfer their operations to the virgin forests of the adjoining state, South Carolina, where the same destructive methods were applied by the same men or their descendants. In this way, and for these reasons, the center of the industry has gradually moved southward and then westward as evidenced by the relative prominence of the ports for exports of the products; first Wilmington, N.C., then Charleston, S.C., then Savannah, Ga., and now the latter, together with Jacksonville, Fla., and the gulf ports, Tampa, Fla., Pensacola, Fla., Mobile, Ala., Gulfport, Miss., New Orleans, La., and others.

#### FRENCH IMPROVEMENTS

The steady growth of the American industry received a serious check during the Civil War. The consequent scarcity of the products was accompanied by an abnormal increase in their value. This enhanced valuation led Hugues, a Frenchman, to propose a less wasteful method for the French forests than the hole dug in the sand. He proposed as a substitute a clay pot, holding about one pint. This pot was supported on its bottom by a large nail driven into the tree and on one side of its upper rim by a strip of sheet zinc, approximately 2" x 4", slightly curved and driven into a corresponding upwardly inclined cut in the wood. This spout served to direct the oleoresin into the pot. At first his proposition was scoffed at and the peasants amused themselves by breaking the little pots. It is a pitiful

commentary that Hugues died in poverty; but his ideas lived and gradually became adopted in France.

#### AMERICAN IMPROVEMENTS

As the knowledge of the new method in France spread to this country, numerous efforts were made to apply similar forms of apparatus to the American system of chipping, but for many years such efforts failed. No less than fifteen patents were issued in the United States on this subject, but no one of them proved a commercial success.

Eleven years ago the writer began a series of field experiments on a small scale in the turpentine forests of South Georgia. One feature of these experiments was the use of a modification of the Hugues system, consisting of two separate metallic gutters, inserted in upwardly inclined cuts in the tree, along which the oleoresin flows. The upper and shorter gutter is separated at its lower end about one inch from the lower gutter and empties into it. The lower gutter extends from two to three inches beyond the center of the angular scarified surface formed in chipping, and serves as a spout to convey the oleoresin to a cup suspended from a nail just below the end of the gutter. These cups are made of either well burned clay or galvanized iron, and have a capacity of one quart.

Attracted by the promising character of these preliminary experiments, the U. S. Bureau of Forestry began a series of field tests of the apparatus on a large scale, the work being under the immediate supervision of the writer. Before the end of the first season of testing it was evident that the apparatus was a practical success, and the results attained, both as to quantity and quality of oleoresin, justified the hope of immediate commercial introduction of the system. But the habits of long years made difficult the adoption of such an innovation. This ultra-conservatism was slowly overcome and the adoption of the new system spread rapidly. Only a few years more will be required to witness the complete replacement of the "box" by the "cup" system in American forests. A detailed account of these experiments is given in Bulletin No. 40 and Circular No. 34 of the U. S. Bureau of Forestry.



With the main points at issue settled, namely—improved yields both in quantity and quality of the products and preservation of the trees, other forms of apparatus were devised to meet the objections of some of the operators to certain points in the cup and gutter system. Many of these have never proved practical, but some have been introduced on a considerable commercial scale.

The successful outcome of the experiments on the relative yields from the "box" and the "cup" system led the United States Forest Service to further experiments in more conservative treatment of the trees in chipping. Comparative studies were made of the yield from deep and shallow chipping and the latter found to give the greater yield during a period of four years of operation. Other experiments showed that a less rapid rate of ascent of the trunk also gave larger yields, and experiments combining these several modifications of present practices showed a largely increased yield. A final set of experiments pointed clearly the rational way to a perpetuation of the naval stores industry in America. The details of this investigation are given in Bulletin No. 90 of the United States Forest Service.

#### DISTILLATION

In the matter of distillation, only slight advances have been made in America. The uniform process consists in the use of a large copper kettle and condensing worm. The charge for a distillation averages nine to ten barrels of crude turpentine. The kettle is heated by free flame and during the distillation a small stream of hot water from the top of the condenser tub is admitted through an opening in the upper part of the kettle, thus facilitating the removal of the volatile oil. The condensed spirits of turpentine and water separate in the receiver, owing to difference in specific gravity, and the lighter spirits of turpentine is transferred to oak barrels, well coated with glue on the inside. No effort is made to redistill this product, and it always comes upon the market contaminated by a small amount of resin carried over mechanically during distillation. After most of the volatile oil has passed off, the still cap is removed, excess water in the kettle boiled off, and the molten rosin drawn off

through a tap in the bottom of the kettle onto a coarse wire filter, then through a second filter of fine mesh wire overlaid with cotton batting. The molten rosin is then dipped into wooden barrels luted with clay and solidifies on cooling. In this condition it is shipped to market.

The usual method of controlling the distillation is by the sound heard at the mouth of the condenser worm. Within the past three years a number of American operators have substituted for this method that of thermometer control with very excellent results.

In France, much more progress has been made in the art of distillation. Among the French distilleries there are three distinct types: first—a system closely resembling the American; second—distillation solely by steam in steam jacketed vessels; and third—a mixed system in which there is direct contact of fire with the kettle during the first stage of the distillation, then replacement of this by mixed injection of steam and hot water. By this means, a constant temperature is maintained, enabling the complete removal of all spirits of turpentine without danger of scorching the rosin.

It can readily be understood that in France, under proper methods of forestry, with conservative tapping of the trees and provision for systematic reforestation, a distillery can look forward to a permanent supply of raw material. Hence there is justification for the more costly plants and more efficient methods of distillation; but in America, where under past methods the industry shifts so rapidly so great an outlay of capital for this purpose would not be justified. There is no doubt that with an excellent "stiller" very good results can be obtained under the American system, but the personal element of the stiller enters into the question and this could be easily avoided without any great outlay of capital by adopting the French system of mixed injection.

Quite recently M. Castets has erected near Dax, France, a distillery which combines the features of continuous distillation in a partial vacuum and condensation by pressure of the waste spirits of turpentine vapors from the ordinary condenser in a

second condenser attached to the first, thus increasing notably the yield of volatile oil and improving the quality of the rosin.

#### THE INDUSTRY IN OTHER COUNTRIES

There is no need of any especial consideration of the Spanish industry which has developed considerably during the past decade. The operations are essentially the same as the French, and the same species of pine, *pinus maritima*, is exploited.

In Austria the industry is more limited and is even more destructive than by the old American system; a "box" being cut in the base of the tree, *Pinus Laricio*, and the trunk of the tree scarified for at least fifty per cent of its circumference, the oleoresin being directed towards the center of the scarified surface by thin wooden strips inserted in downward cuts in the tree.

In Russia the chief tree exploited is *Pinus Sylvestris*. Climatic conditions do not admit of the usual process of collecting the crude turpentine at regular intervals. Instead, the trees are scarified in Spring over a space about three feet high and almost encircling the tree. During the year a mass of hardened rosin collects on this surface. In the Winter it is scraped from the tree and distilled for its volatile oil and resin. This process is repeated for five years. The tree is then felled and the resinous portion of the tree subjected to destructive distillation. In other districts no effort is made to collect the rosin from the trees annually, but this is allowed to remain until the end of the fifth year of scarification. The tree is then felled and that part containing the rosin distilled first at a low temperature to obtain the volatile oil, then at a more elevated temperature to obtain tar and charcoal by destructive distillation of the wood.

The spirits of turpentine from Germany, Sweden, and Finland, seems to be a product solely of the destructive distillation of resinous wood.

The production of naval stores in India and other tropical countries is at present on too small a commercial scale to call for any detailed discussion here.

## WOOD SPIRITS OF TURPENTINE

Among the various departments of the naval stores industry in America none has had a more varied and interesting career than that of the production of "wood spirits of turpentine" by destructive distillation of resinous wood. Years ago considerable capital was invested in plants for utilizing the by-products formed during the destructive distillation of "fat lightwood." None of the plants were commercially successful and for awhile nothing was heard of the industry. But with the increase in price of spirits of turpentine resulting from the formation of the Turpentine Operators Association in 1902 a fresh impetus was given to the "wood spirits of turpentine" industry. At first somewhat crude methods of destructive distillation were advocated, and as the promoters of this industry appealed largely to local interest in having stumps for distillation removed from fields suitable for cultivation, a double impetus was received. Much enthusiasm was aroused, and a number of plants constructed. But the industry received a serious blow in the refusal of the varnish makers to use the impure "wood spirits of turpentine" manufactured, by the failure to find a market for many of the heavier oils and the coke, and by the destruction by fire of many of the improperly constructed plants.

The price of spirits of turpentine continued to rise and led to the development of the steam extraction process for manufacture of wood spirits of turpentine. After thorough grinding, the wood is treated in iron retorts with steam, and the volatile oil distilled, no effort being made to obtain any other product. By one redistillation of the product a very high grade spirits of turpentine is obtained, equal, if not superior, to that from the living tree. Unfortunately, the yield is not sufficiently large to make the process remunerative.

Quite a different process is employed by those plants which utilize a bath of molten rosin for removal of the spirits of turpentine from the wood, with subsequent distillation of the volatile oil from this bath. Such plants seem to have met with a fair measure of success.

More recently, extraction processes have been developed

which employ low boiling petroleum products as the extractive. Such plants recover both the spirits of turpentine and the rosin from the ground wood, and have a great advantage in the present very high value of rosin. These plants are also utilizing the refuse from the straining of rosin at the distilleries in the woods, a product formerly burned on the waste piles, but now bringing nineteen dollars per ton. This method is adding a considerable amount to the annual output of rosin.

The most recent development is a plant for destructive distillation of wood in retorts heated by jackets filled with high boiling petroleum fractions. By this means the fire risk is practically completely eliminated and the results indicate that by means of the complete and ready temperature control of the oil jacket larger yields of better products can be obtained.

#### ANNUAL PRODUCTION OF NAVAL STORES

No subject connected with the naval stores industry admits of so little accuracy of statement as does that of statistics on the total annual production. The most careful estimates are at best only approximations. This is unfortunate, for in the past it has frequently led to speculative manipulations of the market and the temporary establishment of values which had no legitimate basis depending on supply and demand.

The following table of annual production is given therefore, as an approximation only, but it is believed to be a reasonably accurate approximation:

	Spirits of Turpentine (barrels 52 gallons)	Rosin (barrels 500 lbs.)
America.....	600,000	2,100,000
France.....	100,000	350,000
Spain.....	25,000	87,500
Austria.....	3,000	10,500
Other countries.....	50,000 (?)	(?)
Total estimated production....	778,000	2,548,000

## PRODUCTION OF CRUDE TURPENTINE PER TREE

Here again definite figures are difficult to give; for there is no reliable information concerning the number of trees in operation. Furthermore, there is often very wide variation in the producing power of adjacent trees of the same species, size, and crown. But from the data in the publications of the United States Forest Service, an average American pine, worked under the cup system, will produce, during four years of operation, an annual average of ten pounds of crude turpentine and two and a half pounds of "scrape," the proportionate yield being considerably greater during the first and second than during the third and fourth years of operation.

The average daily flow of crude turpentine during one week from a freshly chipped surface on such pines is shown in the following table, the results having been obtained during the summer of 1901 on trees near Statesboro, Georgia:

Day	Yield per tree (grams)			Average yield (grams)	Per cent average yield
	1	2	3		
1	113.0	46.5	89.0	82.8	62.9
2	22.5	7.5	16.0	15.3	11.6
3	13.5	6.5	16.0	12.0	9.1
4	9.0	5.0	17.0	7.0	5.3
5 & 6	9.0	5.0	23.0	12.3	9.3
7	1.0	2.0	4.0	2.3	1.8
Total	168.0	72.5	165.0	131.7	100.0

## TSCHIRCH'S VIEWS ON RESIN FLOW

As to the seat of resin production and cause of resin flow, most valuable and important views have been advanced by Prof. A. Tschirch in his book "Die Harze und die Harzbehälter," 2nd edition. Tschirch has shown that the seat of resin production is a mucilaginous layer lining the inner walls of the resin ducts. These ducts he divides into two classes: First—primary

ducts, whose resin is to be considered a true physiological product. Such ducts occur irregularly and in varying number in any pine. They play only an insignificant role as producers of commercial crude turpentine. Second—secondary resin ducts which form in large numbers in the outer layers of the new wood after a tree is wounded, both above and below the wound. Their oleoresinous exudate is, therefore, a pathological product. It is from such pathological ducts that the great bulk of crude turpentine is obtained.

The application of these views to practical problems in the turpentine forests has already yielded important and fruitful results.

#### FUTURE OF THE INDUSTRY

During the past few years the statement has frequently been made that from present indications the naval stores industry must cease to exist, at least as a large industry, within the next twenty years. While it is true that there are danger signals which must be heeded, such pessimistic views do not seem to be well grounded.

Certainly in France and consequently in Spain, where the same system is in operation, the industry has been placed upon a self-perpetuating basis.

In America we have been prodigal with our wealth of virgin forest.

But it must be remembered that until the last decade these forests have had a very low commercial valuation. The average price for well timbered lands in our southern states not many years ago was approximately one dollar per acre, land, timber, and all. Indeed, the popular term applied to all holders of large tracts of such lands was "land poor," as expense of taxation, protection, etc., exceeded any hope of probable profit. This condition was largely due to lack of transportation facilities, insecurity of title, low price of naval stores and lumber, lack of knowledge of the farming value of much of the land on which these forests stood, and the belief that the forests were inexhaustible.

Now conditions have entirely changed. Railroads penetrate

every portion of the territory, titles have been cleared, prices of naval stores have brought wealth to the operators, the lumbermen from Michigan, Wisconsin, and other northern states have turned from the rapidly disappearing white pine forests of the north to those of the southern yellow pine; where forests once stood farms have been developed which surpass in fertility any other portion of the southern states, and a clear knowledge has been gained that the forests are by no means inexhaustible. Furthermore, the spirit of conservation of natural resources has made itself felt in this field as well as in those of minerals, water power, etc.

The consequence of these changes has been a very rapid enhancement in the value of such holdings. And with increased valuation comes naturally the desire to protect and use conservatively. Unquestionably the stand of virgin forest will still further diminish, for the demand for farm lands is active, the call for lumber imperative, and the danger of tropical storms along the Gulf Coast ever present. With such diminution in supply will come still further enhancement in values and still more conservative methods of operation.

So much for the present stand of virgin forest. If the situation were limited to this alone, the outlook might be considered gloomy. But it must be remembered that there are vast tracts of cut-over lands in portions of the southern states whose clay sub-soil lies so deep that the lands are not suited to agriculture. On such lands the longleaf pine, with its long tap root, prospers. Magnificent forests once covered every acre of such lands and fortunately tree planting is not required to reproduce such forests. Nature alone will again cover this territory with a wealth of forest, provided Nature is given an opportunity; for the most superficial observer who travels through this territory will testify that where conditions have been favorable natural reproduction has brought again splendid, though small, young forests.

Against this willingness of Nature to restore this rich heritage to us, stand three agencies:

First, and of least importance, the consumption by hogs of the delicately flavored and nutritious seed of the longleaf pine.



This is a real factor in certain somewhat restricted districts. The constantly spreading sentiment for "stock laws" will check this evil.

Second, and of the very greatest importance, the destructive action of the ground fires, Fig. 7, which annually sweep over the entire turpentine belt. Such fires destroy the myriads of young seedlings which can readily be seen springing up in the wire grass which surrounds them on every side. The seedling devotes the greater part of its early energies to sending down its long tap root through the deep sands rather than to strengthening its stalk above ground; hence, in most cases, it is not able to withstand the constantly recurring ground fires. The doctrinaire may rail against the evils of such firing of the woods, but from one who has lived among the turpentine camps there comes no word of reproach against the turpentine operator who "burns the woods." His all is invested on the outer surface of his trees. A serious outbreak of fire during midseason means financial ruin. The carelessness and sometimes viciousness of laborers is too serious a risk to run with a mass of dead wire grass covering every foot of his territory. Naturally he protects himself by burning this grass when he is prepared for it, after "raking season."

Where then is the hope for reforestation? In the realization of the value of the waste cut-over lands where turpentine operations cannot be carried on for lack of timber. Such lands have now but little value, but the lesson of France shows that even there a reasonable income begins from artificial reproduction within a period of twenty years and then rapidly increases. With our warm southern climate the prospect for rich returns from such investments should be even greater than in France.

Third, the greed of man. If we are to have a self-perpetuating industry, even stock laws and the reforestation of waste lands will not avail if a practice on the part of turpentine operators during the past two years continues. The abnormally high price of spirits of turpentine two years ago led to a wild scramble for timber for increased operations. At the same time the efficiency of the cup system was just gaining wide recognition. Realizing that a tree too small to have a "box" cut in it could

be worked with a cup hung upon it, the operators throughout the whole region proceeded to cup every small tree to which access could be gained. In many cases new farms were opened on old abandoned territory where natural reproduction had furnished thrifty young forests. The result was over-production of crude turpentine. The temporary benefit to the consumers in the drop in values following this over-production was dearly bought, for the price was the destruction of young forests which in time should have produced their full share of the world's need of spirits of turpentine and rosin. Common sense must and will govern in this matter. It is only necessary for the operators to realize that the yield from such saplings does not meet the cost of production, then the practice will cease.

Surely the above considerations justify an optimistic view of the future of the naval stores industry. But experiment, demonstration, statistics, and knowledge of progress made in other lands, must lead the way for the man in the woods.

## SHELLAC ANALYSIS AND THE DETECTION OF SMALL AMOUNTS OF COLOPHONY IN SHELLAC

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The adulteration of shellac with colophony or common rosin has been extensively practised in recent years, though during the past two or three years it has not been so conspicuous and flagrant as formerly; doubtless owing chiefly to the relatively lower prices which have prevailed in the shellac market for the pure grades during this period.

While the best marks, bearing certificates, can, as far as the writer has observed, be accepted as free from sophistication, many of the intermediate grades are liable to contain added rosin in variable amounts, and the cheaper grades, especially some varieties of button-lac, are still subject to flagrant adulteration with large amounts of rosin.

The analytical examination of shellac has been carried out more extensively in recent years, owing to the improved chemical methods which have been devised for the determination of adulteration, and because of a better understanding between buyers and sellers of the extent of this adulteration in the past.

The price of commercial shellac is dependent upon several conditions, chiefly its color, freedom from dirt, etc., as well as its content of added rosin, but the chemist is seldom called on to pass upon the purity of a given sample of shellac in other respects than the extent of its adulteration with rosin, and it is to the detection and determination of this substance in shellacs that improvements in methods have been mostly directed.

When the proportion of rosin present in admixture with shellac is large no difficulty is encountered, even by a person with small experience, in recognizing its presence through readily discernable physical properties, and its detection and determination in moderate amounts only, can be accomplished by chemical means with

reasonable accuracy and without any particular difficulty or uncertainty; but when the amount of rosin present is small, say in the neighborhood of one per cent or less it has not been possible hitherto to establish its presence in a complete and satisfactory manner by any of the tests that are generally well-known.

It is not my intention to review or even refer to all the various methods which have been proposed for the examination of shellac for commercial purposes, and after a few remarks on the so-called analytical constants of shellac and colophony, and some of the qualitative reactions by which the latter may be detected when in admixture, I shall confine my descriptions to those methods for its estimation in shellac which are at present most extensively in use in the United States, and which form naturally a prelude for the subject of the second part of the title of this paper.

“Analytical Constants” of:

	<i>Shellac</i>	<i>Rosin</i>
Acid Number . . . . .	60-65	155-170
Saponification Number . . . . .	195-210	165-180
Ester Number . . . . .	aver. 150	0-12
Iodine Number (Hübl) . . . . .	7-11	aver. 125
“ “ (Wijs) . . . . .	14-18	“ 228

As a means of estimating the extent of adulteration with rosin it will be readily observed that the determination of the iodine number has a decided advantage; the acid and ester values of a sample of shellac are useful as checks on the iodine absorption results, but owing to the limits of these values for shellac and rosin being nearer than in the case of their iodine numbers, they do not afford so useful a basis for calculation of the rosin present as the latter figure.

For the qualitative detection of rosin in admixture with other resins, the well known Liebermann-Storch reaction, which is the only one described in most books treating of the subject, has hitherto been almost exclusively relied upon for this purpose.

It is however, not very sensitive and besides has other disadvantages. Its limit of sensitiveness for rosin in shellac being about 2%, that is to say, shellacs yielding Wijs iodine values

below 22-24, may not give a positive reaction when this test is applied; so that until quite recently there has been no satisfactory way of confirming the presence of rosin in shellacs containing small amounts of it as indicated by the iodine figures obtained upon them.

There is, however, another qualitative test for rosin which is far more sensitive and reliable than that of Liebermann-Storch, viz:—Halphen's Color Test, which, as pointed out by Foerster<sup>1</sup> can be applied directly to shellac, best however, in the manner described by me in a former paper.<sup>2</sup> By this means using 2 grams of shellac and 15 c.c. of ether as little as 0.5% rosin can be detected without difficulty. Still smaller amounts may be detected by this reaction as I shall bring out later on in this paper.

Now we will turn to the methods of analysis which have found most favor in this country for the determination of the extent of adulteration of shellac with rosin, and first I shall refer to the Wijs-Langmuir Iodine method.

This process was originally suggested for use upon oils and fats by Wijs and later was adapted for use upon shellac by Langmuir<sup>3</sup> and more recently the method has been recommended, practically without change, by a committee of the American Chemical Society<sup>4</sup> as the most reliable of those in use up to the time of their report.

The process consists of the following procedure: 0-200 gm. of the finely ground sample is introduced into a dry 250 c.c. bottle with a ground stopper, 20 c.c. of glacial acetic acid of 99% strength is added, and the mixture may be warmed gently until solution is complete (except for the wax). A pure shellac is rather difficultly soluble. 10c.c. of chloroform is added and the solution cooled to 21-24°C. (72°F.); 20c.c. of Wijs solution is then added from a pipette with a narrow orifice. The bottle is closed and set aside for exactly one hour in a darkened place (Presence of considerable rosin will be revealed by solution having taken on a red-brown color). During the period the bottle should be

<sup>1</sup> Ann. Chim. Anal., 14, 14 (1909).

<sup>2</sup> Jour. Ind. & Eng. Chem., 3, 86 (1911).

<sup>3</sup> Langmuir, J-S-C-I, 24, 12 (1905).

<sup>4</sup> Jour. Amer. Chem. Soc. 29, 1221-27 (1907).

partially immersed in water, the temperature of which is carefully maintained at 72° F. At the end of the hour the bottle is removed from the basin and 10 cc. of a 10% potassium iodide solution added and the excess of iodine titrated immediately with N-10 thio-sulphate solution using starch solution as an indicator.

With a little practice the end-point is sharp, most of the coloring matter of the shellac being retained in the chloroform which has separated.

A blank determination should be made at the same time with 20 cc. of the acetic acid, 10 cc. of chloroform and 20 cc. of the Wijs solution. After obtaining the number, the percentage of rosin is calculated by means of the following formula:

$$X = \frac{100(M-S)}{R-S} = \frac{100(M-18)}{228-18}$$

"M" being the iodine number obtained on the sample examined.

When all the proper precautions are carefully observed, particularly as set forth in a recent paper by Langmuir and White (*J. S. C. I.*, 30, 786 (1911)), this method has given excellent results, and is of especial value, since in the hands of different analysts, after a little experience, closely agreeing results upon the same sample can be readily obtained.

The objections to the use of the process are, first, that it is likely to give results below the truth, and second, that the method of ascertaining the amount of rosin is an indirect one and any other substance having a high iodine figure will be counted as rosin; the rosin itself is not separated from the shellac and consequently cannot be separately examined for identification.

A process with this end in view has, however, been devised by McIlhiney.<sup>1</sup> It depends upon the fact that rosin is soluble in petroleum ether, while shellac is not. Although it is not practicable to extract the rosin from solid shellac with petroleum ether, the latter may be used to separate the two resins when they are dissolved in a suitable solvent. Such a solvent is absolute alcohol or glacial acetic acid, either of these solvents being miscible with

<sup>1</sup> *Jour. Amer. Chem. Soc.* 30, 867 (1908) and 7th Inter. Cong. App. Chem. Section 1-99 (1909).

petroleum ether. To the solution water is then added which causes a separation into two layers since the alcohol upon dilution is no longer miscible with the petroleum ether, and by further addition of water the shellac is gradually precipitated from its alcoholic solution. The petroleum ether carries with it the rosin, and the wax, which was contained in the shellac, provided sufficient petroleum ether was used to dissolve it, and also a small amount of some of the resinous constituents of the shellac itself. There are several methods which may be used to effect a separation of the shellac-wax from the rosin, but the most convenient is to treat the petroleum ether solution of the two with an alcoholic alkaline solution which removes the rosin and leaves the wax dissolved in the petroleum ether, from which it can be recovered and determined if desired. From the alkaline solution of the rosin the latter may be recovered, after the removal of the alcohol by evaporation, by acidifying and extracting the acidified solution containing the precipitated rosin acids with a solvent such as ether, separating the ethereal layer and evaporating off the solvent to obtain the rosin which may then be weighed.

The steps of the procedure may be briefly described as follows: 2 grams of the shellac is dissolved in 20 cc. of absolute alcohol or glacial acetic acid, with or without gentle heating. After cooling 100 to 300 cc. of petroleum ether, having a boiling point not higher than 80° C. are added in small portions at a time and with constant agitation. It is important that the addition of petroleum ether be made slowly and with stirring in order that the shellac which is partially precipitated after the first portions of the petroleum ether have been added may not carry out with it mechanically any of the rosin (or wax) contained in the solution. 100 cc. of water is then slowly run in, also with constant agitation. This causes the liquid to separate into two layers and ensures the complete precipitation of the shellac. The necessity for agitation during this stage is again to ensure the collection into the petroleum ether of all the rosin. The liquid is then poured off from the flask in which the previous operations have been conducted into a separatory funnel. The layers readily separate and the aqueous-alcohol layer is drawn off. The petroleum ether portion is washed with a little water, and may be filtered and

evaporated off for weighing the residue of wax and rosin. One procedure at this juncture is to titrate the rosin after solution of the residue in alcohol with N-5 or N-10 caustic alkali and phenolphthalein as an indicator. The average combining equivalent of rosin does not vary greatly from 346, the figure used for this titration in the Twitchell process for the estimation of rosin in admixture with fatty acids.

It is better, however, to proceed to an actual separation by treating the petroleum ether solution directly after transferring into a clean separator, filtering if necessary, with 25 cc. of N-5 caustic soda in 50% alcohol. By this means, after one or two treatments the rosin is completely extracted from the petroleum ether, together with traces of resinous matter from the shellac itself which were originally taken into solution in the petroleum ether. After drawing off the alkaline layer, and evaporating off the alcohol, the rosin is precipitated by acidifying the liquid with a mineral acid and extracting the precipitated rosin with either ether or petroleum ether, which after separation from the acid liquid in a tapped funnel is evaporated off and the residue weighed.

By this process it is practicable to actually separate, exhibit and examine by appropriate confirmative tests the rosin which has been added to the shellac as an adulterant.

As previously stated the petroleum ether dissolves traces of the resinous matter of pure shellac, and from my experience this always amounts to about 1%, and may amount to as much as 2%, consequently the mere obtaining of a weighable residue at this juncture is not absolute proof of the presence of adulteration; and in the case of the presence of only small amounts of rosin or certain other foreign resinous substances, it becomes necessary to apply some further reliable and characteristic test for its identification.

We now have such means at our disposal in the very sensitive Halphen color-test before referred to. By applying this reaction to the residue of the ethereal extract of the precipitated resin acids in the McIlhiney process in the manner described in my previous paper,<sup>1</sup> it is possible to detect without difficulty as little

<sup>1</sup> Jour. Ind. & Eng. Chem., 3, 86 (1911).



as 0.1% of rosin in a sample of shellac, when 2 grams has been used for the analysis, which is the usual amount taken in the McIlhiney method.

Although in the case of these extremely small amounts of rosin the processes involved for its positive recognition are somewhat tedious and require a considerable degree of careful manipulation, yet in certain cases it may be of importance to answer the question whether a particular sample of shellac does or does not contain rosin. In view of the sensitiveness of this test it would appear that there need no longer be any reasonable grounds for doubt or dispute as to whether a certain sample of shellac is or is not free from this foreign resin.



## BENZOL AND THE COAL TAR DISTILLATES AND THEIR APPLICATION IN THE PAINT TRADE

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In a book written in 1867, by Charles F. Crockett, and recently published in conjunction with the English translation of Bottler's book on German Varnish Making by A. H. Sabin, there appears an N.B. following the formula for a furniture japan:

"However by using a portion of No. 1 Coal Tar Naphtha and less Benzine, this japan will mix with raw oil."<sup>1</sup>

Elsewhere in the little book he refers to No. 2 Coal Tar Naphtha, and in speaking about asphaltum paints, he very tersely remarks that No. 2 Coal Tar Naphtha may be used in place of Turpentine, in order to cheapen the mixture. No. 1 could be used to better advantage but is more costly. From this, when you consider that No. 1 Naphtha is a product similar to 90% water-white Benzol of this day, and No. 2 would correspond to the prevailing straw-colors, it will give some idea as to the relative costs of these two varnish and paint materials forty years ago as compared to now. It was necessary for Mr. Crockett to use a crude Benzol to have a price lower than Spirits of Turpentine, while for the past year, 90% water-white Benzol has been selling from one-fifth to one-half the price of Turpentines.

The strides that have been made by the producers of Coal Tar Naphthas are comparable with the demand from paint and varnish makers. This can be roughly figured when we consider that in Mr. Crockett's time two grades were known, No. 1 and No. 2; that is, refined and crude. To-day there are on the market ten refined Coal Tar Distillates ranging in boiling point from 82° to 200° C., and five crude fractions of approximately

<sup>1</sup> "German and American Varnish Making," Prof. Max Bottler of Wurzburg; Alvah Horton Sabin. John Wiley & Sons, New York.

the same range. The direct cause of this is the demand of the paint and varnish manufacturer on the tar distiller, and is definite proof that these solvents are much more in vogue than in the days when Turpentine was cheap and plentiful. For example, where Coal Tar Naphtha was used then in order to enable a japan to mix with an oil, no one would have ever employed a high boiling fraction to give a brushing quality or "length" to a varnish made with "short" thinners.

The era of the Benzols in the paint and varnish trade may truly be said to have begun with varnish removers. Of course, many manufacturers were well aware of the solvent power and the working qualities of Coal Tar Naphthas before that time, but there was a prejudice as to odor, and danger as to fire risk, so that the trade was loth to accept goods which smelled strongly of Benzol. But the introduction of the paint removers tended to familiarize people with the odors, and then, too, the use of crude gas drips and other very bad smelling hydrocarbons has made the refined goods smell quite pleasant by comparison. This has been a very good feature of this class of goods, which consume a very large percentage of the Benzol used by the paint trade; but there has been also another condition brought about by their vogue that is not so desirable. When the higher boiling Naphthas were first offered as paint materials, people were inclined to regard anything with Benzol in it as a paint remover. The reasoning is not sound, for the presence of oil or resin in Benzol inhibits its action on oxidized bodies, such as paint or varnish films.

The profitable handling of paint removers at a time when Linseed Oil, Turpentine, and most profitable paint and varnish materials were advancing, led to the seeking of other specialties, and a very large number of these newer materials are made with the use of some one of the Coal Tar Distillates. Probably one of the most generally known of these specialties is the penetrating stain. Benzol is employed as a solvent for oil soluble anilines in such instances.

This field, while dominated by three or four manufacturers, belongs essentially to the paint trade, and many painters make their own stains for each job; hence it is very hard to form an

estimate of the amount of Benzol consumed in these preparations, but from the consumption for 1909-10 & 11 of the principal manufacturers it has been possible to estimate an increase of 58% from 1909-1910, and from 1910-1911 65% represents the percentage increase. This increase is characteristic of the use of Benzols in the specialty lines, so that now the manufacturer of paints carries a much larger line, due largely to the versatility of Benzol. Where formerly the principal product was paint and varnish remover, we now find offered:

Oil Soluble Stains (Penetrating).

Enamels: Pigment in Damar Benzol Varnish and Asphaltum Benzol Varnish, as the stove pipe enamels.

Rubber Paints: Insulating proposition.

Spirit Varnish: Insulating & Shellac Substitute.

Flat Wall Coats: Wood Oil and Pigments.

Bronzing Liquids with varnish and cellulose bases.

Concrete Paints: Both the unsaponifiable gum and wood oil varieties.

N.B. "No attempt has been made to enumerate all the specialties in which Benzol is employed, as many are specialized products by certain manufacturers and while in many cases the suppliers are familiar with the uses, it was not considered fair to divulge them."

These few will serve as examples of the way that the manufacturers have made use of the various properties of the Coal Tar Naphthas. In each case selected it can be readily seen that the grade of Benzol is chosen for its particular properties. Strong solvent power, brushing quality, the slowness or quickness of evaporation, penetration or flash point have been considered in the choice.

This class of goods very likely consumes the bulk of Benzols in the paint trade, and next comes a line where some peculiar property is made use of to correct some defect in a material already in use. This for instance, is very strikingly seen in the use of turpentine substitutes of a petroleum origin. Here no Coal Tar Distillate can compete on price, yet many manufacturers who know their solvents well have been able to make use of the

solvent action and complete drying of Benzol by adding a small percentage, thus increasing the efficiency of their substitute, and not materially increasing the cost. This sort of thing is very often done in goods that tend to thicken or liver, and it can be considered very intelligent practice.

In almost this same class comes the only use of Benzol in a true paint that is a pigment ground in a suitable oil of a drying nature. Early in the use of the more modern woods in building it was advocated to let woods of a sappy and resinous nature such as cypress and yellow pine, go unpainted, but the use of panels unpainted on test fences soon changed this idea, and the problem was attacked from the painters' standpoint. It was found that if a suitable priming coat was applied little or no difficulty was experienced with the succeeding coat or coats. The addition of a small amount of Coal Tar Naphtha to the Linseed Oil of the priming coat was found to give the requisite penetration; but so far this has been rather the painters' specialty than the manufacturers', as the writer has never encountered but one prepared paint on the market intended for priming work of this sort.

It has also been suggested to use Benzol or higher boiling homologue in the priming coats of paints to be used on surfaces where mold and mildew are to be encountered, and thus employ the germicidal power of a Coal Tar Distillate, or use a Naphtha to convey a small percentage of phenol into the pores of the surface to be painted.

While as yet no data is available on this proposition, it is mentioned as one of the instances where the various Coal Tar Distillates are being applied to the paint problems of to-day.

## COBALT DRIERS

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The cobalt compounds which are generally offered on the market to-day, may be divided into two classes. In the first are cobaltous Oxide, Acetate, Sulphate, Chloride, Nitrate, Hydroxide, and Basic Carbonate. In the second class, are various grades and qualities of resinates (sometimes called sylvinates), both fused and precipitated, oleates or linoleates, oleo-resinates, tungates and resino-tungates, besides some other liquid preparations composed in whole or part of the foregoing.

From the varnish manufacturer's standpoint the substances in the first division are crude materials which are utilized in the production of the compounds in the second class, and also in the preparation of some varnishes, liquid driers, drying oils, and the so-called paint oils. The materials enumerated under the second class, are the result of a varnish maker's labor, and when properly made and used in mixtures to which they are adapted, give very good results.

The inorganic salts of cobalt do not directly come under the scope of this paper, and thus will not be directly considered except inasmuch as their use as crude material affects the driers into whose composition they enter.

It is only within the past year that the cobalt driers have been offered to the American paint and varnish manufacturers. Up to the present time, their use is not general, first, because of the very high price, and second because their use is not thoroughly understood and many experimenters have had unsatisfactory results and therefore refused to further consider the introduction of the new material. Furthermore, not all of the cobalt driers, whether liquid, paste, or solid, now offered for sale are properly made and truly adapted to the purposes for which they are recommended. This situation in addition to unsatisfactory results

obtained by some of those experimenting, would naturally have a retarding effect on the introduction of a new type of material.

The salts of cobalt which are at our disposal in commercial quantities, are all of the cobaltous or divalent type. It has been found that although they can be readily used in the manufacture of driers and worked like the various compounds of manganese, lead, zinc, calcium, aluminum, etc., the organic compounds formed, which are the basis and active principles of the so-called driers, are not efficient while in the cobaltous state. The cobaltic combinations however, are very active driers, and it is for the formation of trivalent cobalt compounds that we strive in the making of driers. This transformation can be effected in several ways. By blowing cold, heated, or ozonized air through the hot cobaltous drier stock, or by the introduction of liquid or solid oxidizing agents. The use of cold or even heated air is a very long and tedious operation if carried out to the extent to which it is necessary in order to get the maximum strength in the drier, and greatly adds to the cost of an already expensive material. The use of the liquid or solid oxidizers can be carried out successfully and in a comparatively short time, although even when great care is exercised the batch of material is in danger of catching fire.

Since driers are used in a number of industries in which drying oils form part of the material produced, and since the operating methods of the various manufacturers are widely divergent, the siccatives or driers adapted to each will in many instances show widely different characteristics, not merely in form but also in composition.

Since the paint manufacturer and also the practical painter who mixes his own paints from paste colors and raw or treated oil, are the principal consumers of what are generally known as driers, the materials adapted for their use may be first considered. The driers will in practically all instances, be in the liquid state either very fluid, of heavy consistency or of a semi-paste nature. In composition, they will mostly consist of resinates, tungates, oleates, or linoleates, or combinations of the three. For the drying of linseed oil, when the proper driers are selected, little or nothing can be asked in addition to those known at present.



When the general lead, manganese and other prevalent metallic driers are well chosen raw linseed oil can without any difficulty be made to dry by the addition of from 5 to 10% or even less, the time of drying under average weather conditions being from 10 to 24 hours. By the use of cobalt driers, the same drying effect can be obtained when only from 1 to 3% of a liquid drier is used. I am not yet prepared to say positively what the ultimate effect of cobalt driers is upon paint films, but from my experiments, I am led to believe that cobalt has not the harmful progressive oxidizing action that some of the usual manganese lead compounds have. It has also been noticed that although a cobalt drier may be fairly dark in color, it will not have as darkening effect as one of the usual driers of like color would have upon a white paint. The cobalt driers likewise, show the same phenomena as some of the others when used in excessive amount; that is that although the paint film will set up well in the usual time, the drying action apparently reverses and the film remains tacky.

The terms applied to liquid driers are often uncertain and apt to be misleading. There are no general standards for strength or consistency, and, it must be admitted, many of the materials found on the market contain more volatile thinners than is conducive to obtaining a maximum drying effect with a minimum quantity of drier.

The value of the Cobalt specialties depends not on their power to dry Linseed Oil, but on their ability to make the lower priced semidrying oils act like it.

Soya, Fish, and even Corn and Cottonseed oil are adaptable for use in paint, and when correctly treated increase its durability. Dr. Maximilian Toch has published the results of his extensive research and experimental work with both Fish and Soya Oils, and there describes the types of driers suitable for them.

In the making of waterproof fabrics, insulating coatings, etc., both liquid and solid driers are used. In the linoleum, oilcloth, patent leather, artificial leather and similar industries, the semi-liquid, paste, and solid driers are in demand since for these products the manufacturers cook the oils and varnishes in their own factories.

The paste and solid driers must essentially be considered under

the caption of crude materials because they must be churned or cooked in the oils or varnishes in which they are used.

The methods of making both the solid and liquid driers are in general similar in the first stage of the process, and thus may be described under the same headings.

#### *Resinate of Cobalt; Precipitated and Fused.*

This is correctly made by saponifying rosin or colophony with caustic soda or sodium carbonate, care being taken to avoid an excess of the reagent, and then precipitating with a solution of some salt of cobalt. The chloride or sulphate serve best for this purpose. The precipitated resinate, or as it is sometimes called, rosinate or sylvinate, must then be thoroughly washed, and then pressed and dried. This will yield a pinkish fairly fluffy powder when ground, which will readily dissolve in oil at a low temperature. The fused variety is made by melting the dried resinate in a kettle and then pouring into cooling pans. The operation is performed more rapidly by taking the cakes from the presses and driving off the water and fusing in one operation.

#### *Cobalt Oleates or Linoleates.*

The basis of this class is generally linseed oil, although Walnut, Perilla, Soya, and some other oils may be used. The oil is thoroughly saponified with caustic soda and like the resinate, precipitated with a salt of Cobalt. The material is then carefully washed and pressed. It may be melted to form a dark viscous heavy fluid.

Several samples of cobalt linoleate which I examined consisted of bodied linseed in which small amounts of inorganic cobalt salts had been dissolved. Another was of the same order with the addition of volatile solvents.

True linoleate of cobalt, when fused with varnish gums and dissolved in volatile oils, yields an excellent drier.

#### *Oleo-resinates.*

This type of drier is made by melting together the precipitated resinate and linoleate, sometimes with the further addition of fused fossil gum-resins.

### *Tungate of Cobalt.*

Like the linoleates, the tungate of cobalt is made by saponifying pure China Wood Oil (Tung Oil) with caustic soda, care being taken to avoid excess of caustic, and then precipitating with a salt of cobalt. The tungate is then washed thoroughly, pressed and generally dried and fused. Great care is necessary in the preparation of a tungate since it oxidizes very rapidly, and the oxidized material is useless.

Like the linoleate of cobalt, the tungate may be fused with the resinates to form what may be called a resino-tungate.

In general the foregoing substances are incorporated in oils by means of heat, the combining temperature being between 300° and 500°F. The amount necessary will vary from about 1-2% to 5%. In order to make *liquid driers*, the paste or solid driers can be melted alone or in combination with gum-resins, bodied linseed oil, or both, and then thinned to liquid consistency with volatile oils.

Among other cobalt salts, some of the chemical manufacturers offer the acetate, with directions for its use as a drier. All agree that between two and four tenths of one percent are necessary to dry linseed oil. The oil should be at a temperature between 300° and 400°F., and be carefully stirred until all the salt is dissolved. Soya and China Wood Oil may be similarly manipulated.

It is still a little too soon to make a positive statement as to how oils thus treated with the acetate withstand wear and exposure.

Cobalt Oxide, like the Acetate, can be directly added to oil during boiling. It however dissolves slowly and necessitates heating to high temperature; the resulting product is also very dark, and mostly consists only of bodied oil. Rosin also will directly combine with cobalt compounds on heating together in a suitable kettle or container. The product possesses a number of objectionable features. It still is mostly unchanged rosin, has become much darker and lost considerably in weight due to volatilization. I have tried the effect on oils of quite a number of Cobalt compounds, but found none equal in efficiency to those described in the foregoing.



# THEORY AND PRACTICE OF THE PAINTING OF THE MODERN STEEL PASSENGER CAR

BY J. W. LAWRIE

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Since the very general introduction of the steel passenger car into our railway service, new problems in painting and preservation of the steel have been brought to our attention. It is true that the problem of the preservation of steel is not in itself new to us, but the artistic preservation and protection of steel from corrosion, etc., is a new problem. A railway passenger coach must not only be painted carefully, but it must be painted so as to present a pleasing appearance to the eyes of the traveling public. This effect is arrived at by the color, lustre, harmony of color, etc., and thus some of the pigments which have great value for steel protection cannot be used, and others that do not have merit for steel protection must be used merely on account of the color they possess. The railways in general have retained the same standard colors for steel cars that they had for wood cars. The consideration of the protection of steel has been secondary to the color of the finished coach. Fortunately, this consideration has not been felt for certain colors, because we have found good inhibiting pigments which harmonize with the color desired and afford good protection to the steel.

Paints for steel have different functions, in many respects, than those for wood. In painting steel we do not have the absorption into the pores, but to only an extremely limited extent, compared to that which we have in painting wood. For this reason there must be some other way adopted for getting the strong clinging effect that the pores of wood afford as an anchorage for the paint coats. Once we have the priming coat well anchored, the subsequent coats, if properly made and well applied, anchor themselves one on the other, all finally depending for their adherence on the fastness of the priming

coat and the strength and elasticity of the paint film. With steel we have only to a very limited extent inter-crystalular crevices, most minute in size and depth. These do not afford a firm anchorage, nor is the penetration of the paint into these crevices of much value for anchorage. Sandblasting steel gives a slightly roughened surface, which aids materially in holding the paint to the steel. It is almost necessary to assist an oil paint with something which is a better adherer to steel than linseed oil. This we find in varnishes. For this reason we find in all steel primers a certain amount of varnish. At the same time the pigments which have answered for wood may or may not do for steel. Depending on the color, we may have more or less pigment to get proper opacity, for dark colors less, for light colors usually more pigment is necessary than in the paints used for wood. It has been established in a practical way, as well as experimentally, that the fewer the number of paint coats on steel which will give the maximum protection the longer wearing and better service will the paint coating give.

In general, we can functionate the properties of both the pigment and the vehicle for painting steel.

The pigment must give us the color and shade desired, opacity, thickness of film; it affects the life of the paint, both by its actinic action due to its color absorption, etc., and its chemical effect on the oils or vehicle. It should be such as to give the maximum inhibition of corrosion on the steel.

Corrosion itself may be due to several factors. Moisture must be present for continuous corrosion, acid gases and oxygen assist, and any free acid, such as is used in pickling steel is a strong inducer of corrosion. When we consider these causes, then we can attempt to get ways of overcoming the effects of these causes and so approach perfect inhibition of corrosion. It must be borne in mind, however, that inhibition of corrosion is only one of the desirable qualities of a paint for steel.

The vehicle has for its fundamental functions, the binding of the particles of pigment together, and the cementing of this bonded material onto the steel surface. It gives life to the paint and gives the finish effect desired as to lustre, etc. It must also

be such as to exclude from the steel surface all moisture and gases.

Both pigment and vehicle have additional functions other than those given. These mentioned are the ones of greatest consideration in the study of proper paints for steel protection.

There are essentially two or perhaps three great classes of pigments as regards their effect on steel. These classes can be called the Electrical, the Chemical and the Passifiers. Examples of the passifiers are the Chromates, which seem to render the steel immune to oxidations.

In line with the electrolytic theory of the corrosion of steel, the differences in electrical potential produce a current of electricity in the direction of the high to low, or also positive to negative. The different pigments show such differences in their relation to steel, and for this reason if we use pigments which are positive to steel, then in any flow of current we would have the positive material going into solution and the negative material, or, in this instance, the steel, protected. Such pigments would therefore be inhibitors of corrosion of steel. Those of the same potential, or neither positive or negative to steel, would be neutrals and those negative would be accelerators.

The chemical pigments are those which through their particular chemical properties, such as acidity, either direct or through hydrolysis, neutrality, or alkalinity, affect the steel so as to inhibit or accelerate corrosion. It is practically established that there is a minimum alkalinity below which there is no inhibition, and also with too strong alkalinity the action of the pigment on the vehicle oils is so pronounced that such pigments are detrimental to the life of the paint. Practically all pigments belong to both the electrical and chemical classes. A pigment may be positive to steel, and yet in itself or by hydrolysis be so acid in action that instead of being, as we would expect, an inhibitor, it is instead, a strong accelerator of corrosion. In the same manner, a negative pigment may be sufficiently alkaline as to become an inhibitor. Many pigments are both positive and alkaline, and therefore extremely good inhibitors. Others are neutral, either through opposing electrical and chemical properties (as applied to inhibition, etc.), or are neutral of them-

selves in all respects. Again, other pigments are negative and acid, and so strong accelerators. There are, of course, all grades and stages in these valuations. It is, however, possible by test to identify the different properties of the different pigments and combinations of pigments, and so classify them as to their actual value for inhibiting corrosion.

The knowledge of these classes is worth having, but not of great importance, unless we have satisfactory methods of determining to which class each and every kind of pigment or mixture of pigment belongs. It is possible to measure directly differences in potential between pigments and steel, and also the relative acidity or alkalinity, either as a direct property or as one produced by hydrolysis. These tests can be applied directly to most pigments, but not to all. There is one test which can be considered final and fair. That is, an actual exposure test of the pigments combined into paints and applied to steel panels under differing exposure and weather conditions. It must be admitted at once that such tests are not absolute, but their relative value cannot be disputed. It is impossible from the results of such tests as those at Atlantic City to say that the American Vermilion is 10 times as good a pigment as some other pigment which would be rated at 1. The relative fact is that American vermilion is a first-class inhibitor of corrosion, whereas the paint rated at 1 is not an inhibitor and is probably one of the negative pigment paints, and therefore an accelerator. It is extremely tedious, however, to wait four or five years for such an exposure test to give reliable results. Events and truths in paint grinding history are moving much too fast and some other means must be had for testing out these pigments and vehicles in a shorter time and yet with a reasonable amount of assurance that the results so obtained check up the actual exposure or railway service wear.

I have been experimenting for a long time with the so-called razor blade test for both pigment and vehicle. The test is made by completely separating the pigment from the vehicle by solvents and the centerfuge, so that there is no trace of the vehicle left with the pigment. The pigment is then re-ground until all of it passes through a 100-mesh sieve. It is then made



into a stiff paste, with water, spread out on a square of filter paper and the emiered razor blade is wrapped up in the pigment in such a manner that the pigment is in intimate contact with the surface of the blade all over. Here is where many fall down on the test. The wrapping up of the blade properly has much to do with the success of the experiment. The blades are now left for about 21 days, being kept moist all the time. They are then cleaned, re-weighed, and the loss in weight, together with the appearance of the blade, give the value of the pigment for steel protection. I have followed the results so obtained with outdoor exposure panels, and have seen the conclusions arrived at from the razor blade test check with wonderful accuracy the results obtained on exposure. As examples of these checks I give the relative values placed on some of the Atlantic City steel panels and the losses on the razor blades:

	Loss Razor Blade	Atlantic City rating
American Vermilion . . . . .	.0005	10
Sublimed White Lead . . . . .	.0015	9
Corroded White Lead . . . . .	.0247	2½
Red Lead . . . . .	.0003	9
Zinc Chromate . . . . .	.0004	9

I have made these tests on over 200 different pigments and mixtures of pigments, with the exposure test for a check. The results indicate that when properly carried out the blade test is reliable and of great value where time is such an important factor as in large testing laboratories.

In like manner the vehicle can be tested for its value as a resister of moisture and gases. The emiered and weighed razor blade is dipped into the separated vehicle and given two coats, with proper drying intervals. The blade is now subjected to alternating treatments with water and moist sulphur-di-oxide, and carbon-di-oxide gases. This treatment is continued for a period of eleven days. The blades are then cleaned and re-

weighed. The appearance and loss in weight give the relative value of the vehicle as a resister of moisture and gases. Here we also use the filmometer with great success. This particularly where we are called upon to test paints from competing companies, and designed for the same purpose. The test of the resistance of the film to acid and gas penetration is of extreme importance. We have in railway service to contend with sulphur-di-oxide and carbon-di-oxide gases, as well as an almost continuous presence of moisture. For this reason the paint must be able to exclude these gases and moisture. This exclusion depends largely on the nature of the vehicle. Straight linseed oil or soya bean or other like oils will not exclude completely. If, however, we add a gum varnish to the oil the porosity is largely stopped. This, of course, is more or less perfect, according to the amount of varnish used, its kind, etc. At the same time the physical condition of the pigment must be considered, as too coarse a pigment will practically always leave a porous film. Too much varnish on the other hand, especially in a priming coat, will leave a glossy surface, to which the second coat will not adhere well. At the same time it is well established that varnish will not carry a large amount of pigment and give successful outdoor surface. It is for this reason that there have been so many failures with the so-called "quick process methods" of finishing steel cars.

We have made many tests to establish the value of baking the paints on steel cars. Our results, and practical experience, based on these tests, has shown that the life of the baked paint on steel is prolonged wonderfully and also the adherence to the steel itself is very much better. At the same time the baking has the additional value of making the vehicle much more impervious to moisture and gases than the same vehicle unbaked. Numerous experiments with certain kinds of vehicles baked gave a resistance in this way of almost three times that of the same vehicle unbaked. The mechanical difficulties of baking an entire car are large. We are at the present time experimenting in this direction. In this respect, the removable sheathing of the modern Pullman is of a decided advantage, as it can be readily taken off, the paint removed, the sheathing re-painted, baked

and placed back again on the car as before. There are some other difficult problems involved in the baking of the paint. It is the best practice at the present time to bake the surfacer. This baking produces an extremely hard and brittle coat. Up to the present, when it is necessary to refinish such a car, we have not found any chemicals which will successfully remove this baked surfacer. It is, however, possible to remove all coating over the surfacer and then rebuild up again in the regular manner. Here again the problem of baking the entire car is paramount and so far we have not solved the problem with entire success.

The baking temperature and length of time baked have a great deal to do with the life service of the paint. There is, for most vehicles, a minimum heat necessary to produce the internal changes in the vehicle, which give it the valuable properties so desired. This change has also a time factor. In general, the lower the temperature and the longer the time the paint is baked, the better the wear, service and resistance to moisture, and the more elastic the film. Twelve hours at 180 deg. Fah. are better than five hours at 280 deg. Fah.

There is no longer any argument with regard to the preparation of the steel for painting. Wherever possible sandblast. Pickle only when no other means affords itself to remove scale and rust. Pickling with sulphuric acid gives under our usual factory methods the best accelerator of corrosion of any agent met with in regular railway service. Capillary attraction is an extremely powerful force. The sulphuric acid by this force enters the spaces between the crystals of the steel and is held very tenaciously. A mere dipping in a bath of water or several baths of water fails to remove all the acid and with the hygroscopic nature of sulphuric acid an ever increasing area of steel is subjected to acid action. The whole sheet begins to corrode under the paint coat. Even with a paint which is inhibitive and moisture-proof such action will soon destroy these valuable properties. The action of the acid is cyclic and almost unending. Ferrous sulphate is readily converted to ferric sulphate and with moisture to ferric hydrate. Under these conditions the ferric hydrate is precipitated out of solution and does not re-act further with the acid. The acid is re-generated and again re-acts with

the steel, etc. The ferric oxide formed is electro negative to steel and with moisture and acid a current is established, carrying iron ions from the steel into solution. These are precipitated out as more ferric hydrate or oxide and so again the action proceeds ad infinitum. I would rather pickle with hydrochloric acid than with sulphuric acid even at a higher cost, because this acid is not hygroscopic; it is volatile at a low temperature and its capillary force is small compared to that of sulphuric acid. It can therefore be washed out with greater ease and sureness and can ultimately do less harm if not entirely obliterated. If you have to pickle with sulphuric acid, then wash with a stream of hot running water, so as to overcome by heat, force and dilution the capillary strength of the acid. Treat with lime water and wash again, dry and oil.

There is one feature of steel car building that is generally neglected. The outside surface of the steel is taken care of in a more or less respectful manner, but the inside of the sheet is usually given a coat of slush paint and the scale is seldom removed. Oil may be on the surface, or rust already formed. This treatment is certainly to be condemned. The inside of the outside and the outside of the inside sheets form a box with little ventilation, but usually holding a great deal of moisture. The paints used are seldom good resisters of moisture, and as a result corrosion starts and is aided by the conditions until there is often danger that the inside of the sheet will corrode through before the paint on the outside has seen decent service. As color is of no interest in this case it is easily possible to apply a good inhibiting and moisture resisting paint on these unseen sides of the sheets of steel and so prolong the life of the car very much. It is also a matter of general safety to properly paint this material, as it is impossible to get at the surface for repainting after the car is in service.

Where moulding abuts on steel sheets it is usual to interpose sheet copper between the two pieces of steel. This is to produce as near a water tight joint as possible. The fact remains that the joint is never entirely water tight. Copper is electronegative to steel and the steel therefore goes into solution and rapid destruction takes place. I have seen siding renewed on many

cars in less than 9 months, and the destruction could be traced directly to this electrolytic effect. Aluminum on the other hand is electro-positive to the steel and so it goes into solution and saves the steel. It soon coats over with oxide and thus the reaction is largely diminished. The steel itself is entirely protected. This substitution of Aluminum for copper was made entirely as a result of the electrolytic theory and the test of its worth by means of the well-known ferroxyl agaragar test of Cushman, Gardner and Walker. The copper in contact with the steel in the agar jelly caused the flow of current and the liberation of iron ions, which with the ferri-cyanide gave the characteristic blue-green color. With the aluminum under the same conditions there was formed the pink, due to hydroxyl ions and the white aluminum ferricyanide.

There are several essential properties which should be possessed by the different kinds of paint used on steel. The usual procedure is first, sandblast, next prime, and following usually a second but different primer; then filler and surfacer, color and varnishes. The essentials of a good first primer or first coat of paint on steel are that it adhere well to the steel, present a good surface for the second coat, and that it have a pigment that is a good inhibitor of corrosion. It is not essential that the vehicle be altogether gas and moisture proof, although it is better so. The second coat should adhere well to the first one. It should be primarily a paint that is a good excluder of gases and moisture. It does not have to have a strongly inhibiting pigment, but it is better with such a pigment. It is usual after the application of the fillers and surfacers to rub down to a smooth finish with water and pumice. This treatment requires undercoats, which will resist the water and next to the steel a pigment that will prevent corrosion, even if some moisture gets through the outer coats. It has been possible to get better results from two coats instead of a single primer combining all qualifications. It is more practical also to get the resistance to moisture by making both coats moisture proof than by depending on the second coat alone.

The fillers or surfacers are designed to give a film such that it can be rubbed down to a smooth surface without tare and

still be flexible. Most of them are fairly brittle and all of them are hard. The brittleness is increased with the baking. It is, however, possible to make a surfacer which will be hard enough to rub well and still be very elastic. Such an elastic surfacer will give to the paint coats as a whole, much better wear and freedom from checking than a more brittle and non-elastic surfacer. The coats of color, etc., following the fillers are never or seldom baked. It is very difficult to hold the shades and finish constant when we bake the finishing color coats and varnishes.

I have tried to show the theory of steel car painting as it has been applied with some success in a practical manner on a large scale. We are using the tests and theories described every day and with increasing confidence in their practical value. There are still many new phases of the work to be thought out and problems to be solved. We need more men with a little time for the practical theoretical work of the proper protection of the steel passenger car.

## KÖNNEN ANSTRICHE ROSTFÖRDERND WIRKEN?

VON ERIK LIEBREICH

*Berlin, Germany*

Die Ansichten über die Entstehung des Rostes auf Eisen haben in den letzten Jahren eine grosse Umwandlung erfahren. Früher führte man die Entstehung dieses für die Eisentechnik so gefährlichen Feindes einzig und allein auf chemische Angriffe zurück: man nahm an, dass der Sauerstoff der Luft das Eisen zuerst oxydierte und alsdann hinzutretende Feuchtigkeit zur endgültigen Bildung von  $\text{Fe}(\text{OH})_2$  führte. Auch wurde—wie sich später zeigte—irrtümlich angenommen, dass die Anwesenheit von Kohlensäure zur Bildung von Rost notwendig sei. Heute, wo die Chemie physikalischer, wenn ich so sagen darf, geworden ist, oder wo Chemie und Physik Hand in Hand Probleme in Angriff zu nehmen anfangen, haben die Anschauungen über die Ursachen des Rostens eine völlige Neugestaltung gefunden.

Vorbereitend für diese Umwandlung war die von Arrhenius aufgestellte Lehre der Ionenspaltung von Electrolyten und die von Nernst gegebene Theorie des Lösungsdruckes. Die Früchte, die die Electrochemie seitdem pflücken konnte, gehören zu den schönsten Errungenschaften der physikalischen Chemie. Eine Anwendung dieser neuen Anschauungen auf das Problem des Rostens speciell fand erst verhältnissmässig spät statt. Die wohl von Fechner zuerst aufgestellte Theorie der Lokalströme, welche die schnellere Auflösung von Metallen, wenn diese edlere Verunreinigungen enthalten, dadurch erklärte, dass sich zwischen dem eigentlichen Metall und der verunreinigten Substanz electrolytische Prozesse ausbilden, welche die dabei anodische Grundsubstanz in Lösung gehen lassen,—diese schon in Vergessenheit geratene Theorie wurde wieder aufgenommen, und, weiter geklärt durch die modernen Anschauungen des Lösungsdrucks, auf das Rosten des Eisens angewandt. Hier gebührt vor allen den amerikanischen Forschern Cushman und Gardner das Ver-

dienst durch ihren Ferroxy-Indicator und die damit angestellten Untersuchungen einen strikten augenfälligen Nachweis der electrolytischen Lokalstrom-Theorie erbracht zu haben. Man darf wohl sagen, dass die Zahl der Gegner dieser Theorie von Tag zu Tag abnimmt, obgleich man sich darüber klar sein muss, dass es besonders in der Industrie deren noch eine ganze Anzahl giebt; die Ursache hierfür mag wohl vor allem darin zu suchen sein, dass Verständniss und Interesse für die physikalische Chemie hier oft genug fehlen und dass die schon oft als falsch bewiesene und doch immer wieder auftauchende Ansicht, dass die Farbe nur zu decken braucht, um vor Rost zu schützen, der grösste Feind jedes Fortschrittes auf diesem Gebiete ist. Man muss mit Bedauern konstatieren, dass die Industrie der Rostschutzfarben, von einzelnen Ausnahmen abgesehen, hinter der wissenschaftlichen Forschung weit zurückgeblieben ist; sie befindet sich hierin im scharfen Gegensatz zu der organischen Farbenindustrie.

Mit der bisherigen Formulierung der electrolytischen Theorie haben die Rostvorgänge von Eisen, welches sich in feuchter Luft oder in einem Electrolyten befindet, eine völlig erschöpfende Erklärung gefunden. Anders scheint es mir jedoch zu sein, wenn man den Ursachen der Rostentstehung unter Anstrichen nachgehen will. Es scheint mir, dass hier eine Erweiterung der bisherigen Theorie notwendig ist, welche sich wohl am einfachsten in der Frage zusammenfassen lässt: Kann man die electrolytische Theorie auf das System Farbe Feuchtigkeit Eisen ausdehnen? Es ist über diese Frage schon Manches geschrieben worden, doch ist es zu einer Klärung vorderhand noch nicht gekommen, zumal die bisher für diese Frage angestellten Versuche physikalisch nicht immer einwandfrei sind.

Wenn man ein Stück Eisen mit einer Farbe bedeckt, so haftet die Farbe nicht an allen Stellen des Eisens. Es lässt vielmehr die dem Eisen zugewandte Seite der Farbschicht kleine Vertiefungen oder Höhlen frei. Hiervon kann man sich am besten überzeugen, wenn man z. B. eine Farbe auf Glas streicht, und dann mit der Luge bei günstiger Beleuchtung betrachtet, oder wenn man ein Zinkblech streicht, welches man nachher in starker Salpetersäure auflöst, so dass man die Farbhaut frei erhält. Diese kleinen Höhlen werden sich wohl zweifelsohne in einer



zum Teil von den äusseren Umständen abhängenden Zeit mit Feuchtigkeit anfüllen, da bekanntlich Feuchtigkeit und Wasser von der Farbhaut aufgesaugt werden; man hat wegen dieser Eigenschaft auch die gestrichene Farbe schon mit einem Schwamm verglichen. Aber selbst, wenn im wesentlichen eine Zufuhr von Feuchtigkeit von aussen nicht stattfindet, so kann solche in diese Hohlräume bei dem Trockenprozess des Leinöls gelangen, worauf ich kürzlich hingewiesen habe,<sup>1</sup> da ja das Leinöl während seines Trockenprozesses fortdauernd Wasser abspaltet.

Eine ähnliche Annahme, wie die des Bestehens kleiner Hohlräume, werden wohl diejenigen Autoren, welche sich mit der Frage eines electrischen Stromflusses zwischen Eisen und Farbe befasst haben, stillschweigend auch gemacht haben, wofern nicht in besonderen Fällen anzunehmen ist, dass sich die ganze Farbhaut vom Eisen teilweise durch dazwischendringende Feuchtigkeit abhebt.

Die Möglichkeit des Vorhandenseins eines Electrolyten ist also gegeben. Die weiteren Fragen wären, ob Potentialdifferenzen bestehen, wo dieselben liegen, welches ihr Vorzeichen ist und endlich, ob die Widerstände, die in Betracht kommen, so gross sind, dass sie einen Stromfluss verhindern.

Was die Potentialdifferenzen anbelangt, so können dieselben möglicherweise, wie beim ungestrichenen Eisen, innerhalb des Hohlraumes zwischen zwei verschiedenen Stellen des Eisens selbst bestehen.

Für diesen Fall, der wegen der Kleinheit der Hohlräume unwahrscheinlich ist, wäre die ganze Frage auf die ursprüngliche Theorie zurückgeführt.

Anders jedoch, wenn Potentialdifferenzen zwischen dem *Eisen* und *der angrenzenden Farbe* bestehen!

Man unterscheidet hier am besten wohl folgende Möglichkeiten: Erstens die Potentialdifferenz entsteht durch Polarisation; zweitens zwischen Leinöl und Eisen bestehen aus irgend welchen Ursachen schon an sich Potentialdifferenzen; drittens zwischen Eisen und dem in das Leinöl eingebetteten Farbkörper bestehen Potentialdifferenzen und haben die Möglichkeit sich geltend zu machen.

<sup>1</sup> E. Liebreich u. F. Spitzer Zeitsch. f. Electrochemie 1912, p. 24.

Der erste Fall wurde von den Herrn Walker und Lewis<sup>1</sup> an Conservenbüchsen beobachtet und die Ströme coulometrisch gemessen, die zwischen mit Leinöl, Lacken, Farben etc. bestrichenem Eisen und reinem Eisen fliessen. Die genannten Forscher nehmen an, dass die meist porösen Lacküberzüge, die ungesättigte Verbindungen enthalten, auf den nascierenden Wasserstoff durch Absorption depolarisierend wirken und so Spannungsdifferenzen zwischen lackfreiem und lackiertem Eisen herbeiführen. Ob diese Erklärung ausreichend ist, mag zweifelhaft erscheinen, da die einzelnen Farben, welche doch sämtlich Leinöl enthalten, in diesem Falle gleiche Strommengen hätten liefern sollen. Jedenfalls bleibt aber die interessante Tatsache bestehen, dass messbare Ströme zwischen dem lackierten und unlackierten Eisen flossen.

Hieran schliesst sich zugleich die zweite Frage an, nämlich die, ob etwa zwischen Leinöl an sich und Eisen Potentialdifferenzen bestehen. Zu diesem Zwecke habe ich versucht die Potentialdifferenzen einer mit Leinölfirnis überzogenen Glasplatte gegen Eisen zu messen. Die Versuchsanordnung war dabei folgende: Die Firnisplatte tauchte in ein Bassin ein, welches mit dem Electrolyten gefüllt war, sie wurde an einer Klemmschraube aus Messing so befestigt, dass einige Centimeter der Platte bis zur Klemmschraube frei über der Flüssigkeit herausragten; zwischen Messing und Platte wurden kleine Eisenplättchen zwischengelegt, um bei etwaigem kapillarem Aufstieg des Electrolyten bis zur Klemmschraube keine falschen Potentialwerte zu erhalten. Eine Eisen-Electrode befand sich in demselben Bassin der Firnisplatte gegenüber. Die Messungen wurden mit einem Quadrantelectrometer (1 Volt = 17,4 cm) ausgeführt. Als Electrolyt im Bassin wurde eine schwach mit  $H_2SO_4$  angesäuerte 1-10 n-KCl Lösung genommen. Die Messung gegen eine Eisenelectrode aus gewalztem Blech, das noch teilweise Hammerschlag hatte, ergab folgendes Bild: Im ersten Moment trat ein Ausschlag von ca.  $-17,5\text{cm} = \text{ungefähr } -1,0 \text{ Volt}$ , ein (das Vorzeichen bezogen auf die Leinöl-Electrode), und zwar so, dass das Eisen positiv, d.h. edel im Vergleich zu der Leinöl-Electrode war. Dieser Ausschlag ging alsdann unter starkem Schwanken bis auf

<sup>1</sup>W. H. Walker u. W. K. Lewis Journ. of Ind. and Engr. Chem. 1. 754. 1909.

im Mittel  $-\frac{1}{2}\text{cm} = -0,03$  Volt zurück und stellte sich dort eine Zeit lang ziemlich constant ein, um dann gegen O zu tangieren. Aehnlich war das Bild mit einem frisch geschmirlgelten dünnen Eisendraht. Der erste Ausschlag betrug  $\text{ca} -22\text{cm} = \text{ungef.} -0,125$  V, und tangierte dann, nach einem Aufenthalt bei  $-2\text{cm} = -0,11$  Volt, wieder gegen O. Man kann wohl in Anbetracht dieser Resultate vielleicht sagen, dass das Leinöl sich als schwach rostschtzend erweisen kann, wenn auch die zu gunsten des Eisens auffallenden Potentialdifferenzen in ihren endgültigen Werten äusserst gering sind und praktisch nicht in Frage kommen dürften. Welches der Vorgang an dem Leinölfirnis ist, ob ein chemischer oder physikalischer, darüber kann man sich ohne Weiteres kein Bild machen.

Die ersten hohen Potentialdifferenzen, die man nach dem Eintauchen der Platte beobachtet, deuten darauf hin, dass sich die Leinöl-Electrode im ersten Augenblick wie eine Gas-Electrode verhält. Es scheint demnach, dass wenn Ströme zwischen einer mit Leinöl bestrichenen und einer unbestrichenen Eisenplatte beobachtet werden können, die Ursache hierfür, wie die Herren Walker und Lewis annahmen, tatsächlich in irgend einer Polarsiationserscheinung zu suchen ist. Zwischen dem Leinöl an sich und dem Eisen bestehen, wie ja auch von vorneherein anzunehmen ist, keine Potentialdifferenzen; das Leinöl ist eben indifferent.

Verschiedentlich wurde—um auf die dritte Frage zu kommen—in der Praxis und in der Litteratur die Vermutung ausgesprochen, dass zwischen Farben und Eisen Potentialdifferenzen bestehen; besonders wurde dies von der Bleimennige behauptet. Strikte Beweise hierfür sind jedoch meines Wissens bisher noch nicht erbracht worden. Ragg<sup>1</sup> hat zwar zwischen mit Farben bemalten Glasplatten und Eisen Ströme nachgewiesen und empfiehlt auch einen solchen Nachweis ganz allgemein für die Güte von Anstrichen. Die Farben, mit denen er diese Versuche ausführte, enthielten jedoch alle metallischen Zinkstaub; ob der von ihm vorgeschlagene Versuch bei gewöhnlichen Farben messbare Ströme giebt, erscheint, nach in derselben Weise von Herrn Spitzer und mir angestellten resultatlosen Versuchen

<sup>1</sup>M. Ragg Jahrbuch der Schiffbautechn. Ges. Berlin 6, 389 (1905)

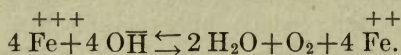
zweifelhaft. Dieser negative Ausfall beweist aber nichts gegen das Bestehen von Potentialdifferenzen zwischen Farben und Eisen, da alle Versuche, um Ströme zu messen, bei der Kleinheit der in Frage kommenden Potentialdifferenzen und der Grösse des Widerstandes der Farbe bei einer derartigen Versuchsanordnung, zu keinem Resultate führen dürften.

Der Nachweis der gesuchten Potentialdifferenzen ist eben nur mit einem empfindlichen Electrometer möglich.

Es lag mir daran zuerst festzustellen, ob einer der gebräuchlichen Farbkörper ohne Leinöl gegen Eisen oder gegen die Hg-HgCl Normalelectrode Potentialdifferenzen aufweist. Ich wählte hierzu anfangs Eisenoxyd ( $\text{Fe}_2\text{O}_3$ ) später auch noch Zinkoxyd ( $\text{ZnO}$ ) Bleicarbonat ( $\text{PbCO}_3$ ) und Bleimennige ( $\text{Pb}_3\text{O}_4$ ).

Die Herstellung von Electroden aus diesen Substanzen wurde in liebenswürdiger Weise von Herrn Wunsch mit einer eisernen cylindrischen Presse ausgeführt. Die in Stangenform gepressten Stücke hatten einen Durchmesser von 1 cm. und eine Länge von ungefähr 3–4 cm. Die Messungen wurden mit dem vorher erwähnten Electrometer und einem Compensationsapparat von Siemens & Halske nach der Compensationsmethode in bekannter Weise ausgeführt. Der Electrolyt, in den die Electrode tauchte—wieder neutrale 1-10 n-KCl-Lösung—enthielt  $\text{Fe}_2\text{O}_3$  als Bodenkörper, nachdem er hiermit ordentlich durchgeschüttelt worden war. Die Lösung wurde später zuerst mit NaOH schwach alkalisch und nachher mit  $\text{H}_2\text{SO}_4$  schwach sauer gemacht. Als gegenelectroden wurden die Hg-HgCl-Normalelectrode oder Eisenelectroden benutzt.

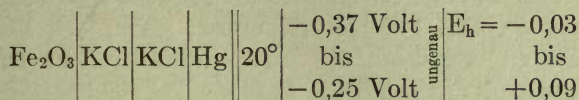
In der neutralen und schwach alkalischen Lösung waren die gemessenen Potentialdifferenzen äusserst inconstant, sie wurden ständig kleiner. Als Grund hierfür ist es möglich anzunehmen, dass die OH-Jonen Concentration infolge des sich an der  $\text{Fe}_2\text{O}_3$ -Electrode abspielenden Vorganges, stetig geringer wird. Es ist nämlich wahrscheinlich, dass dieser Vorgang folgender ist:



Es spricht auch hierfür, dass in saurer Lösung die Potentialwerte gegen die Normalelectrode absolut constant wurden und sich jederzeit reproduzieren liessen.

Die Resultate waren im Einzelnen folgende:

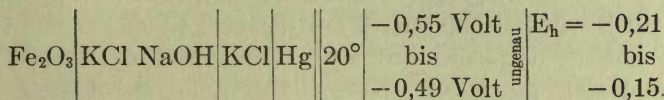
A.  $\text{Fe}_2\text{O}_3$ -Electrode in neutraler Lösung



d.h.:  $\text{Fe}_2\text{O}_3$  ist um ca. 0,3 Volt unedler oder zinkischer als Hg.

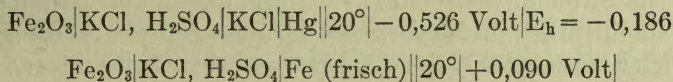
Anmkg.: Um die Werte auf die Wasserstoff Normal-Electrode  $E_h$  zu beziehen, sind den gefundenen Werten +0,337 Volt zuzuzählen.

B.  $\text{Fe}_2\text{O}_3$ -Electrode in schwach alkalischer Lösung (1 cm.<sup>3</sup> 40% NaOH auf 1,5 l. neutraler 1-10 n-KCl Lösung)



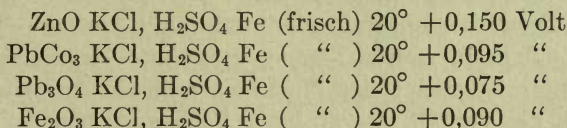
d.h.  $\text{Fe}_2\text{O}_3$ -ist um ca. 0,5 Volt unedler oder zinkischer als Hg.

C.  $\text{Fe}_2\text{O}_3$ -Electrode in saurer Lösung (1 cm.<sup>3</sup> 10%  $\text{H}_2\text{SO}_4$  auf 1,5 l. neutraler 1-10 n. KCl Lösung)



d.h.  $\text{Fe}_2\text{O}_3$  ist um 0,526 Volt unedler oder zinkischer als Hg, aber um 0,090 Volt edler als metallisches Eisen.

D.  $\text{ZnO}$ ,  $\text{PbCO}_3$ ,  $\text{Pb}_3\text{O}_4$  in saurer Lösung



Die Werte für Eisen mit Hammerschlag sind stets um ungef. 0,02 bis 0,04 Volt grösser.

Die Farbkörper sind also alle um gegen 0,1 Volt edler als Eisen. Dies erscheint im ersten Augenblick überraschend. Die Erklär-

ung mag aber die sein, dass die Farbkörper sehr wenig positive Ionen (oder vielleicht sogar negative Ionen) in Lösung senden.

Es ist also hiermit nachgewiesen, dass die gebräuchlichsten Farbkörper an sich Potentialdifferenzen gegen das Eisen aufweisen, die zu ungunsten des Eisens ausfallen. Es fragt sich nun nur noch, ob das Leinöl die Farbpartikel nicht bei Anstrichen vollkommen umhüllt, so dass es in Praxi zu Potentialdifferenzen nicht kommen kann. Dass dem nicht so ist, hat seiner Zeit Herr Ragg,<sup>1</sup> durch die weiter oben geschilderten Versuche schon nachgewiesen, und auch Herr Kröhnke<sup>2</sup> berichtet, dass man bei Anstrichen mit Zinkstaub, die sich in schwach mit Salpetersäure angesäuerter Lösung befinden, nach einiger Zeit chemisch Zink in dieser Lösung nachweisen kann.

Um auch diese Frage nochmals nachzuprüfen, versuchte ich eine mit Eisenoxyd-Leinölfarbe bestrichene und über einen Monat getrocknete Glasplatte mit dem Compensationsapparat und Electrometer gegen die Normal-Electrode zu messen. Als Electrolyt nahm ich wieder die schwach saure 1-10 n-KCl Lösung. Der Widerstand der Farbe zwischen dem Electrolyten und der Klemmschraube erwies sich aber zu gross, um nach der Compensationsmethode zu Resultaten zu gelangen; er wirkte wie eine Stromunterbrechung. Ich griff darauf auf das einfache Verfahren zurück die zu suchende Spannung direkt an das Electrometer anzulagen. Dies führte zu einem Resultat. Der erste Ausschlag war, wie bei den Messungen mit Leinölfirniss ein verhältnissmässig grosser; er entsprach einer Potentialdifferenz von ungef.  $-0,78$  Volt, (das Vorzeichen auf die Farbe bezogen). Alsdann stellte sich das Electrometer ziemlich constant auf ungef.  $-10,0$  cm ein. Dies entspricht einer Potentialdifferenz von  $-0,57$  Volt. Dies wäre ungefähr die Potentialdifferenz  $(-0,55V)$ , die  $Fe_2O_3$  allein in saurer Lösung gegen die Normalelectrode zeigte. Hiermit scheint der Nachweis erbracht zu sein, dass, wenn auch die Verhältnisse an einer Farben-Electrode ziemlich undefiniert sind, es doch im Wesentlichen auf die Farbkörper oder allgemein gesagt, auf die im Leinöl eingebetteten Substanzen ankommt.

<sup>1</sup> M. Ragg l. c.

<sup>2</sup> O. Kröhnke, üb. Schutzanstriche eis. Röhren Leipzig 1910.

Es wäre allerdings nun noch möglich, dass die zwischen Farbkörper und Eisen bestehenden Potentialdifferenzen es zu einer Electrolyse nicht kommen lassen können, weil der electriche Widerstand der Farbkörper zu gross wäre. Ich habe aber schon kürzlich<sup>1</sup> darauf hingewiesen, dass, wenn auch der spec. Widerstand einer gerade trocken gewordenen Eisenoxyd-Leinölfarbe ungef. 5. 106 beträgt, der tatsächliche in Frage kommende Widerstand doch nur verhältnissmässig gering ausfallen wird, da er sich nur auf nach 1-100 mm zählenden Strecken mit beliebig grossem Querschnitt geltend macht. Auch nimmt ja, wie Cushman u. Gardner<sup>2</sup> zeigten die Leitfähigkeit mit dem Feuchtigkeitsgrad der Farben ungeheuer zu. Ein derartiger Einwand ist also nicht zu fürchten und dem Eintreten der Electrolyse steht nichts im Wege.

Wie Herr Spitzer und ich zu zeigen Gelegenheit hatten,<sup>3</sup> nimmt das Rosten von Eisen unter Anstrichen mit zunehmender Anzahl der Anstriche zu. Diese auffallende Tatsache scheint uns darauf hinzudeuten, dass electrochemische Prozesse hier vor sich gehen müssen, die eine eingehende Untersuchung verlangen. Es war uns jedoch bisher nicht gewiss, ob man tatsächlich die Berechtigung hat solche annehmen zu dürfen. Die vorliegenden Untersuchungen stellen somit einen Schritt zu Klärung dieser Erscheinungen dar. Die weiteren in dieser Hinsicht angestellten Untersuchungen werden wir an anderer Stelle Gelegenheit haben zur Discussion zu stellen.

Wie ich ausgeführt habe, liegen die Verhältnisse bei Anstrichen so, dass der eingebettete Farbkörper eine wesentliche Rolle spielt. Es wird daher auf seine Auswahl zweckmässig grosse Sorgfalt zu legen sein. In erster Linie werden indess dabei seine maler-technischen Eigenschaften, insbesondere Weichheit, Deckvermögen und Haltbarkeit zu berücksichtigen sein, und hier wird man wohl von den gebräuchlichen Körpern Zinkoxyd, Eisenoxyd, Bleiweiss und Mennige kaum abgehen können. Man wird jedoch—and dies geschieht auch tatsächlich schon—den Farb-

<sup>1</sup>E. Liebreich u. F. Spitzer l. c.

<sup>2</sup>Cushman u. Gardner. *The Corrosion & Preservation of Iron & Steel* 1910 p. 170.

<sup>3</sup>l. c.

körpern Zusätze geben können, welche das Potential des Eisens günstig beeinflussen.

Den ersten Schritt auf diesem Wege hat man mit dem Zusatz von metallischem Zink-oder Aluminium-Staub gemacht. Theoretisch ist dieses Vorgehen absolut richtig; doch vermögen diese Farben, da die schützende Reichweite dieser Partikel recht gering ist und sie ausserdem, da die Leinölschicht von den Teilchen durchbohrt wird und Feuchtigkeit kapillar in diese kleinen Verletzungen eindringt, keinen effectiven Rostschutz zu gewähren, wie man sich leicht überzeugen kann, wenn man derartige Anstriche in Wasserdampf während 1 bis 2 Tagen längen lässt.

In verbessernder Weise hat man diesen Weg in Amerika und Deutschland jedoch weiter verfolgt.

In Amerika sind es die Farben mit Zusätzen von gewissen Chromsalzen, welche zuerst Wood<sup>1</sup> vorgeschlagen hat. Derartige Farben sind dann von verschiedenen, insbesondere von Cushman und Gardner geprüft und empfohlen worden. Die durch die eindringende Feuchtigkeit sich etwas lösenden Chromsalze passiviren das Eisen und wirken auf diese Weise rostschützend. Es ist nur zu bedauern, dass die geeigneten dieser Salze, dadurch dass sie wie Cushman und Gardner angeben, das Trocknen des Oeles bedeutend erschweren und auch wohl verhältnissmässig sehr teuer sind, in ihrem Wert herabgemindert werden.

Diese beiden Gründe machen es leider nicht möglich diese ausgezeichneten Rostschutzmittel in dem Procentsatz der Farbe beizumengen, der nötig ist, damit seine panivierenden Eigenschaften in vollem Umfange zur Geltung kommen können; immerhin wird auf diesem Wege des Passivierens noch mancher Fortschritt zu erreichen sein.

Der in Deutschland eingeschlagene Weg ähnelt dem in Amerika eingeschlagenen. Hier wird die Eigenschaft des Eisens benutzt in nicht concentrirten alkalischen Lösungen ein verhältnissmässig edles Potential anzunehmen. Diese Verhältnisse sind von Mugdan<sup>2</sup> genau untersucht worden.

Nach diesem Beobachter liegt die von ihm ausgesprochene

<sup>1</sup>Wood, Am. Soc. Mech. Eng. Trans. 1895, 16, 671.

<sup>2</sup>M. Mugdan, Zeitschrift, f. Electrochemie 1903, p. 442.



Vermutung nahe, dass das in  $\text{Na}_2\text{SO}_4$  gemessene Wasserstoff Potential von  $-0,25$  Volt (gegen die H—H-Normalelectrode gemessen) denjenigen Wert angiebt, welcher die die Rostung beschleunigenden und verhindernden Lösungen trennt, woraus folgen würde, dass die Bedingung des Eisenangriffes primär wasserzeretzung wäre. Dies stimmt mit seinen Beobachtungen überein. Es würde demnach praktisch darauf ankommen das Eisen mit solchen Lösungen zu umgeben, in denen es gegen die Wasserstoffnormalelectrode einen edleren Wert als  $-0,25$  Volt zeigt. Da das H-Potential in alkalischer Lösung noch unedler wird, ( $-0,74$ ) so ist eine Rostgefahr für das Eisen in alkalischen Lösungen mittlerer Concentration nicht vorhanden, in denen es Potentiale von  $+0,06$  Volt (in z. B.  $0,05$  n-NaOH) annimmt. Erst in ganz concentrischen Laugen zeigt es wieder ein wesentlich unedleres Potential ( $-0,88$  Volt), so dass Icht die Bedingungen eines Angriffes wieder gegeben sind, was auch mit den Tatsachen übereinstimmt.

Ich hatte Gelegenheit mich mit der rostschtützenden Wirkung von Farben mit Zusätzen solcher Art zu befassen, wobei sich insbesondere diejenigen Alkaliverbindungen als geeignet zeigten, welche bei Zutritt von Wasser direct NaOH oder KoH abspalten. Es sind dies besonders die Amide der Alkali-Gruppe. Vergleichende Rostungsversuche zeigten, dass Farben mit diesen Zusätzen eine unvergleichlich höhere rostschtützende Wirkung zukam, als allen denjenigen deutschen Handels-Farben, welche ich zu untersuchen Gelegenheit hatte. Derartige Farben<sup>1</sup> zeigten aber zuerst den Uebelstand, dass sie sich verseigten und es bedurfte erst längerer Untersuchungen, um dieses Uebelstandes Herr zu werden; nach Ueberwindung dieser Schwierigkeiten scheinen mir insbesondere die erwähnten alkalischen Zusätze ein vorzügliches Mittel zu sein, um das Rosten unter den Anstrichen zu verhindern, wie sich dies auch aus praktischen Versuchen ergeben hat.

Die in dieser Arbeit mitgetheilten Potentialmessungen wurden mit den Mitteln des physikalisch-chemischen Instituts der tech-

<sup>1</sup>Diese nach mir benannten Farben werden von den ebenfalls nach mir benannten Rostschutz-Farwerken in Reinickendorf bei Berlin hergestellt, welche ausschliesslich derartige Farben fabrizieren.

nischen Hochschule zu Danzig ausgeführt, die mir Herr Professor F. Krüger in liebenswürdigster Weise zur Verfügung stellte. Ich möchte Herrn Professor Krüger an dieser Stelle meinen ganz besonderen Dank hierfür aussprechen. Die übrigen erwähnten Untersuchungen führte ich im Wesentlichen der technischen Mittelschule der Stadt Berlin zusammen mit Herrn Dr. F. Spitzer aus, welchem ich ebenfalls meinen Dank für seine Mitarbeit auszusprechen gerne Gelegenheit nehme.

## HERRING OIL

ABRAHAM LUSSKIN

*New York City*

Within recent years the subject of fish oils has received considerable attention first from the leather and soap manufacturers and subsequently from the paint chemist. Hitherto fish oil played the role of a rather unimportant by-product in the course of fertilizer or "scrap" production, for which there seems to have been always a large demand.

As the peculiar properties and industrial possibilities of fish oils became more thoroughly appreciated in the light of investigations carried out by progressive manufacturers, the fish oil industry received a new lease of life and grew until it rivalled in importance the fertilizer industry to which it had previously been a tributary.

Of all the numerous varieties of fish oils which have at one time or another appeared upon the market, Menhaden Oil alone seems to have established itself on a firm basis in the manufacture of special kinds of heat-resisting paints. Its application, therefore, is no longer an experiment; it is an established fact.

Latterly, attention has been more particularly directed toward seal, whale, cod, porpoise, and herring oils, with a view to investigating their utilizability in the industries. Of these, seal, cod and porpoise body oils have proved to be in many ways as good as menhaden oil, but are beyond the reach of the paint manufacturer on account of considerations of price.

Whale oil, which is now obtainable in the form of a clear, pale material, comparatively free from objectionable odors, has not as yet been successfully manipulated to give very good drying results.

In the treatment of fish oils, several considerations must be constantly kept in mind in order to obtain the best results:

1. The oil must be free from high melting point glycerides or fatty acids; or, to use the technical term, the oil must be "winter pressed." Most fish oils contain a large amount of saturated glycerides of the nature of palmatin which separate from the

oils on standing for any length of time at a low temperature. When these have been removed from the oil, the resulting product is found to be much more amenable to successful treatment than it otherwise is. It would seem that these high melting point fats tend to retard or to prevent the drying of fish oils, giving films which remain greasy for a very long time.

2. Very frequently, oils are received which have a high content of free fatty acids. In the case of one sample of herring oil, this was as high as 41.9. Under such circumstances, it is perfectly evident that the drying of the oil would be very largely inhibited. In addition, such an oil, used as a paint vehicle, in conjunction with pigments like red lead, white lead, and zinc oxide will, in a very short space of time, "liver" up and form the lead and zinc soaps of the fatty acids. This was very largely responsible for the poor results obtained with the fish oils which were first introduced on the market. The free fatty acids are formed when the oil, extracted from the fish by boiling in water, is subjected to the action of the decomposition products from the bodies of the fish for a longer time than is absolutely necessary to break open the oil-containing cells.

3. Finally it must be remembered that driers, which serve very well for vegetable drying oils, will not, in general, function properly, when utilized for fish oils. The tungate driers, and particularly the Cobalt tungates, can generally be depended upon in the case of oils which do not yield to the action of the ordinary linseed oil driers, provided, however, the two conditions named above have been satisfied.

The writer recently had his attention called to several grades of herring oil, which, at first glance, appeared desirable from the paint manufacturer's standpoint. Accordingly an investigation was started to test its adaptability for paint purposes, and to compare its behavior with that of Menhaden oil.

Herring oil occurs in the bodies of *Clupeus C.* and *V.* (Japanese herring varieties) and *Clupeus harengus* (European or North Sea herring).

The plan of extracting the oil from herring is the one which is universally used in the fish oil industry, viz., extraction in boiling water.

Two representative samples of herring oil, furnished by two of the leading oil concerns in the States, were experimented with in conjunction with menhaden and other fish oils. The following analytical constants were obtained:

No.	Color	Odor	Sp. Gr. 15° C	Acid Value	Iodine Value
#1 Herring Oil	Very Pale	Good	0.9240	2.4	137.9
#2 Herring Oil	Dark Brown	Bad	0.9210	41.9	136.1
Blown Oil #2	Deep Red	Almost None	0.9654	25.7	89.94
Winter-Pressed } Refined } #2 *	Extremely Pale	Fair	0.920	39.4	136.1
#1 Crude Whale Oil	Very Pale	Good	0.9230	0.6	136.1
#1 Filt. Whale Oil	Very Pale	Good	0.9203	2.3	125.0
#2 Filt. Whale Oil	Pale Amber	Very good	0.9222	14.5	142.9
Porpoise Body Oil	Very Pale	Very good	0.9268	2.8	132.3
Menhaden Oils					
Ext. Bleached Winter Oil	Very Pale	Fair	0.9272	0.5	150.4
Bleached-Refined	Pale Amber	Not Bad	0.9308	5.7	161.2
Regular	Deep Red	Bad	0.9284	8.4	165.7

Crude herring oil, even though very dark in color, yields a very clear, pale product when treated with Fuller's earth for a short time at about 250° F., and then for some time longer, at the temperature of boiling water. In addition the odor is considerably improved.

In the case of the crude herring oil listed above, the sample was kept for several hours at about 60 F. to permit high-melting fats to separate out. The portion which remained liquid corresponded to a winter-pressed oil. Since the acid and iodine numbers were practically unchanged it seems that the solid fats

\*The part of the table below the asterisk (with exception of the acid values), is from a paper on Fish Oils delivered by Mr. M. Toch before the Amer. Chem. Soc. Dec. 1911 and published in the Journal of Industrial and Engineering Chemistry.

contained saturated and unsaturated compounds in about the same proportion as the crude oil.

Another sample of the oil was heated to 320° F. and blown with air for about 8 hours. The effect produced on the constants are shown above. The oil was very heavy and viscous but had the deep red color which fish oils so readily assume. It must be noted also that the "fishy" odor was very faint. The reduction in acid value would seem to indicate that the oil contained fatty acids which were volatile at the temperature of blowing.

Attempts to dry the samples of herring oil did not prove successful, even when very powerful driers were used. This cannot, however, be interpreted to mean that herring oils are, in general, not capable of drying.

Porpoise body oil and menhaden oil, under similar conditions, dried satisfactorily.

The blown herring oil could very well be used for the production of smoke-stack paints, and for paints intended to resist the "Chalking" action of salt air. Herring oil is at present used to a certain extent in leather manufacture together with some of the other fish oils like menhaden and whale oil. In regard to herring oil, as with many of the other materials which are being introduced from time to time, the final word cannot be spoken until many more specimens have been examined and given a fair test.

# MOISTURE AND THE DRYING OF THE LINSEED OIL FILM

HANS MANNHARDT

*Heath & Milligan Mfg. Co., Chicago, Ill.*

It is a well known fact that a linseed oil film does not dry properly in damp weather. The subject has been discussed by a number of investigators and as their experimental modes of procedure have differed, their conclusions have been somewhat at variance. It is believed that the apparatus employed in this experiment differs from those of previous experimenters.

Compressed air tap 2 liter water trap 2 liter bottle containing concentrated $H_2SO_4$ Safety bottle Wash bottle, 100 cc 50% Na OH $CaCl_2$ bottle 100 g NaOH. $Ca(OH)_2$ Safety bottle Wash bottle, 100 cc conc. $H_2SO_4$ 2 Mohr bulbs, conc. $H_2SO_4$	}	Purifying train
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$CaCl_2$ bottle charged with	{ 300 grams silica flour and 30 grams "boiled" linseed oil }	} Reaction Bottle #1
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Mohr bulb, conc. $H_2SO_4$ Mohr bulb, conc. $H_2SO_4$ 20 cm. straight—one bulb tube, soda lime U-tube, pumice and $H_2SO_4$	}	Absorption train #1
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Reaction Bottle #2 like R. B. #1.....	Reaction Bottle #2
Absorption train #2 like A. T. #1.....	Absorption train #2

3 Bulb—U-tube—conc. $H_2SO_4$ .....	Safety tube
$3\frac{1}{2}$ liter aspirator bottle.....	Suction

Necessary stoppers were of sound cork thoroughly soaked with paraffine wax at 100° C. and sealed in place with paraffine wax. Joints between the contiguous pieces of apparatus were made with fresh pure gum-tubing wired in place and blank experiments were made to ascertain the efficiency of the purifying train and various joints.

*The object* of this train of apparatus was to establish whether conc. H<sub>2</sub>SO<sub>4</sub> and soda-lime could retain those products of linseed oil which retard its drying.

*The oil used*, when one gram was spread uniformly through ten grams of silica flour, gained 16% in weight in 18 hours at 20°C.

Usually about seven liters of *purified air* passed through the apparatus in the course of an eight-hour day. The apparatus remained idle on Saturdays and Sundays.

*Organic volatile.* The sulphuric acid in each of the Mohr bulbs immediately following the reaction jars, was colored to about the color and depth of a tenth-normal iodine solution. The next Mohr bulb contents were not colored.

*Observations.* The first Mohr bulbs of the two absorption trains apparently absorbed all the "H<sub>2</sub>O, etc.," and the small gains in weight of the next Mohr bulbs was considered as being derived from the soda-limes following and therefore added to the gains in weight due to "CO<sub>2</sub>, etc."

The following weighings were taken:

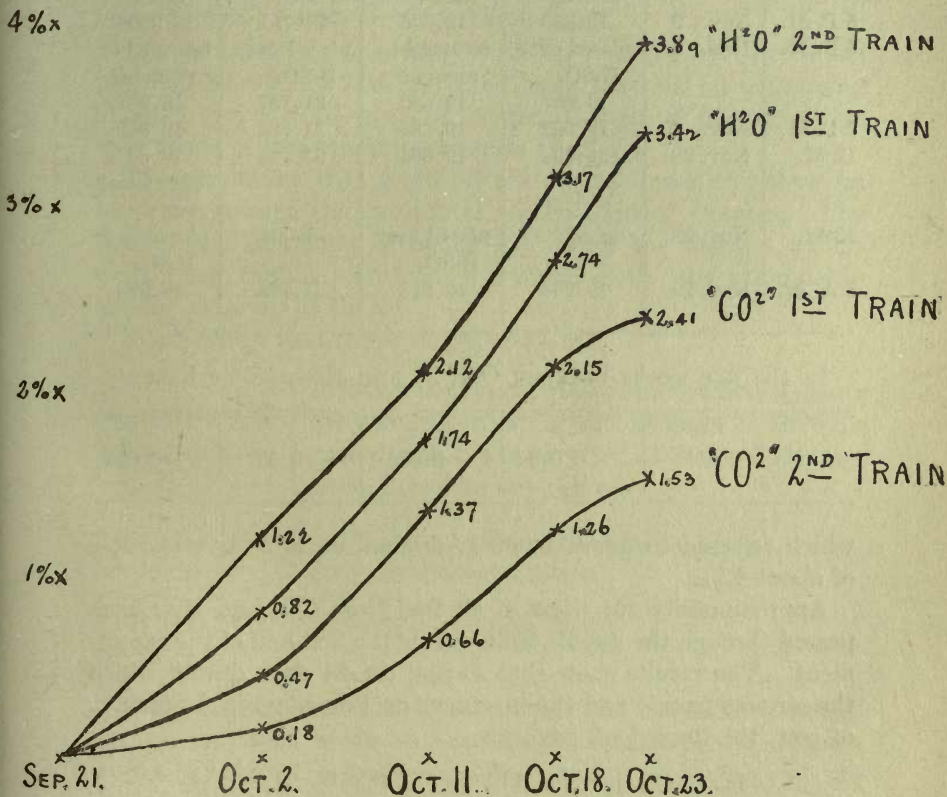
Increments "H <sub>2</sub> O etc."	Train #1	Increments "CO <sup>2</sup> etc."			
		H <sub>2</sub> SO <sub>4</sub>	NaOH. Ca(OH) <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	
0.245	9-21 to 10-2	.003	.097	.042	Column of silica and oil about six inches deep
0.276	10-2 to 10-11	.000	.229	.040	
0.299	10-11 to 10-18	.000	.202	.032	
0.205	10-18 to 10-23	.000	.052	.027	
1.025				0.724	

"H<sub>2</sub>O" plus "CO<sub>2</sub>" equals 1.749 g.



	Train #2				
0.366	9-21 to 10-2	.002	.017	.034	Column about eight inches deep
0.270	10-2 to 10-11	.001	.113	.030	
0.315	10-11 to 10-18	.000	.150	.031	
0.215	10-18 to 10-23	.001	.059	.022	
1.166				0.460	

"H<sub>2</sub>O" plus "CO<sub>2</sub>" equals 1.626 g.



While these curves show that the oxidation was by no means completed, the two Ca Cl<sub>2</sub> jars were opened at the end of the experiment and 10,000 grams at once weighed out from the top and from the bottom of each jar and placed in shallow dishes.

		Top #1	Bottom #1	Top #2	Bottom #2
4 P. M.	Oct. 23	19.940	19.720	21.800	19.030
5 P. M.	Oct. 23	19.930	19.713	21.790	19.025
9 A. M.	Oct. 24	19.910	19.692	21.769	19.005
9 A. M.	Oct. 25	19.907	19.687	21.764	19.002
9 A. M.	Oct. 30	19.902	19.684	21.764	19.002
9 A. M.	Oct. 30	placed over H <sub>2</sub> SO <sub>4</sub>	placed over H <sub>2</sub> SO <sub>4</sub>	placed over H <sub>2</sub> SO <sub>4</sub>	placed over H <sub>2</sub> SO <sub>4</sub>
5 P. M.	Nov. 2	19.893	19.666	21.755	18.990
5 P. M.	Nov. 2	placed over H <sub>2</sub> SO <sub>4</sub>	returned to room air	placed over H <sub>2</sub> SO <sub>4</sub>	returned to room air
		19.897	19.680	21.757	18.997
3 P. M.	Nov. 6	19.902	19.684	21.762	19.002
12 M.	Nov. 28	19.904	19.684	21.763	19.004
					Foggy weather
12 M.	Nov. 28	in air	placed over H <sub>2</sub> SO <sub>4</sub>	in air	placed over H <sub>2</sub> SO <sub>4</sub>
8 A. M.	Nov. 29	19.903	19.673	21.762	18.993

In the five weeks between Oct. 23 and Nov. 28 we have—

		-0.036	-0.036	-0.037	-0.026
--	--	--------	--------	--------	--------

which referred to about 0.900 g. original oil is an average loss of about 4.0%.

Approximately 161 liters of air free from CO<sub>2</sub> and H<sub>2</sub>O were passed through the double train during the first half of the experiment. The results show that during the 21 days during which the air was passed and the intermediate Saturdays and Sundays of rest, the linseed oil gave up:

in CaCl<sub>2</sub> jar #1 0.65% C., 0.38% H.  
in CaCl<sub>2</sub> jar #2 0.34% C., 0.43% H.

and if the jars and contents had been weighed before and after the run, we would also know whether any oxygen was given off by the oil. This could easily be done by some future investigator.

1 gram of water is sufficient to saturate—

108 liters of air at 10° C. 760 m.m.	} Meyers Groses Konvers, Lexikon, "Luft feuchtig- keit" s. 809
58 " " " " 20° C. 760 m.m.	
33 " " " " 30° C. 760 m.m.	

As the laboratory temperature averaged 20° C. with little variation during this experiment, the air coming off the reaction jars was about one-third saturated with moisture, a low humidity, very favorable for the drying of linseed oil.

The actual drying or setting of the linseed oil must have taken place on September 21st and 22nd, each reaction jar consuming about 5 grams or 3½ liters of oxygen, though no measurements were made of this presumptive state of affairs.

The curves for H<sub>2</sub>O given off are almost linear and show no tendency toward the horizontal at the 23rd of October. The further loss in weight of about 4% which the linoxyn underwent from October 23rd to November 29th was presumably largely made up of H<sub>2</sub>O.

It is possible that the drying consists of:

PERIOD "A" 9-21-10-2	} Fixation of oxygen, little decarbonization, some dehydrogenization, about 49 liters of air were passed into the apparatus; 36 liters of air may be sufficient to dry the oil
PERIOD "B" 10-2-10-18	
PERIOD "C" 10-18—	} Dehydrogenization chiefly

If the reaction jars had been weighed and the other determinations had been made at more frequent intervals the process would have given a further insight into the mechanism of the drying of linseed oil.

Presumably, combustion determinations of the carbon and the hydrogen in linoxyn have been made with the air-dry product and this certainly is open to some criticism owing to the moderate hygroscopicity of the linoxyn.



## THE DECOMPOSITION OF LINSEED OIL DURING DRYING

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There are various statements in the literature on linseed oil that during the process of drying carbon dioxide is given off. The authors have failed to find the record of any definite experiment indicating the amount of this constituent which is evolved during the drying process. No definite information could be found with reference to the amount of water evolved. Experiments have been conducted to ascertain the increase in weight of linseed oil during drying, the assumption being that this increase in weight is due to the absorption of oxygen. It is evident that if volatile constituents are given off during the drying process, the increase in weight will not give a true measure of the oxygen absorbed.

In order to secure more definite information with reference to this very interesting and important reaction, an experiment was carried out in which pure, dry air was conducted over a weighed amount of linseed oil. The increase in weight of the linseed oil was ascertained and the moisture and carbon dioxide given off was absorbed and weighed so that the total amount of oxygen which combined with the linseed oil could be calculated.

The linseed oil used for this purpose was a sample of the oil prepared under the direction of Committee E of the Society of Testing Materials. Four samples were prepared under the direction of this committee under conditions which seem to absolutely guarantee that the samples taken are pure linseed oil. Four samples were received from Mr. G. W. Thompson, sealed and packed exactly as they were sent out by this committee for analysis.

The full description of the method of preparing these samples, as well as the analysis, may be found in the report of Committee

D of the Society of Testing Materials. The sample upon which our experiment was conducted was pressed from the seed by the National Lead Company April 1909. On the 25th of April when our experiment was begun, the oil was clear but there was a slight sediment in the bottle. The bottle was thoroughly shaken when the portion experimented on was weighed out.

5.336 grams of the linseed oil was transferred to a weighed Florence flask of 400 cc. capacity. In order to expose this large amount of oil in a thin film to the gases of the air 3.866 grams of glass wool were placed in the bottle. By previous experiment, this amount had been found just sufficient to soak up the oil after the walls of the flask has been covered by a thin film. A similar flask was used as a counter-poise in all the weighings so as to eliminate the error due to air displacement and films of moisture on the surface of the glass.

The flask containing the linseed oil was connected up in a series of tubes as follows. A glass tube extended into the open air so as to avoid acid fumes and impurities from the laboratory air. The air was first passed through a large tower containing soda lime and caustic potash in lumps, then through a Geissler bulb containing strong caustic potash solution; then through a U tube containing concentrated sulphuric acid and glass beads. The air thus freed from carbon dioxide or other acid gases and water, passed into the flask containing the linseed oil through a tube extending to the middle of the flask. The exit tube, passing out from the upper part of the flask conducted the air into a weighed U tube containing concentrated sulphuric acid and glass beads, thence into weighed Geissler bulbs containing strong caustic potash solution; then through a weighed U tube containing concentrated sulphuric acid and glass beads, then through another sulphuric acid tube to an aspirator, holding 75 liters. This aspirator drew 7.5 liters of air through the apparatus at night and 7.5 liters during the day; the flask containing the oil, the sulphuric acid tubes and the Geissler bulb being weighed morning and evening.

Before the experiment was started, the apparatus was tested over a long period of time by drawing air through in the manner indicated, and weighing the tubes night and morning until it

was certain that all sources of error had been eliminated and that the various weighed tubes had become constant. The flask designed for the linseed oil then received its charge of weighed linseed oil, and the experiment continued for 74 days. The results of the experiment are given in tabular form.

The determinations bracketed are doubtful on account of slight errors such as spattering of the liquid in the tubes, etc. Table II was calculated from Table I by adding together the daily increases in weight, so that the figures given for each day give the total quantity on that day. Table III was calculated from Table II by dividing the various quantities by the weight of oil taken, 5.366 grams.

TABLE I  
Daily Record of Weights Taken

Days	Increase in weight of oil Grams	Water given off Grams	Carbon Dioxide given off Grams
1st.....	0.0254	0.0306	0.0156
2nd.....	0.0060	0.0156	0.0106
3rd.....	0.0044	0.0236	0.0138
4th.....	0.0060	0.0316	0.0244
5th.....	0.0102	0.0088	0.0270
6th.....	0.0140	0.0118	0.0124
7th.....	0.0178	0.0334	0.0080
8th.....	0.0286	0.0164	0.0038
9th.....	0.0276	0.0218	(0.0084)?
10th.....	0.0156	0.0102	0.0128
11th.....	0.0374	0.0292	0.0094
12th.....	0.0454	0.0364	0.0072
13th.....	0.0274	0.0202	0.0063
14th.....	0.0696	0.0438	0.0095
15th.....	0.0796	0.0246	(0.0074)?
16th.....	0.0756	0.0200	0.0054
17th.....	0.0650	0.0098	0.0000
18th.....	0.0478	0.0156	0.0078
19th.....	0.0600	0.0230	0.0066
20th.....	0.0636	0.0150	0.0042
21st.....	0.0408	0.0270	0.0058
22nd.....	0.0354	0.0212	0.0056
23rd.....	0.0400	0.0560	(0.0056)?
24th.....	0.0184	0.0272	0.0057
25th.....	0.0112	0.0356	0.0079
27th.....	0.0114	0.0268	0.0052
28th.....	0.0108	0.0088	0.0010
30th.....	0.0156	0.0260	0.0090
32nd.....	0.0064	0.0304	0.0022
35th.....	0.0082	0.0202	0.0078
38th.....	0.0058	0.0130	0.0028
41st.....	0.0092	0.0046	0.0028
44th.....	0.0071	0.0061	0.0035
48th.....	0.0054	0.0057	0.0038
51st.....	0.0058	0.0072	0.0018
53rd.....	0.0040	0.0086	0.0026
57th.....	0.0032	0.0043	0.0020
62nd.....	0.0012	0.0068	0.0025
74th.....	0.0011	0.0052	0.0007



TABLE II  
*Total Amount of Quantities Determined*

Days	Increase in Weight of oil Grams	Water given off Grams	Carbon Dioxide Given off Grams	Total Oxygen Absorbed Grams
1st.....	0.0254	0.0306	0.0156	0.0716
2nd.....	0.0314	0.0462	0.0262	0.1038
3rd.....	0.0358	0.0698	0.0400	0.1456
4th.....	0.0418	0.1014	0.0644	0.2076
5th.....	0.0520	0.1102	0.0914	0.2536
6th.....	0.0660	0.1220	0.1038	0.2918
7th.....	0.0838	0.1554	0.1118	0.3510
8th.....	0.1124	0.1718	0.1156	0.3998
9th.....	0.1400	0.1936	0.1240	0.4576
10th.....	0.1556	0.2038	0.1368	0.4962
11th.....	0.1930	0.2330	0.1462	0.5722
12th.....	0.2384	0.2694	0.1534	0.6612
13th.....	0.2658	0.2896	0.1597	0.7151
14th.....	0.3354	0.3334	0.1692	0.8381
15th.....	0.4150	0.3580	0.1766	0.9496
16th.....	0.4906	0.3780	0.1820	1.0506
17th.....	0.5556	0.3878	0.1820	1.1254
18th.....	0.6034	0.4034	0.1890	1.1958
19th.....	0.6634	0.4264	0.1964	1.2862
20th.....	0.7270	0.4414	0.2006	1.3690
21st.....	0.7678	0.4684	0.2064	1.4426
22nd.....	0.8032	0.4896	0.2120	1.5048
23rd.....	0.8432	0.5456	0.2176	1.6064
24th.....	0.8616	0.5728	0.2233	1.6577
25th.....	0.8728	0.6084	0.2312	1.7124
27th.....	0.8842	0.6352	0.2364	1.7558
28th.....	0.8950	0.6440	0.2374	1.7764
30th.....	0.9106	0.6700	0.2464	1.8270
32nd.....	0.9170	0.7004	0.2486	1.8660
35th.....	0.9252	0.7206	0.2564	1.9022
38th.....	0.9310	0.7336	0.2592	1.9238
41st.....	0.9402	0.7382	0.2620	1.9404
44th.....	0.9473	0.7443	0.2655	1.9571
48th.....	0.9527	0.7500	0.2693	1.9720
51st.....	0.9585	0.7572	0.2711	1.9868
53rd.....	0.9625	0.7658	0.2737	2.0020
57th.....	0.9657	0.7701	0.2757	2.0115
62nd.....	0.9669	0.7769	0.2782	2.0220
74th.....	0.9680	0.7821	0.2789	2.0290

TABLE III

*Total Amount of Quantities Determined in Percentage of Oil Taken*

Days	Increase in weight of oil Per cent	Water given off Per cent	Carbon Dioxide given off Per cent	Total Oxygen absorbed
1st.....	0.47	0.57	0.29	1.34
2nd.....	0.59	0.86	0.42	1.94
3rd.....	0.67	1.30	0.74	2.72
4th.....	0.78	1.88	1.20	3.97
5th.....	0.97	2.06	1.70	4.72
6th.....	1.23	2.27	1.98	5.44
7th.....	1.56	2.90	2.08	6.55
8th.....	2.09	3.20	2.16	7.45
9th.....	2.61	3.61	2.31	8.52
10th.....	2.90	3.80	2.55	9.25
11th.....	3.60	4.34	2.73	10.65
12th.....	4.44	5.02	2.86	12.30
13th.....	4.76	5.40	2.98	13.30
14th.....	6.25	6.21	3.16	15.60
15th.....	7.73	6.67	3.29	17.70
16th.....	9.14	7.05	3.45	19.60
17th.....	10.35	7.21	3.45	21.00
18th.....	11.21	7.50	3.52	22.30
19th.....	12.31	7.84	3.66	24.00
20th.....	13.51	8.23	3.74	25.50
21st.....	14.30	8.72	3.85	26.95
22nd.....	14.94	9.10	3.95	28.00
23rd.....	15.70	10.18	4.05	29.50
24th.....	16.00	10.67	4.16	30.90
25th.....	16.25	11.30	4.30	31.90
27th.....	16.41	11.80	4.41	32.70
28th.....	16.65	12.00	4.43	33.10
30th.....	16.95	12.50	4.60	34.00
32nd.....	17.10	13.05	4.64	34.80
35th.....	17.21	13.41	4.78	35.50
38th.....	17.35	13.66	4.83	35.80
41st.....	17.50	13.73	4.89	36.20
44th.....	17.65	13.82	4.95	36.50
48th.....	17.75	13.95	5.03	36.80
51st.....	17.80	14.10	5.05	37.00
53rd.....	17.90	14.26	5.10	37.30
57th.....	17.95	14.35	5.14	37.50
62nd.....	18.00	14.48	5.20	37.70
74th.....	18.05	14.55	5.21	37.80

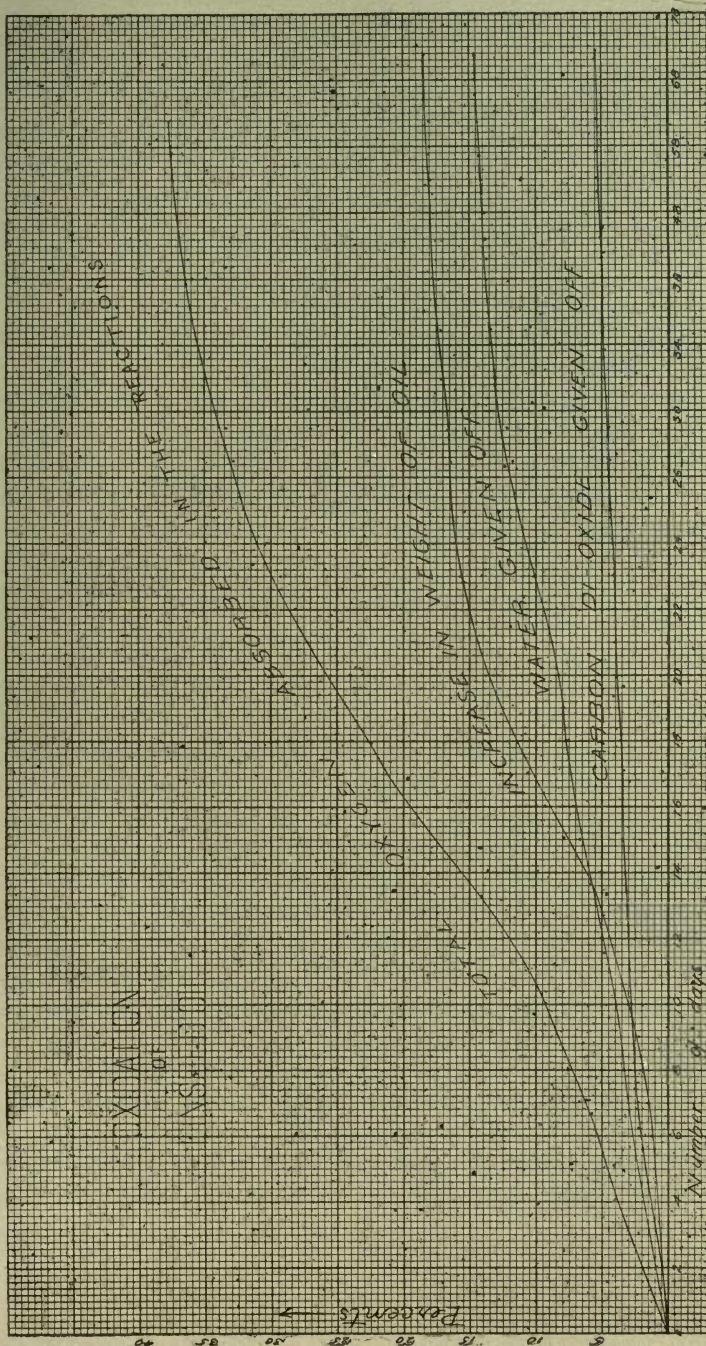
It will be noted that moisture and carbon dioxide were given off almost immediately in fairly large quantity. The oil which was slightly yellow in the beginning soon became colorless and gradually acquired a dark yellow color. Volatile matter also began to be evolved from the linseed oil. This was ascertained from the observation that small oily drops collected in the neck of the flask. The weighed sulphuric acid tube also gradually acquired a brown color which ultimately became black. This would, undoubtedly, produce an evolution of sulphur dioxide, which would be absorbed by the caustic potash solution in the Geissler bulb. Only toward the end of the experiment did the sulphuric acid tube which followed the Geissler bulb acquire a dark color. It is reasonable to suppose, therefore, that little, if any, volatile matter escaped absorption and that, therefore, while the increase in weight of the absorption tubes does not correctly represent the amount of water and carbon dioxide evolved, it does represent the total volatile matter given off by the oil, so that the increase in weight of the oil, plus the increase in weight of the absorption tubes represents the total amount of oxygen absorbed by the oil, and that experiments in which the increase in weight of the linseed oil film is noted, do not represent correctly the amount of oxygen absorbed. On the accompanying plate, a curve is drawn representing the amount of oxygen absorbed in the reaction. This was obtained from the increase in weight of the oil, plus the increase in weight of the absorption tubes. Another curve is given, showing the amount of water evolved, and another one showing the amount of carbon dioxide evolved. The accuracy of these curves and more especially the one representing the amount of water evolved, is vitiated by the fact that a volatile organic substance was produced. This volatile substance, however, is probably high in hydrogen, and an attempt will be made in the future to isolate a larger quantity of this constituent and identify it.

The composition of linseed oil is generally given as follows: Carbon 76%—Hydrogen 11%—Oxygen 13%.

Neglecting the error due to the volatile oil given off, the linseed oil lost 1.87% of its carbon and 14.73% of its hydrogen.

At the time this paper was written, the flask and the absorption tubes had not yet become constant in weight. The experiment will be continued until constant weight is obtained.

It was believed that the results, though incomplete, were of sufficient interest for publication.





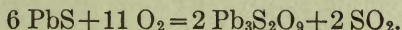
## THE MANUFACTURE AND PROPERTIES OF SUBLIMED WHITE LEAD

JOHN A. SCHAEFFER

*Picher Lead Co., Joplin, Mo.*

The manufacture of sublimed white lead, the commercial name for the basic sulphate of lead prepared by the sublimation process, depends directly upon the oxidation of galena, the sulphide of lead, when subjected to intense heat in an oxidizing atmosphere. The combustion under these conditions proceeds with violence resulting in the formation of a white sublimate, which when purified is known as sublimed white lead.

The reaction which occurs in this oxidation of galena may be written as follows:—



This formula  $\text{Pb}_3\text{S}_2\text{O}_9$  or  $2 \text{PbSO}_4 \cdot \text{PbO}$  is analogous to the generally accepted formula for the basic carbonate of lead— $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . Commercial sublimed white lead, however, contains a higher percentage of lead sulphate than that required for the above theoretical formula. While the formation of the theoretical basic sulphate of lead is entirely feasible, its manufacture has not proven commercially advantageous. The conditions for the oxidation of the sulphide of lead are, consequently, so adjusted that a compound showing about 16 per cent. of lead oxide is obtained. The conversion of a small percentage of the lead oxide, present in the theoretical basic sulphate of lead, to lead sulphate undoubtedly results from a reaction between the lead oxide and the sulphur trioxide which forms from the oxidation of a certain amount of sulphur dioxide. A small percentage of zinc oxide is formed at the same time from the sphalerite, the sulphide of zinc, which is present in almost all non-argenti-ferous lead ores. It is maintained that the presence of about 6 per cent. of zinc oxide enhances the value of the pigment.

Coke, of a hard compact variety is used as fuel, while iron, in the metallic form, and limestone serve as fluxing materials together with the silica present in the ore. Any metallic lead which forms from a reduction of the lead compounds by the coke, at the intense heat continually maintained in the furnace, is separated from the readily fusible slag by a difference in their specific gravities.

Blue Fume, the fume known commercially as sublimed blue lead, is frequently added to the charge. This fume is formed in the smelting of lead ores and is recovered by the bag room process. It is found to contain about 35 per cent. of lead oxide and about 50 per cent. of lead sulphate. This fume pigment, sublimed blue lead, is rapidly finding extended use as a paint pigment for the protection of iron and steel. Its composition renders it extremely valuable as charge material and being a product of sublimation is extremely reactive when subjected to the conditions found in the oxidizing furnaces.

The method of charging the furnaces varies with atmospheric conditions and the life and temperature of the furnace, charges being formulated to meet these conditions.

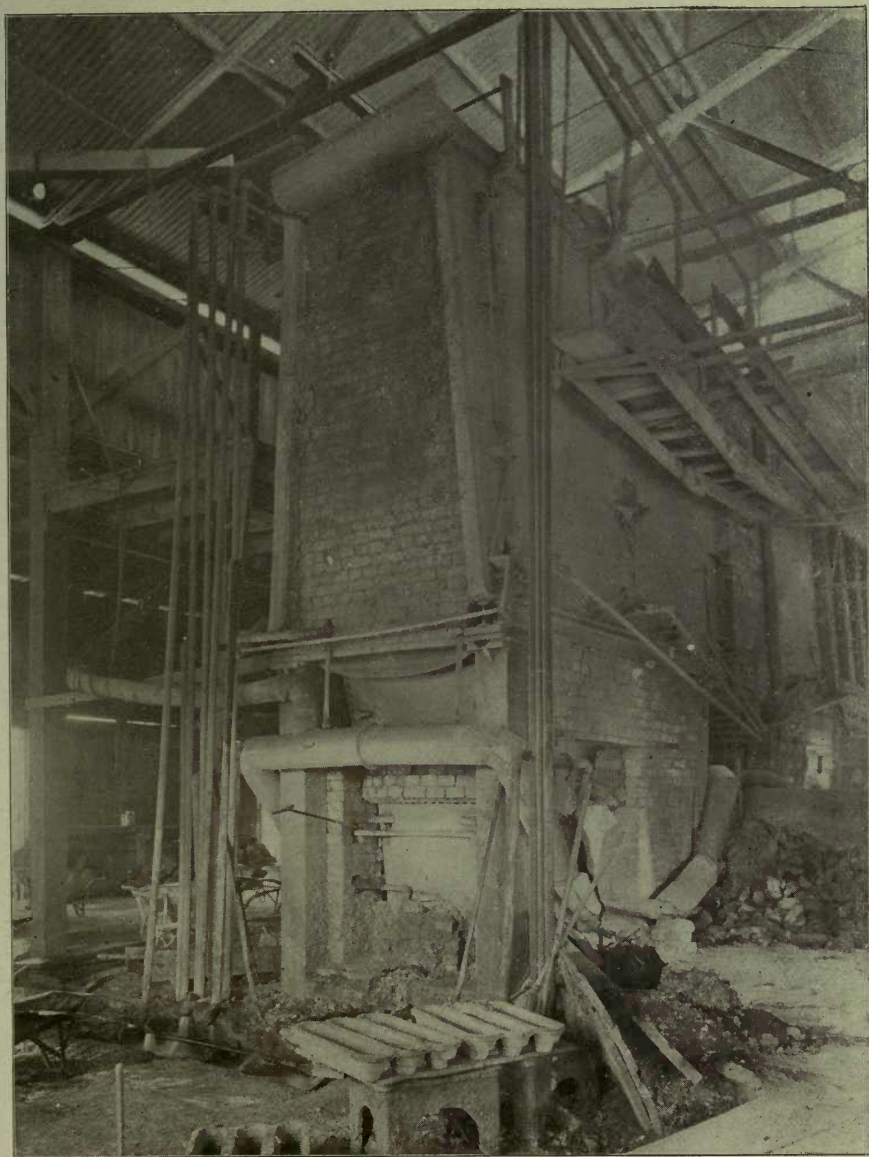
By following the charge from the raw materials to the finished products, the general working conditions can be best understood.

The oxidizing furnaces, two being considered a unit, consist of oval iron water-jackets, four feet in height, open at both ends, the upper end being five feet in length and three and one-half feet in width.

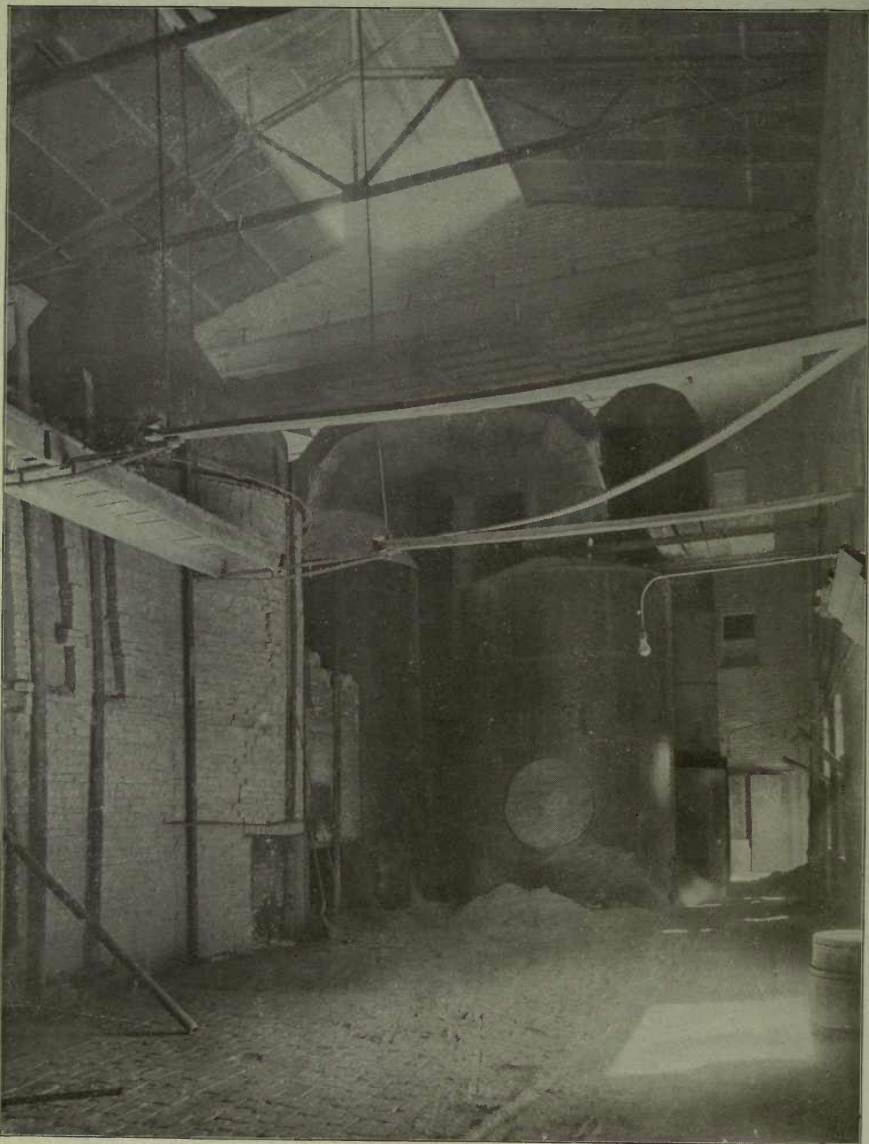
This water-jacket is securely built in a brick structure, on a solid brick base, and has a small opening in front which serves as a tap hole for the continuous removal of slag and metallic lead and their separation by the difference in their specific gravities. An oxidizing atmosphere is maintained by blowing air through tuyere holes entering near the base of the furnace. The feed door of suitable size and form is placed at one side of the furnaces.

The brick work surrounding the water-jacket or furnace proper is extended upward so as to form a large combustion chamber, which is in some cases water-jacketed.





View of the furnace with combustion chamber above. The trough for the separation of metallic lead from slag is seen in front of the furnace.



View showing "beehive" with "goose-necks" in the distance.

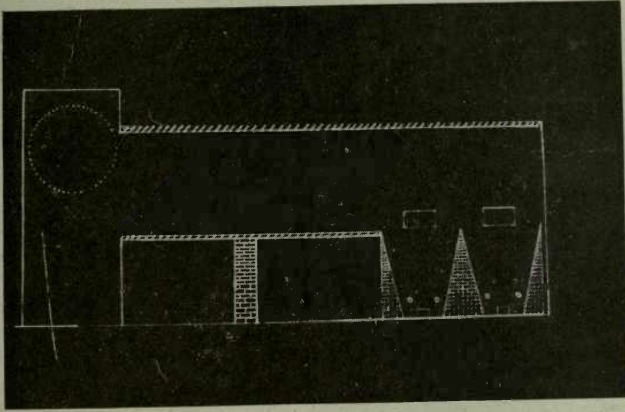


Diagram showing the location of the furnaces in relation to the combustion chamber and "beehive."

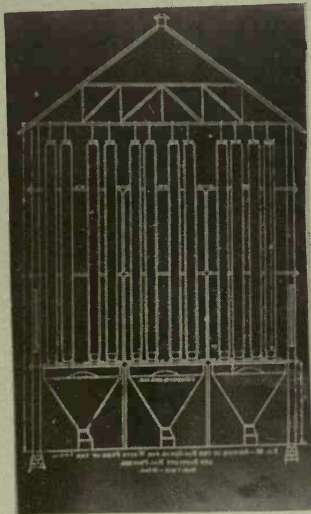


Diagram showing the arrangement of the bag room.



The hoppers into which the sublimed white lead falls from the bag room.

Immediately upon feeding the charge into the furnace, the fire of which is maintained at a point of incandescence, the reactions theretofore described occur with great violence and the volatilized lead passes upward into the combustion chamber.

Suction is maintained by a powerful fan placed between the bag room and the "goose-necks" which draws the condensed fume onward through the cooling system, finally driving it into the bag room where it is deposited.

The cooling system is built so as to produce maximum cooling effect by the introduction of baffles which prevent the easy passage of the fumes into the bag room. After the fume has passed out of the bee hive, where it is condensed and purified, it is drawn through the "goose-necks," large inverted U shaped pipes resting on hoppers, by the large suction fans and thence forced into the bag room.

The bag room is of a special type somewhat similar to those used in the collection of all fumes.

In the sublimed white lead bag room, however, are found three rows of hoppers (Cut #5), each hopper carrying 24 bags. The pressure of the fan forces all the gases through the cloth of the bags, while the sublimate is deposited. Occasional shaking throws the fume into the hopper where it is packed for shipment.

Sublimed white lead as it is removed from the hoppers is white in color. Much fume, however, which is unsatisfactory and not suited for use in the various arts is deposited in the portion of the cooling system preceding the suction fan. This fume is contaminated with a small percentage of coke, ash and other impurities, and being of a higher specific gravity than pure sublimed white lead, is readily deposited before reaching the fan, by a careful adjustment of the suction. The fume becomes darker in color the nearer the approach to the furnace. As a charge material the sublimate is excellent owing to its very finely divided condition.

Sublimed white lead, being a fume product consists of very fine amorphous particles, in size about one thirty-five thousandth of an inch in diameter. Its specific gravity is found to be 6.2.

In composition it shows approximately 78 per cent. of lead sulphate, 16 per cent. of lead oxide and 5.5 per cent. of zinc

oxide. That the lead oxide present is chemically combined as a basic sulphate of lead, the sulphate of lead present in excess of the amount required for the theoretical formula being present as neutral sulphate of lead, is held by practically all authorities. Chevalier claims the formula of  $Pb_3S_2O_9$  for the fume resulting from a furnace roasting lead sulphide.

According to Toch,<sup>1</sup> we find, that "A Mixture of precipitated lead sulphate, litharge and zinc white is approximately the proportions found in sublimed lead, when ground in oil and reduced to the proper consistency, dries totally different from sublimed white lead; in fact, sublimed white lead when ground in raw linseed oil takes two days to dry dust free, but the mixture just cited will dry sufficiently hard for repainting in twelve hours, because lead sulphate is a fair dryer and lead oxide a powerful one. The oxysulphate having the same composition, behaves totally different from the mixture." A mixture of the neutral lead sulphate with two per cent. of sublimed litharge, the finest and palest oxide of lead yet prepared, shows a yellow color not approached by any sublimed white lead yet made.

When sublimed white lead is subjected to the heat of the blow pipe it is only reduced to metallic lead, when intimately mixed with charcoal, with the greatest difficulty. It shows only slight darkening in an atmosphere containing appreciable amounts of hydrogen sulphide gas. When used in colored paints containing chemically reactive tinting materials it exhibits chemical inertness. The tinctorial power and opacity is directly lowered with a decrease in the percentage of lead oxide.

When chalking is noted in paints containing high percentages of sublimed white lead, it is found to differ from that noted in the case of other white lead pigments. According to Holley,<sup>2</sup> we find, "When ordinary white lead begins to chalk vigorously, it will be found that the paint film has lost its elasticity, and has become brittle and friable throughout; also, that the luster of the film under the chalk-like coating has entirely disappeared. A sublimed white lead film, on the other hand, retains much of its original elasticity under the chalk coating, indicating that the

<sup>1</sup> Chemistry and Technology of Mixed Paints: Maximilian Toch, page 19.

<sup>2</sup> Zinc and Lead Pigments: Holley, page 115.

disintegration is confined to the surface, and it is possible that the retention of the 'chalk' on the surface gives some protection to the unaffected coat below."

The pigment in common with other white lead compounds, finds its greatest value when compounded with zinc oxide and a small percentage of inert pigment of a crystalline nature, as these pigments tend to overcome those factors which militate against the use of the pigment alone.

Sublimed white lead is a pigment extensively used in the compounding of the finer grades of rubber goods.

The pigment has been found to practically inhibit corrosion on iron and steel even after long exposures, and ranks favorably with all other pigments yet prepared for the elimination of this decay. In consequence, it is rapidly finding its predicted place among paint pigments not only as a protective coating for wood but as a preservative for iron and steel.





(Abstract)

THE EXAMINATION OF THE OLEORESINS FROM  
SEVERAL SPECIES OF PINE NATIVE TO  
THE WESTERN STATES

BY A. W. SCHORGER

*Forest Products Lab., Madison, Wisconsin*

*Western yellow pine (Pinus ponderosa) from California*

The oleoresin had a specific gravity of 1.0290 at 15° and gave on analysis: volatile oil 18.5%; rosin 79.5%; trash 0.8%; water 1.2%. The volatile oil had the following properties:  $d_{15} 0.8625$ ;  $n_{D15} 1.4772$ ; and  $[a]_D = -41.34^\circ$ . About 70% distilled between 168–172° and consisted largely of Beta-pinene as proven by oxidation to nopinic acid m. p. 126°. Alpha-pinene was isolated from the first fraction: m. p. of nitrosochloride 103°; m. p. of nitropiperidine 118°. Limonene was isolated from the fraction boiling between 174–178.6° by means of its tetra-bromide m. p. 104°, and dihydrochloride, m. p. 50° C.

The rosin contains about 90 per cent abietic acid crystallized from alcohol and hydrochloric acid; m. p. 159–160°;  $[a]_D = -225.39^\circ$ ; formula  $C_{20}H_{30}O_2$  determined from analysis of its silver salt. Resin crystals obtained from the colophony by crystallization from acetone only melted at 155°. The rosin distilled between 245 and 265° C. at 22 mm. The crystals obtained from solution in acetone melted at 150–151°;  $[a]_D = -156.82^\circ$ . The original rosin had the following properties:  $d_{15} 1.068$ ; acid No. 148.8; sap. No. 161.3; ether No. 12.5.

*Western yellow pine (P. ponderosa scopulorum) from Arizona*

The oleoresin contained: volatile oil 19.6%; rosin 75.0%; trash 3.8%; water 1.6%. The volatile oil had the following properties:  $d_{15} 0.8639 - 0.8672$ ;  $n_{D15} 1.4723 - 1.4729$ ;  $[a]_D = +36.96^\circ$  to  $+37.44^\circ$ . It contained from 60–70% Alpha-pinene, m. p.

of nitrosochloride  $103^{\circ}$ ; about 5% of Beta-pinene, m. p. of nopinic acid  $125^{\circ}$ ; and 20–25% limonene, m. p. of tetrabromide  $104.5^{\circ}$ ; of dihydrochloride  $50^{\circ}$ .

The rosin,  $[a]_D = -88.93^{\circ}$ , contained about 90% abietic acid crystallized from alcohol and hydrochloric acid; m. p. of abietic acid crystals  $159^{\circ}$ ;  $a_D = -252.35^{\circ}$ ; formula  $C_{20}H_{30}O_2$ , determined from analysis of silver salt.

#### *Digger pine (P. sabiniana)*

The oleoresin had:  $d_{15^{\circ}} 1.0265$ ;  $a_{D20^{\circ}} = -3.62^{\circ}$  for an 8.45% alcoholic solution. It gave on analysis: volatile oil 11.4%; rosin 83.5%; trash 3.3%; water 1.8%. The volatile oil had the following properties:  $d_{15^{\circ}} .6971$ ;  $n_D 1.3903$ ; b. p.  $96.1-98.8^{\circ}$  for the first 95%. The oil consists almost entirely of normal heptane since 90% had the following average values: b. p.  $98.5^{\circ}$ ;  $d_{15^{\circ}} 0.6881$ ;  $n_{D15^{\circ}} 1.3898^{\circ}$ .

The rosin had the following properties:  $d_{15^{\circ}} 1.073$ ; acid No. 156.7; sap. No. 176.5; ether No. 19.8. The original rosin could not be crystallized. However, the product obtained by distilling the rosin under reduced pressure crystallized readily from acetone; m. p. of crystals  $151-152^{\circ}$ ; formula  $C_{20}H_{30}O_2$  from analysis of silver salt. Resin crystals obtained from the crude oleoresin using acetone as the solvent melted at  $131^{\circ}$ ;  $[a]_D = -274.91^{\circ}$ ; when crystallized from alcohol and hydrochloric acid the crystals melted at  $158-159^{\circ}$ . The silver salt contained 26.44% of Ag; calculated from  $Ag(C_{20}H_{28}O_2)$ , 26.37%.

#### *Sugar pine (P. lambertiana)*

The oleoresin,  $d_{15^{\circ}} 1.0420$ , contained: volatile oil 16.4%; rosin 75.3%; trash 3.4%; water 4.9%. The volatile oil had the following properties:  $d_{15^{\circ}} .8658-.8663$ ;  $n_{D15^{\circ}} 1.4727-1.4728$ ;  $[a]_D = +29.93^{\circ}$ . The oil boiled largely below  $165^{\circ}$  and contained approximately 70–75% Alpha-pinene, m. p. of nitrosochloride  $103^{\circ}$ ; 5% Beta-pinene, m. p. of nopinic acid  $125^{\circ}$ ; 2–3% of a terpene, b. p.  $169-174.5^{\circ}$ ,  $d_{15^{\circ}} .8550$ , which appears to be phellandrene; 2–3% of what is apparently an aliphatic hydrocarbon, b. p.  $194-201^{\circ} C.$ ,  $d_{15^{\circ}} .7549$ ,  $n_{D15^{\circ}} 1.4249$ ; 10–12% of a sesquiterpene, agreeing closely with "aromadendrene" in color reactions

and physical properties: b. p. 250–255° at 739.9 mm.,  $d_{15^\circ}$  .9238,  $n_{D15^\circ}$  1.5006,  $[a]_D = +108.85^\circ$ .

The rosin had the following properties:  $d_{15^\circ}$  1.078; acid No. 142.7; sap. No. 152.6; ether No. 9.9. Crystalline resin acids were not obtained.

*Lodgepole pine (P. contorta)*

The oleoresin,  $d_{15^\circ}$  1.0210, contained: volatile oil 14.7%; rosin 77.7%; trash 2.5%; water 5.1%. The volatile oil had the following properties:  $d_{15^\circ}$  .8518–.8549;  $n_{D15^\circ}$  1.4860–1.4862;  $[a]_D = -57.81^\circ$ . The oil consists almost entirely of Beta-phellandrene. The rectified oil had: b. p. 60° at 11 mm.;  $d_{15^\circ}$  .8460;  $n_{D15^\circ}$  1.4861;  $[a]_D = -35.53^\circ$ ; m. p. of nitrite 103°.

The rosin had the following properties:  $d_{15^\circ}$  1.061; acid No. 131.2; sap. No. 139.6; ether No. 8.4. On crystallization from alcohol and hydrochloric acid about 80% of abietic acid crystals were obtained: m. p. 159–160°; formula  $C_{20}H_{30}O_2$ , from analysis of silver salt.

*Pinon pine (P. edulis)*

The oleoresin,  $d_{15^\circ}$  1.0238, contained: volatile oil 20.0%; rosin 76.5%; trash 0.9%; water 2.6%. The oil had the following properties:  $d_{15^\circ}$  .8680;  $n_{D15^\circ}$  1.4707;  $[a]_D = +55.35^\circ$ . It contains approximately 70–75% Alpha-pinene, m. p. of nitrosochloride 103°; about 5% Beta-pinene, m. p. of nopinic acid 123°; and 15–20% of d-cadinene having: b. p. 135–140° at 20 mm.;  $d_{15^\circ}$  .9173;  $n_D$  1.4925;  $[a]_D = +44.28^\circ$ . The cadinene dihydrochloride melted at 118° and gave  $a_{D20^\circ} = -5.43^\circ$  for a 5.94% ethereal solution.

The rosin had the following properties:  $d_{15^\circ}$  1.060; acid No. 155.2; sap. No. 164.1; ether No. 8.9. It distilled between 240–255° at 10mm. pressure. Neither the original rosin or distillate could be crystallized. With acetone as the solvent, crystals were obtained from the crude oleoresin, m. p. 129–130°; the latter when crystallized from alcohol and hydrochloric acid melted at 137°;  $[a]_D = -151.83^\circ$ ; the silver salt contained 26.46% Ag; calculated for  $Ag(C_{20}H_{29}O_2)$ , 26.37%. The rosin is assumed to consist of amorphous acids of the above formula.



THE TECHNOLOGY OF VARNISH MANUFACTURE  
WITH NOTES ON AN IMPROVED  
SCIENTIFIC PROCESS

BY J. CRUICKSHANK SMITH AND GASTON DE PIERRES

*London, England*

It was in England towards the end of the 18th Century that the first varnish manufactory on a large commercial scale was established. In the early days of the industry, amber was the sole fossil resin employed. The amber was fused; to the fused mass was added some linseed oil; the whole was 'cooked,' and the solution of resin in oil was diluted with spirits of turpentine. Since that time an ever increasing number of fossil resins have been introduced into commerce and all have found some use in varnish making.

Today amber is but little used in the manufacture of varnish, and thus it has come about that while the chief raw material of the industry has changed the method of procedure by which the fusion, solution, and dilution are carried out has persisted without any important modification down to the present time. In Germany, Belgium, and even in England to a slight extent, several so-called improvements have been introduced. These consist for the most part in 'running' a small quantity of rosin in the gum-pot prior to the introduction of the hard resin. This procedure has been found to assist and expedite the fusion of the resin; but whether it can be described as an 'improvement,' in the technical sense, is a matter in which opinions differ.

In spite of the fact that varnish-making is a chemical industry very few chemists have devoted themselves with any degree of thoroughness to investigating the principles which govern it. On the other hand considerable attention has been paid to the chemistry and technology of linseed oil. It is true that Mr. C. Coffignier has conducted interesting investigations on the resins. He has determined their solubility in various media and their

acidity numbers, but although his results may form the starting point for further scientific research they have not as yet enabled us to put them to an industrial use. However, one fact appears to be established by Mr. Coffignier's researches, namely that the higher the acidity number of a resin the less satisfactory from a practical point of view is a varnish prepared from it. Arguing from this we might say that the best varnish would be produced by a resin which was as nearly as possible neutral, a condition which never obtains in practice. Kauri, it should be noted, is an exception to the rule.

If we consider the fusion of resin as it is effected in the ordinary process of 'running' in the gum-pot, it may be regarded as essentially a process involving partial dry distillation of polymerised terpenes. It may be likened to dry distillation of wood or coal with the differences that in the case of the resin the distillation is arrested at a definite point and that the valuable product is contained, not in the distillate (as in the case of wood or oil), but in the residue which is left in the gum-pot. As in the distillation of wood or coal the vaporised portion contains carbon dioxide and ethylic compounds while the distillate contains acetic and pyrolygneous acids, naphthalene, hydrobenzene and, in short, that whole range of compounds derived from the polyterpenes to which we apply the name 'copal oil' or 'varnish fumes.' It must not be imagined that the acids which are found in the copal oil exist as such in the original resin, any more than acetic or oxalic acid is contained as such in wood or cellulose. The lower acids named are decomposition products, in the one case of cellulose and in the other of the polymerised terpenes.

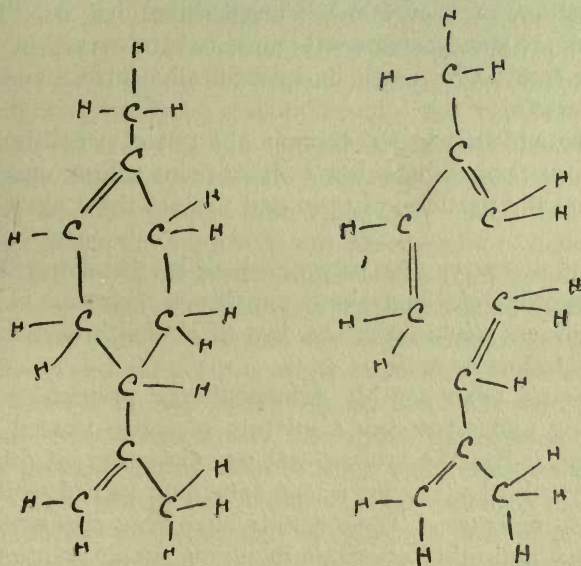
The composition of copal oil varies comparatively slightly from whatever resin it is derived. The chief difference we have observed in various samples lies in their viscosity, which has no relation to the acidity number and which is determined by causes which will be dealt with later. It will be seen, then, that the usual process whereby a resin is fused or 'run' is one which results in a very definite decomposition and splitting of the complex polyterpene bodies contained in the resin.

Nevertheless in the conventional method of varnish making this fusion and incipient distillation process could not be avoided

because the resin had to be rendered wholly soluble not only in spirits of turpentine but also in linseed oil, and this result could only be achieved (under the conditions which surround the conventional process) by subjecting the resin to strong direct heat.

The practical result aimed at in subjecting a hard resin to heat is to de-polymerise it, that is, to convert it into bodies of simpler constitution and lower molecular condensation than those possessed by the higher members of the polyterpene series. Thus the polymerised terpenes of high molecular weight which may be represented by the general formula  $(C_{10}H_{16})_x$  are in effect polymers of dipentene  $C_{10}H_{16}$  which again is a polymer of pentene (isoprene)  $C_5H_8$ , the first members of the series.

The splitting of a dipentene molecule into two pentene molecules by means of heat under suitable conditions may be expressed graphically thus:—



It must therefore be admitted that the conversion of a body of complex chemical constitution into bodies of simpler constitution by means of direct heat unmodified by any other condition cannot be regarded as technically correct inasmuch as it involves incip-

ient destructive distillation and an inevitable loss of sensible qualities of valuable raw material. The process of 'running' a resin, as carried out in the historic way, necessarily involves this result. The temperature produced in the gum-pot frequently approaches 350° C., and no organic compound of complex constitution can withstand such a temperature without decomposition. In proof of this one need only recall that sometimes the contents of the pot take fire spontaneously. It is true that this happens but rarely when the operation is in the hands of an experienced gum-runner, but the fact that the phenomenon can and does occur affords conclusive proof that over-heating and consequently excessive decomposition do take place.

It would appear then that some modification of the conventional historic method of varnish manufacture might be adopted with advantage in order to eliminate the crude and wasteful decomposition of the resin. Consideration has convinced us that there are two fundamental points to be observed in order to obtain a result which will be scientifically correct and practically successful:—

(1) The addition to the resin in the pot of a substance of a stable nature possessing a low melting point whose function it is to envelop the particles of resin and protect them against over-heating.

(2) The discovery of a solvent which by dissolving the more soluble portion of the resin is capable of bringing about the solution of less soluble portions, just as alcohol brings about the solution of ether in water.

About sixty years ago Mr. Schutzenberger prepared a varnish by heating under pressure a mixture of copal, linseed oil and turpentine. But the product was unsatisfactory; it dried very slowly, remained tacky for a long time, and turned white when exposed to moisture. These results have been confirmed many times since and other processes involving simple solution under pressure have never, so far as we are aware, yielded satisfactory results. Mr. Henry Terrisse has investigated the cause of Mr. Schutzenberger's failure. He heated re-distilled spirits of turpentine under a pressure of 20 atmospheres for two hours in an autoclave at a temperature of 295 C. At the end of the operation



the autoclave and its contents were allowed to cool, when it was found that the pressure gauge still recorded a pressure of  $3\frac{1}{2}$  atmospheres. When the safety valve was opened the presence of a hydrocarbon gas was observed. The gas burned with a white flame and was found to possess properties characteristic of ethylene. The contents of the autoclave, which were originally spirits of turpentine, had been converted into a viscous oily liquid with a disagreeable empyreumatic odour. This liquid on distillation yielded fifty percent of volatile spirit, the remainder consisting of a gummy residue. Evidently therefore the original turpentine had undergone a process of resinification similar to but more complete than the resinification which takes place when turpentine is exposed to the air.

The experiment has been repeated, various hard resins being substituted for turpentine. Thus in the case of Zanzibar copal fused at  $300^{\circ}\text{C}$ . in an autoclave under a pressure of 14 atmospheres a pressure of  $1\frac{1}{2}$  atmospheres was registered when the temperature had fallen to the original figure. The liberated gas consisted almost wholly of carbon dioxide, and the fused gum residue was slightly tacky and somewhat friable in texture.

With congo similar results were obtained. A maximum compression of 20 atmospheres was registered, which fell to  $4\frac{1}{2}$  atmospheres when the autoclave was nearly cold. In this case the fixed gases produced were carbon dioxide and inflammable hydrocarbons. The fused residue from both the resins treated in this way were soluble in linseed oil, and varnishes made from them dried well and did not turn white in presence of moisture.

Finally linseed oil was heated in an autoclave at  $300^{\circ}\text{C}$ . The pressure registered scarcely rose above the normal. After two hours heating the oil became very tacky and dried with difficulty. This was probably due to some re-action in which acrolein and free glycerine play a part. These experiments appear to show conclusively that the flaw in Mr. Schutzenberger's process was the presence of turpentine. We arrive therefore at the following conclusions:—

(1) The ordinary hard resins are capable of being depolymerised with comparative ease under pressure.

(2) The process of fusion is however still too severe and causes decompositions which are undesirable.

(3) In order to ameliorate the process of fusion and prevent secondary decompositions there should be present some substance with a low fusion point which will dissolve the products of the fusion at the moment of and *pari passu* with their formation. In this connection it must be remembered that the complete fusion of a hard resin does not take place at one definite temperature (as in the case of a homogenous substance of definite chemical composition) but proceeds gradually throughout a range of 50 or even 100 degrees.

(4) Such a substance must be of stable constitution and not liable to decomposition under the conditions of fusing.

(5) It must be cheap and easily procurable.

At first phenol appeared to conform to these requirements and experiments made with it were quite successful. The price of pure phenol is however a drawback, and naphthalene was finally adopted as a material which conforms to the above mentioned requirements, and it has proved in every way satisfactory.

The pressure during the fusion need not exceed 6 atmospheres. When the process is complete and the autoclave is cold the pressure falls to normal. After the naphthalene has been removed by distillation the fused gum is found to be very hard, to be quite free from tack, and to be capable of being mixed with quite large proportions of linseed oil. The resulting varnish shows no tendency to crack and withstands the action of extremes of temperatures.

It is easy to conceive the 'mechanism' of the process described. When heat is applied the particles of resin become surrounded by an envelope of liquid naphthalene (the melting point of naphthalene being 79–80° C.). As each particle of resin fuses it is immediately dissolved by the liquid naphthalene and the process goes on until in a relatively short space of time the whole mass of resin, including the most insoluble constituents, is dissolved without any appreciable amount of local overheating or charring.

Here then we have a method of fusion and solution which

results in a depolymerised product without the production of copal oil which in the conventional method of gum-running is the inevitable product of the crude and destructive method which necessitates the loss of no small quantity of valuable material.

An interesting parallel case is that of the formation of salol. When salicylic acid is rapidly heated by strong direct heat it is converted into phenol with liberation of the total theoretical quantity of carbon dioxide. But if the heating is conducted gently on an oil bath there results a conversion of the salicylic acid into the chemically equivalent quantity of salol and no phenol is produced.

The method of which we have outlined the theory and which was originally suggested by Mr. Terrisse has been carefully examined by us. We have been able to confirm the practical results obtained by it and so far as our investigations have gone at present we find that all the ordinary hard resins of commerce can be satisfactorily and economically treated in the manner suggested.

We have also confirmed the work of Coffignier and Terrisse in other directions and have investigated the composition of copal oil. When distilled at normal pressure it yields between the temperatures of 90° and 175° C. distillates of an acid character in which acetic acid predominates. A small quantity of acetone is also given off. Between 175° and 250° the distillate consists of a brownish yellow oil of acid reaction and possessing an acid penetrating odour. From 250 there is a sharp rise of the thermometer to about 310°, at which temperature there comes over a dark olive green oil. A continuous production of water occurs at this point. The thermometer then rises to about 350 and thenceforward the formation of water becomes copious, and the distillation is complete at about 395°. Nearly the whole of the copal oil can be distilled and the residue in the retort consists of a black tarry substance similar in appearance to bitumen and having an acid odour. The greenish oily distillate which comes over after 250 is muddy and has a disagreeable empyreumatic smell and gives an acid reaction. It has a density bordering on but always under 1.0. On standing it quickly clarifies

and separates into two layers, the lower consisting of an aqueous solution of acetic acid and the upper consisting of a mixture of naphthalene or hydro-naphthalene and polyterpenes.

Entirely different results are obtained when the distillation is conducted under reduced pressure. At a pressure equivalent to 15 mm. of mercury under the normal a certain quantity of the lower acids come over between 50° and 75° C. The thermometer then rises rapidly to 150° when the distillate consists of a clear yellow oil of disagreeable odour but *not acid*. Another rapid rise takes the thermometer reading to 225° when a very clear greenish oil passes over. The odour of this fraction is pleasant and reminds one of that of old varnish. At 270° the distillation should be stopped because at this point the formation of water commences, which shows that the residue in the retort is beginning to decompose.

From a litre of copal oil the following quantities of the above-mentioned fractions have been obtained:—

Acid fraction . . . . .	75 cc.
Yellow oil . . . . .	200 cc.
Green oil . . . . .	200 to 250 cc.
Residue . . . . .	475 to 525 cc.

The residue consists of a fused gummy mass rather friable in nature, slightly tacky, and very dark in colour which reminds one (except as regards colour) of the fused product obtained by simple fusion of the resin in an autoclave. From this gummy residue quite good varnish can be made.

It is worthy of remark that all the samples of ordinary copal oil which we have examined yield similar results. From whatever species of copal they have been derived they always yield the same acid fraction, the same yellow and green oils and a solid residue. The solid residue alone varies.

Thus kauri and manilla yield very little residue; Congo yield much more, and so on.

The quantity of residue bears a definite relation to the melting point of the resin or rather to that of the most infusible component part of the resin, and has therefore a direct bearing on the viscosity of the copal oil. If the fusion and distillation





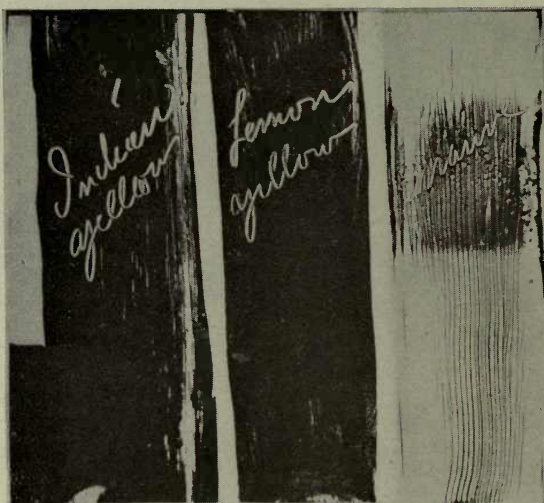




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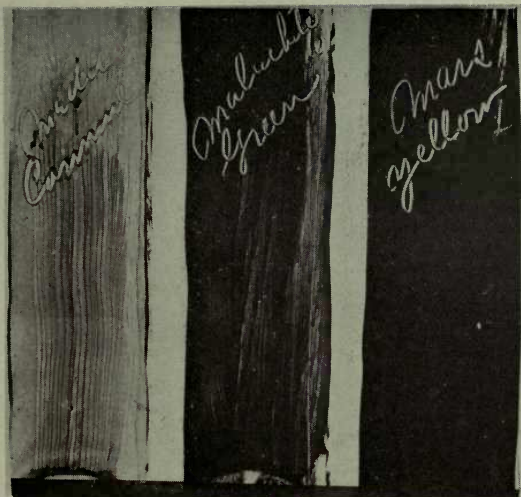
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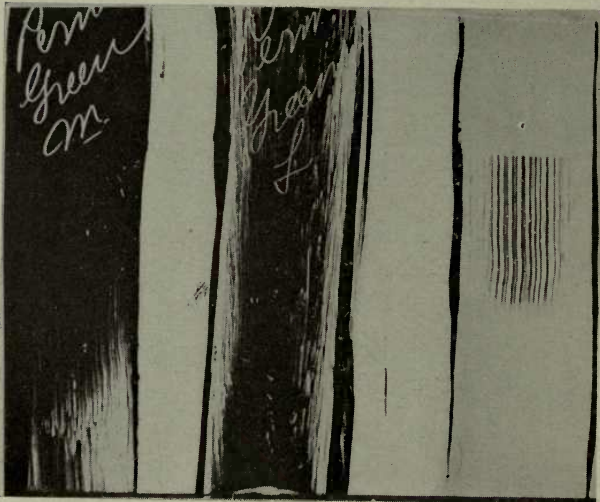
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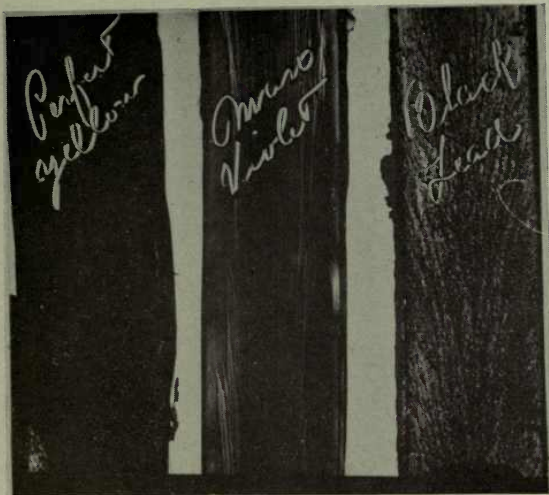
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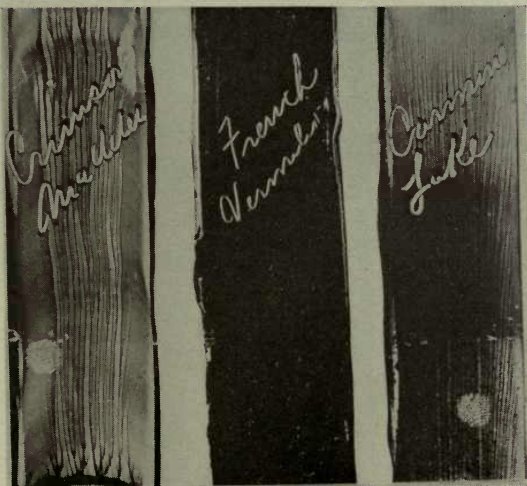
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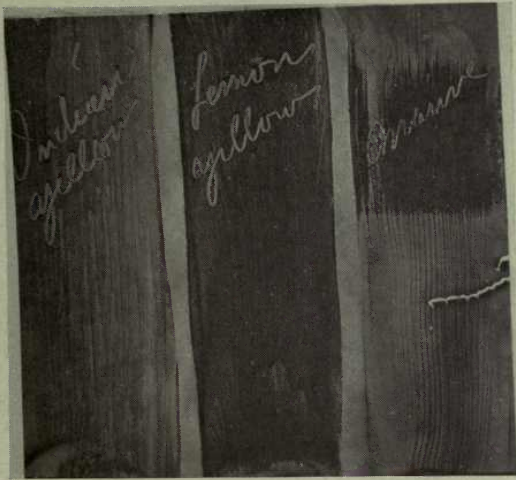
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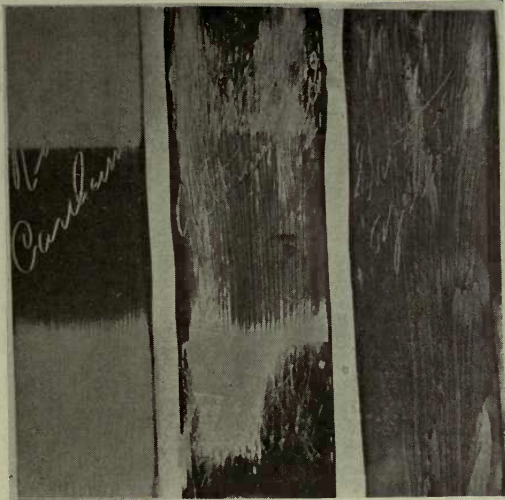
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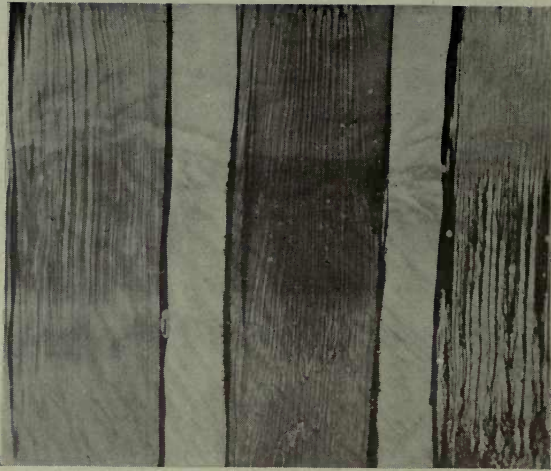
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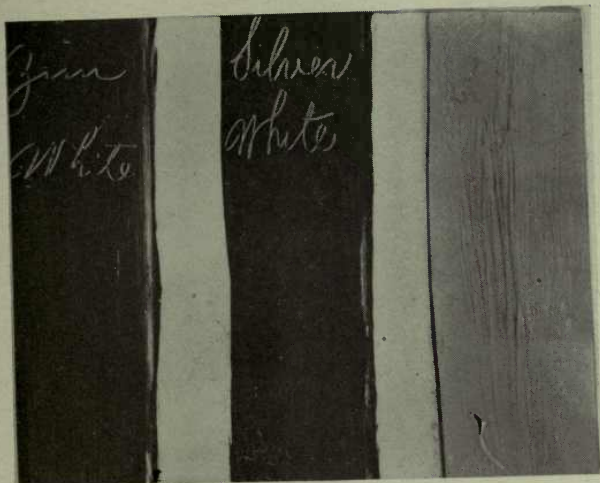


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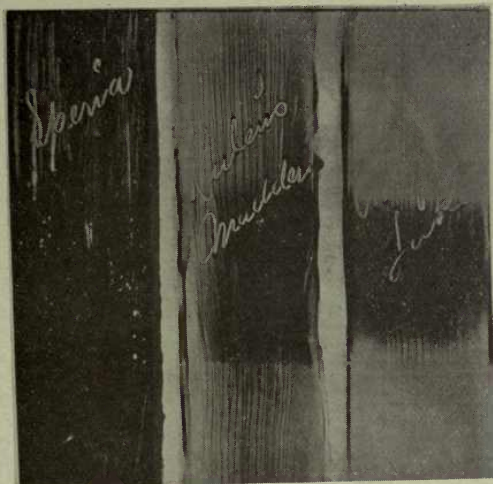




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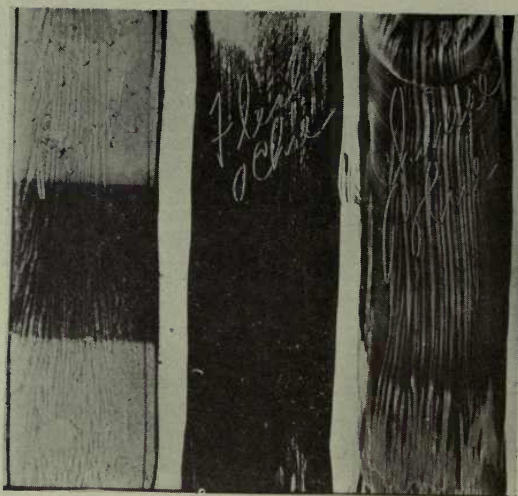
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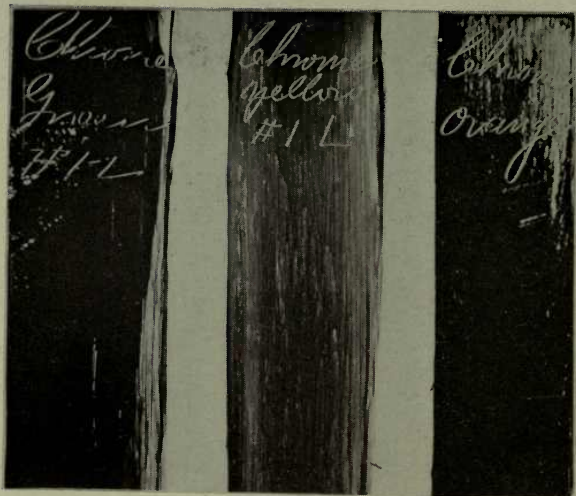
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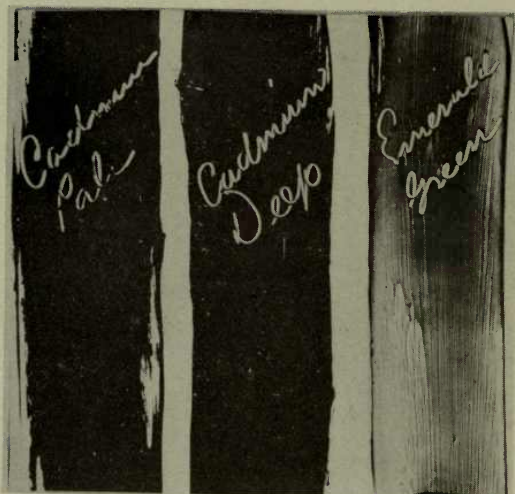
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are carried out with a resin to which has been added a proportion of colophony the acid fraction always increases.

From a survey of the foregoing facts we arrive at some practical conclusions :—

(1) Acids are produced by the action of heat on the hard resins and are found again when the copal oil is fractionated.

(2) The distilling off of the more fusible portion of the resin causes a part of the less fusible and therefore harder portion to be carried over. Just as naphthalene can be driven out of coal tar by means of steam so is part of the hard resin of high melting point carried over by the vaporised terpenes which are produced by the partial decomposition of the resin in question.

The solvent action of the two oily fractions last mentioned has been investigated. The green oil possesses powerfully solvent properties and it has also been established that the green oil is carried over without decomposition by vaporised naphthalene.

In practical varnish-making by the autoclave process it is possible therefore to employ a mixture (in suitable proportions) of the green oil and naphthalene. The former acts as a powerful aid in bringing the hard resins into a soluble form, and the latter can be easily distilled off, carrying with it the added green oil. Hence in the case of certain resins the fusion in the autoclave can be avoided altogether and in other cases much lower temperatures can be used in the autoclave than would otherwise be the case with the result that the varnishes obtained are extremely pale.

It is not claimed that the work of an industrial nature which we have described has added much to our chemical knowledge concerning the nature of the hard resins but it has a very direct bearing on the theory and practice of varnish-making and is not without interest in a large group of chemical industries. Our experiments at any rate go to show that the resins commonly used in varnish-making are similar in their general composition and probably also in their constitution and that they consist essentially of assemblages of polymerised terpenes. We claim that there is abundant evidence at hand to warrant the dissipation

of the fiction that the historic conventional method of gum-running is a necessary or even a defensible process inasmuch as the "acid" which the old fashioned method strove to separate was to a large extent produced by the incipient destructive distillation of the resin itself. We claim also that the depolymerisation (on which the solubility of the fused resin depends) can be brought about by a method which is more gentle in its effects, more under scientific control and capable of producing better and cheaper varnishes than the method which has been the fetish of the mystery-maker and secret-monger for upwards of two hundred years.

In conclusion we should like to point out that in spite of the apparent simplicity of the process and of the principles on which it depends it must be controlled with skill and nicety in order that satisfactory and uniform results may be obtained. The merely theoretical worker who attempts to make good varnish either by this or by any other process will find that he has a long and costly novitiate before him. When it will be granted that the modern varnish factory has little use for the hide-bound rule-of-thumb, so-called practical man, it is equally true that to the dough of organized science must be added the leaven of practical skill—that indefinable turn of the wrist which will always distinguish the clever cook, the good varnish maker, and the successful technical expert.

## THE PERMANENCY OF PAINTING

BY MAXIMILIAN TOCH

*New York*

We are all familiar with the phenomenon that mineral substances which have a distinctive coloring with the exception of one or two which will be mentioned later, show no change of color, and as far as we know have not changed in their appearance for ages. Many of these mineral substances have been used for centuries for decorative purposes either as pigments or as tints. Some of the artificial pigments such as Madder Lake, Bone Black, Lamp Black, Ultramarine Blue, Siennas and Umbers which are simply used to produce their particular shade, have all been regarded as more or less permanent, and are permanent particularly when used alone, and yet, when these pigments are mixed with a drying oil medium they decompose to some slight extent, sometimes through the aid of the decomposition products of the medium, and sometimes because of the influence of brilliant light, darkness, or the gases generated in a large city.

All of the experiments which we have made are not so much for the purpose of proving what is already well known, that certain pigments when exposed to the light change, or when mixed with others to produce chemical effects which are different from their original, but for the purpose of suggesting a remedy which up to now has been more or less empirical, and as far as we know has never been worked out satisfactorily.

Everyone deplors the decomposition of the master pieces of modern paintings, and at the outset it must be impressed upon those who are interested in the subject, that an oil painting of moderate size can be thoroughly protected against the influence of light and noxious chemical gases in the atmosphere, if the back of the painting is thoroughly coated with a non-absorbent or waterproof medium, and if the face of the painting be coated with a hard flexible varnish and the whole hermetically sealed in

a frame with a glass cover, but we are not dealing with prophylactics. We are dealing with remedies, and to that end we exposed a large number of oil pigments on the market under glass, and each pigment was coated on the glass in strips of 3'' long and 1 inch wide, and the centre inch covered with black paper close to the pigment so that light would have no access.

The following is the tabulated result of the photographs obtained:

Illustrations 1, 2 and 3 are well known examples of the work of Sir Joshua Reynolds in the Metropolitan Museum of Art in New York City.

Sir Joshua Reynolds seldom painted two pictures alike. He was continually experimenting with pigments which would secure for him as he thought greater permanency, and as he possessed insufficient knowledge of the composition of the materials with which he worked, he very often mixed pigments which interacted such as ochre and madder lake.

Illustration No. 1 is almost mono chromatic, it having faded into a monotone.

Illustration No. 2 is in a fairly well preserved condition, and the red lips of the child are still red.

Illustration No. 3 has bleached out completely, until the face, breast and fur trimming of the dress are all reduced to the same tone and practically the same color value, and the upper line of the red lips show no line of demarcation. The face and flesh color is practically anaemic in this picture. What was once the portrait of a handsome healthy looking woman is today one mass of faded color.

No. 4 Venetian Red shows no fading.

No. 5 Indian Red shows no fading.

No. 6 Terre Verte is permanent.

No. 7 Indian Yellow is permanent.

No. 8 Lemon Yellow is permanent.

No. 9 Mauve Lake disappeared entirely in four months, excepting in the centre where it was protected from the light.

No. 10 and 11 are two kinds of Brazil wood red which were made up to simulate the lakes used by Sir Joshua Reynolds. They both bleached badly in a short time.



No. 12 is the new color called Harrison Red which is about ten times as strong as English Vermilion. This is a very permanent pigment.

No. 13 is Payne's Grey, a very fugitive color.

No. 14 Yellow ochre which has grown slightly darker on exposure.

No. 15 Yellow lake which is very badly faded.

No. 16 Sepia, not very permanent.

No. 17 Rubens madder. This is evidently a proprietary name, and cannot be a true madder lake as it has faded completely in four months.

No. 18 Magenta Lake very badly faded.

No. 19 Rose Carthame. Not a vestige of this color remained.

No. 20 Ultramarine Blue. This pigment becomes more brilliant on exposure, and darkens considerably when hidden from the light.

No. 21 Strontium Yellow, very permanent.

No. 22 Madder carmine, fairly permanent.

No. 23 Malachite Green, permanent.

No. 24 Mars Yellow, permanent.

No. 25 Carmine 2, fugitive.

No. 26 English Vermilion, darkens considerably when exposed to light, but remained permanent when not exposed.

No. 27 Cerulean Blue, becomes more brilliant when exposed to light.

No. 28 Alizarine Yellow, evidently a misnomer, but is a yellow lake which fades very rapidly.

No. 29 Carnation Lake, entirely bleached in four months.

No. 30 Alizarine Green, evidently a misnomer. It is an aniline green lake, not permanent.

No. 31 and 32 Permanent Green, Medium, and Permanent Green, Light, very permanent colors.

No. 33 Bitumen, evidently not genuine bitumen, as it has completely faded and lost its glaze, for genuine bitumen usually turns dark and shows cracks.

No. 34 Perfect yellow, permanent.

No. 35 Mars Violet, permanent.

No. 36 Black Lead, permanent.

- No. 37 Crimson madder, permanent.  
No. 38 French Vermilion, darkens on exposure.  
No. 39 Carmine lake, faded badly.  
No. 40 Madder lake, deep, shows very slight sign of fading.  
No. 41 Madder lake, pale, shows slight signs of fading.  
No. 42 Lemon yellow, permanent.  
No. 43 Permanent yellow, permanent.  
No. 44 Yellow lake, bleached completely when exposed to the light.  
No. 45 Violet Carmine, permanent.  
No. 46 Indian yellow, permanent.  
No. 47 Lemon Yellow, permanent.  
No. 48 Mauve, very fugitive.  
No. 49 Rose Carthame, very fugitive.  
No. 50 Ultramarine, becomes more brilliant on exposure.  
No. 51 Strontium yellow, very permanent.  
No. 52 Burnt Umber, contains a lake and shows signs of fading.  
No. 53 Bone brown, not permanent.  
No. 54 Mummy, not permanent.  
No. 55 Crimson madder, permanent.  
No. 56 French Vermilion, permanent, but darkens slightly.  
No. 57 Carmine lake, fugitive.  
No. 58 Zinc white, permanent.  
No. 59 Silver white, permanent.  
No. 60 Rose Dore, fugitive.  
No. 61 Sepia, fugitive.  
No. 62 Rubens madder, fugitive.  
No. 63 Magenta lake, fugitive.  
No. 64 Yellow lake, Italian pink, fugitive.  
No. 65 Flesh Ochre, permanent.  
No. 66 Chinese blue, permanent.  
No. 67 Cobalt yellow, permanent.  
No. 68 Cobalt blue, permanent.  
No. 69 Green lake, fugitive.

This green lake which was originally a bright green, changed into a true blue showing that it was made of a permanent blue and yellow lake, the yellow lake having bleached completely.

- No. 70 Brilliant yellow, permanent.
- No. 71 Mummy, fugitive.
- No. 72 Transparent black, permanent.
- No. 73 Purple lake, fugitive.
- No. 74 New Blue, becomes much more brilliant on exposure.
- No. 75 Purple madder, permanent.
- No. 76 Chrome green, permanent.
- No. 77 Chrome yellow, darkens on exposure.
- No. 78 Chrome orange, permanent.
- No. 79 Cadmium, pale, permanent.
- No. 80 Cadmium, deep, permanent.
- No. 81 Emerald green, slightly fugitive.

Many of these colors were duplicated in exposure, and where, for instance, I have given #19 as rose carthame, and #49 as rose carthame, it was due to the fact, that they are the same color but made by two different manufacturers.

All of these exposures were made by pasting a black strip of paper across the middle of a three inch stripe of color, and serve to indicate the effect of light such as would reach a painting inside of a building.

We have not dwelt on the effect on the ultra-violet rays on pigments of this kind, because glass is apparently a permanent bar to these rays.

Yellow lake composed of the quercitron extract precipitated on an alumina base had bleached out completely so that at the end of four months there was nothing left in the bleach to show any trace of color.

The vermilion known as English vermilion which has always been regarded as a perfectly permanent pigment had turned perfectly brown where exposed to the light and remained brilliant where sheltered from the light. This particular experiment was carried out away from any noxious gases, so that the effect produced in this case is one of light entirely.

Yellow ochre alone showed no decomposition whatever.

Green lake which in this instance was a transparent blue similar to artificial cobalt colored with a green dye, became reduced to a perfect blue at the end of four months where exposed to the light but showed no change when protected from the light.

One of the bitumens,—and bitumens notoriously blacken in the light—had bleached out completely, showing that it was an artificial material and not the natural bitumen.

Carmine lake had suffered materially having bleached almost completely when exposed, and French vermilion had blackened much more than the English vermilion.

Crimson madder which in its dry state and as a water color showed no decomposition, began to show a slight deterioration at the end of four months.

The so-called mauve lake disappeared entirely. The mixtures of madder and carmine known as Madder Carmine were also seriously affected.

Prussian blue was one of the most permanent.

Gamboge was much more permanent than was to be expected, but Purple lake was very much bleached and Purple madder considerably affected.

All the artificial ultramarines under their various names seemed unchanged when viewed by transmitted light, whereas a change was quite visible when they were seen by reflected light.

The new pigment known as Harrison Red which has been described in another publication showed no decomposition and the artificial alizarines such as Alizarine Crimson and Alizarine Scarlet which are identical with the natural mediums, showed no trace of fading.

The oxides of iron, such as Indian Red, all of which have a chemical composition of  $\text{Fe}_2\text{O}_3$  Ferric oxide, are changed into a different form, probably  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ . This is particularly noticed when these pigments are mixed with oil media.

Italian pink which is similar to the lake colors, bleaches out entirely, and the brilliant scarlet red known as Rose Carthame suffered such decomposition that not a trace of it was left.

The colors affected by sulphur fumes in the atmosphere such as chrome yellow, chrome green, prussian blue, paris green, emerald green, flake white and white lead when protected from the air showed no decomposition whatever when exposed to light.

All of the blacks, such as lamp black, carbon black, graphite, bone black, and vine black which latter includes all of the charcoals, show no trace of any change.

The illustrations accompanying this treatise were all made on pan chromatic plates which show the relative color value, and in which a faded red or a faded yellow is distinctly shown up and in which the color spectrum from the D line to the ultra red is perfectly visible.

I shall now show you the actual effect of light upon the various pigments treated in this paper, and the ortho chromatic photographs of the faded paintings and color decomposition. Colors were here shown in the stereopticon.

Pastels and water colors are notoriously more permanent than oil paintings. Once a color has become dry, there is nothing but the light to act upon it, but in an oil painting, there is in addition to the light, the generation of water, carbonic acid and formaldehyde, all of which would have the combined effect of decomposing, even to a slight degree, some of the pigments.



## MODERN PAINTING METHODS IN THE NAVY

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The considerations that lead to the use of paint on steel ships are the same in general as those necessitating its use on steel structures on shore. The conditions on ships, however, necessitate more urgent measures for preserving their structures. Corrosion of the steel in ships proceeds more rapidly than on shore and might result, if neglected, in the total loss of the vessels. Sea water, which contains in solution many elements, probably is the strongest corrosive agent with which large quantities of structural steel comes into contact. It, and the moisture from it, serve to set up the electrolysis necessary for corrosion. The black oxide mill scale, which is on all structural steel, unless special precautions have been taken to ensure its being removed, is electronegative to the steel and the corrosive action of the sea water is stimulated by its presence.

To a person not familiar with the effect of sea water on steel work, its power of disintegrating is not always apparent. It is so much greater than the corresponding action of fresh water that, by comparison, the latter may be neglected, and steel ships which are laid up in fresh water basins require little attention to prevent corrosion of their outside bottom plating.

Another characteristic of sea water, which it shares with fresh water, and which unfortunately has not been taken into account, is its action on those paints most generally used on shore and which are made up with linseed oil as a vehicle. Not being a chemist I will not attempt to explain this action beyond saying that the linseed oil film becomes softened by the action of the sea water and the paint ceases to protect the steel under it. As stated, this important defect of linseed oil paints has not been recognized generally either in the Navy or the merchant marine, and such paints continue to be applied on steel in locations exposed

directly to the action of salt water. Although there are many damp-proof and water-proof paints made commercially, their advantages do not seem to have been pointed out with sufficient clearness and force to bring about their general adoption for ship use.

Experience, however, has taught ship owners the world over that they must take energetic steps to prevent deterioration in protecting from corrosion the steel of their ships by the free use of paints, varnishes or cements. Naval vessels have an additional consideration for the use of paint in their desire and the necessity for neatness and cleanliness beyond that achieved ordinarily on vessels of the merchant marine.

Thus paint for the Navy is an important subject and its importance may be pointed out in a striking way by considering the amount and cost of paints used in some cases. During the construction of the 22,000 ton battleship *Florida*, up to the time of first commission there were used a total of about two hundred tons of paint and varnishes. Of this amount about one hundred tons was red lead paint used to protect the steel from corrosion, principally as priming coats, though in some cases it was used alone on the steel work, no finishing coat of paint being necessary. The total cost of all paint and varnish used including the labor of preparing the surfaces and applying the paint was over \$150,000. It should be borne in mind that this amount represents the first painting costs, the value of paints and varnishes used annually by a battleship of this size for keeping the ship painted, exclusive of cost of applying it, is not far from \$15,000.

The above will serve to give weight to my statement that to the Navy, and to the merchants who make a business of supplying painting materials, the general questions of paint used by the Navy, the kinds of materials used, the methods and frequency of application are of vast importance and deserve much more attention than they have received. The chemists who make it their business to determine the qualities and characteristics of paint materials could render an important public service by investigating the subject along scientific lines and telling those of us who are concerned with the use of the paint what are the consider-



ations affecting its choice and what materials can be expected to give best service in the various locations on shipboard. This has not been done heretofore, and shipbuilders use continually paints that not only are not the most suitable but that often serve no useful purpose and even stimulate corrosion. Many such examples could be cited, the most striking being the general use of linseed oil paints alluded to above, red lead paint being used perhaps most often in locations for which it is essentially unfit.

The policies of the Navy Department in the use of painting materials are very conservative and changes are not made readily. The responsible officials must be convinced that changes are desirable and in the interest of efficiency. Such conviction can be carried only by demonstration of superior merit in actual tests, which are scrutinized by persons generally not ready to be convinced easily. These tests of paint are made usually by application on a ship and the determination of comparative results by the same persons is not always possible, due to the removal of the ship to another station. This renders the decision dependent upon the observation of persons who may not be competent to decide and who are frequently not interested in the conclusions. Such tests naturally require several years to produce results and shifting personnel in the interval often nullifies the conclusions reached. The above should serve to indicate the difficulties attendant upon changes in the Navy Department's policies as regards the painting materials and methods prescribed for naval vessels.

In the purchase of its paint supplies, which exceed in value annually over one half a million dollars, the Navy Department makes use of specifications worded accurately to require in most cases the highest grades afforded by the market. Careful inspections and tests are made in most cases to ensure that the materials accepted are as specified. Many of the characteristics mentioned in the specifications no doubt are not essential to the purposes for which the materials are used and manufacturers often have seemingly just ground for complaint in the rejection, for technical deficiencies, of materials which they feel assured would answer fully all practical needs. On the other hand it must be remembered that there is very little authoritative data as regards paint

materials and on which specifications may be used. The naval authorities consequently have been forced to draft their own specifications and apparently they have erred only in doing their work too well and in not accepting changes in ideas until there was in their opinion ample assurance that such changes met with the approval of the trade generally. For this reason some of the Navy's paint specifications have not been changed in many years. The Navy has inherited the traditional conservatism of the practical painter and for many years adhered to the old and staple paint materials, such as red lead, white lead, white zinc, pure linseed oil and pure turpentine. This fact long has been used as an argument against the newer paint materials. Many manufacturers regard the Navy trade so highly as a recommendation of their products that they are willing often to sell them at a slight loss to ensure receiving the contracts, as the care exercised by the naval officials is accepted by the public as an index of merit of those materials that are purchased and accepted. The fact that the Navy Department requires the use of certain paint ingredients doubtless has influenced many ship owners and others to purchase and use the same materials.

In the past five years the naval authorities have awakened to the advances that have been made in the paint trade and have taken some progressive steps, with others in contemplation, and promise to place themselves in the ranks of the progressive paint users.

One of the most important advances in recent years was the change from the custom formerly in vogue of issuing to each naval vessel its paint in the form of the raw ingredients, which then were mixed on board ship by hand as required for use by the ship's painter. Now paint, mixed and ready for use after stirring, is issued. This change was one of the most important and far reaching in its effect that could have been taken. It recognizes primarily the superiority of the compound paints made by machinery according to certain definite formulas over that mixed at haphazard according to the whim of the comparatively ignorant painters on the ships. This, however, was not the most important consideration in making the change. It was recognized that the cost of the Navy's paint could be reduced, without

impairing its quality, by using some of the newer paint materials. This would not have been possible had the ingredients been issued to the painter, for they would have been condemned before even tried. As it stands paints have been made up, issued and used with good results on naval vessels, which contained such ingredients as blanc fixe, barytes, silica, lithopone, petroleum thinners, China wood oil, fish oil, soya bean oil and other materials that many persons regard as rank adulterants. The fetish which binds seafaring men to the use of red lead linseed oil paint has been discredited and paints which cost much less giving better results are being used extensively in its place.

The most important of the changes in materials, that has been made up to the present time, is the discontinuance of the use of turpentine as a thinner for paints. This change was made after full investigation and consideration of the question in all its phases. During the year 1910 the Navy purchased over 70,000 gallons of turpentine at an average cost per gallon of over 78 cents. Early in 1911 the change was instituted and now a hydrocarbon spirit made from petroleum is used almost exclusively for thinning paint. This important step no doubt has had an influence on the trade in general and it is to be hoped that it will serve to reduce the total consumption of turpentine and tend to a conservation of the pine forests being destroyed by the turpentine people to meet the fancy of painters who think it is essential to make good paints and varnishes. This change was not made without opposition, not only from the turpentine manufacturers, but from within the service itself. Many of the master painters in the navy yards attributed to the turpentine substitute faults in the paints that were shown readily to be due to other causes. The ships' people opposed it because they thought that, as the paints issued to them cost less as a result of the use of the substitute, they were consequently less efficient.

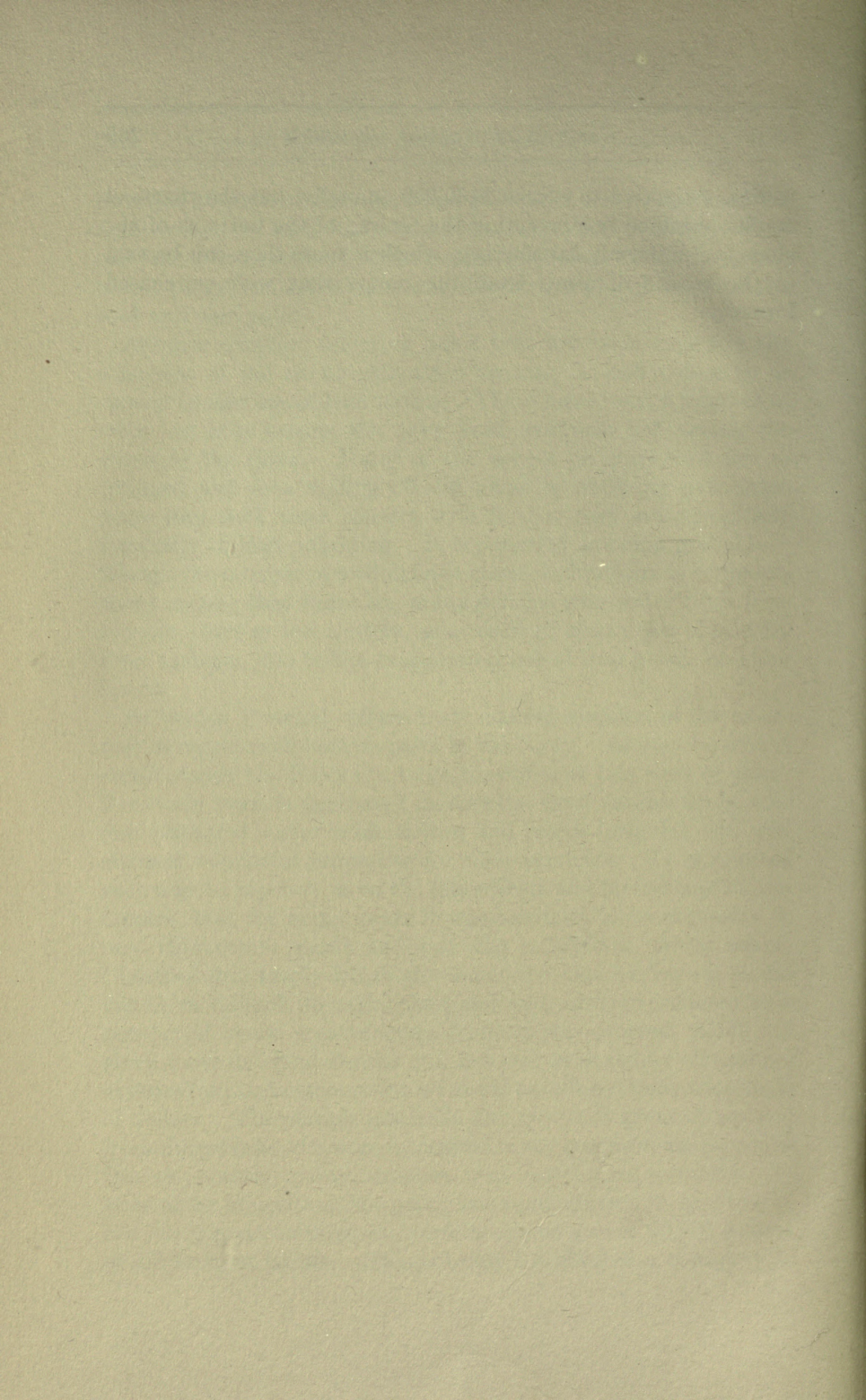
Another innovation that has been made is the introduction, for use preliminarily on one division of the battleship fleet, of a slate color outside paint, having its pigment made of zinc oxide and blanc fixe, with necessary tinting materials. This paint is

intended to supplant the lead and zinc paint slate color used for many years; on tests which have been extended over more than one year it has shown excellent qualities of resistance to the action of salt water, while costing about 35 cents per gallon less than the lead and zinc paint.

Another question affecting paint that has been engaging the attention of the naval authorities recently is lead poisoning as caused by the use of lead paints. There have been a number of cases not only among the navy yard workmen but among the crews of the ships. Many of the spaces on shipboard are so confined and men scaling off old paint or applying new paint come into such close contact with it that they are susceptible especially to lead poisoning. It is regarded as being probable—though the number of well defined cases of plumbism is comparatively small—that there are many persons who suffer from liver trouble, more or less acutely, as a result of absorption of lead by their systems, due to the exaggerated use of lead paints on shipboard.

In closing I cannot refrain from making mention of the situation as regards shipbottom paint in the Navy. As may be understood readily the Navy is a large consumer of this class of paint. For many years it purchased its supplies from various firms, who manufactured under trade names and secret formulas and who claimed wonderful properties for their products. They affected such a great mystery as to the ingredients and methods of manufacture, that for many years it was assumed to be necessary to buy shipbottom paint and pay the exorbitant prices asked. Consideration finally led to the conclusion that perhaps it would not be so difficult to make the paint and, after experimenting a number of years, a satisfactory formula was evolved, which has given most excellent results and has served to reduce the annual expense for shipbottom paint for naval vessels by many thousands of dollars. The change naturally has met with great opposition from the persons who were interested in the contracts under which the shipbottom paint supplies were purchased formerly. In spite of the opposition, the policy has been adhered to, and to-day the Navy manufactures at Norfolk annually over 60,000 gallons of shipbottom paints. This not only has effected a considerable

saving, estimated to exceed \$100,000 annually, but the practical results obtained in preventing the fouling of the bottoms of the ships are uniformly satisfactory, which is more than can be said of the results obtained from the paints that were purchased formerly.



## SUR DEUX NOUVELLES SOURCES DE PINENE

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Au moment où, par suite des besoins croissants de l'industrie, on commence de viviers cotés à exploiter de nouvelles variétés de pins en vue de la production de l'essence de térébenthine, il paraît utile de soumettre à une étude méthodique la matière première de cette fabrication, c'est à dire l'oléorésine ou gemme secrétée par chacun de ces arbres. Cette étude comparative des gemmes de diverses variétés de pins est utile à un double point de vue: d'une part, elle fournit aux industriels des indications sur le rendement en essence volatile des gemmes qu'ils sont appelés à distiller; d'autre part, elle permet de voir quelles sont, parmi les essences volatiles ainsi extraites, celles qui possèdent la composition et les propriétés de l'essence de térébenthine, et par suite ont réellement droit à cette dénomination. Les essences volatiles que fournit la distillation aqueuse de la gemme des pins sont en effet assez différentes les unes des autres par leur composition, et par suite par la manière dont l'industrie peut les utiliser, pour qu'il soit nécessaire de faire entre elles des distinctions: dans ce qui va suivre, nous réserverons, comme l'a fait le Deuxième Congrès international pour la répression des fraudes (Paris, octobre 1909), le nom d'essence de térébenthine à celles de ces essences dont les constituants principaux sont le pinène et le nopinène, c'est à dire dont la majeure partie (80% au moins) passe à la distillation, sous la pression atmosphérique normale, entre 154° et 164°.<sup>1</sup>

Dans un mémoire antérieur<sup>2</sup>, nous avons indiqué les premiers résultats de cette étude en ce qui concerne la gemme de Pin d'Alep; l'examen de nouveaux échantillons de gemme de même origine va nous permettre de compléter, en les confirmant, nos

<sup>1</sup> Compte rendu de travaux du Congrès de Paris, pp. 846 et 1297.

<sup>2</sup> Bull. de la Soc. chim. de France, (4° série), t. 5, p. 931; 1909.

conclusions premières. Nous donnerons ensuite les résultats de l'examen analogue que nous avons eu récemment l'occasion de faire de gemmes de *Pinus Massoniana*, et nous verrons que ces gemmes constituent, comme celles de Pin d'Alep, une matière première avantageuse pour la préparation du pinène pur.

1.—On sait que le Pin d'Alep (*Pinus halepensis* Mill.) est exploité en Grèce, en Algérie et dans le midi de la France. Le tableau ci-dessous donne la composition immédiate des échantillons de gemme, provenant de cet arbre, qui nous ont été envoyés d'Algérie et de Provence.

Echant. n°	Essence	Produit sec	Impuretés solides, eau et perte
1	27,0%	66,7%	6,3%
2	17,3	71,9	10,8
3	14,7	78,3	7,0
4	23,0	70,0	7,0
5	30,0	66,0	4,0
6	25,9	63,1	11,0
7	20,3	non dosés	.....
8	17,6	d°	.....

Dans ces échantillons, le rendement en essence varie, comme on le voit, du simple au double (de 14,7% à 30%). Ces variations paraissent tenir surtout au soin avec lequel la gemme est récoltée, et en particulier au temps plus ou moins long pendant lequel elle reste exposée à l'air. La comparaison des trois derniers échantillons (n° 6, 7, 8) est à cet égard particulièrement instructive: ils ont été récoltés, dans des conditions similaires et garantissant tout particulièrement leur authenticité,<sup>1</sup> sur les mêmes arbres de la forêt domaniale de Touazizine (Algérie), à des époques différentes d'une même saison de résinage (7 juin, 20 août, 11 novembre); la distance que les gouttes de gemme avaient à franchir sur l'arbre avant de parvenir dans le pot était faible en

<sup>1</sup> Nous sommes heureux de renouveler ici nos remerciements à M. Laporte, Conservateur des forêts à Oran, auquel nous sommes redevable de ces échantillons de gemme, ainsi que de l'un des échantillons d'essence dont il est question plus bas.



juin, plus grande en aout, plus grande encore en novembre; aussi voyons nous le rendement en essence baisser progressivement du premier au troisième de ces échantillons.

L'étude des essences provenant de la distillation aqueuse de ces gemmes, ainsi que de quelques autres échantillons d'essence provenant de la distillation industrielle de gemmes similaires, a donné les résultats suivants:

Echantillon n°	Densité à 25°	Indice de réfraction n <sub>D</sub> à 25°	Pouvoir rotatoire (α) <sub>D</sub>
1	0,8556	1,4640	+46°,9
2	0,8568	1,4652	+46°,7
3	0,8556	1,4638	+46°,6
4	0,8557	1,4644	+47°,8
5	0,8561	1,4643	+47°,4
6	0,8548	1,4642	+47°,6
7	0,8546	1,4638	+47°,3
8	0,8549	1,4641	+47°,6
9	0,8553	1,4645	+46°,9
10	0,8552	1,4639	+47°,6
11	0,8562	1,4648	+46°,5

Ces résultats confirment, comme on le voit, ceux que nous avons donnés en 1909: ces essences sont fortement dextrogyres et diffèrent peu les unes des autres. Au fractionnement, elles se montrent très homogènes: sous la pression atmosphérique normale, la majeure partie passe entre 154° et 156°, et les fractions recueillies dans cet intervalle, pendant la distillation d'une même essence, possèdent des constantes physiques à peu près identiques. Voici la valeur de ces constantes pour celles des essences décrites ci dessus dont le fractionnement a été opéré.

Echant. n°	$d_{25}^{\circ}$	$n_D$ à 25°	( $\alpha$ ) <sub>D</sub>
1	0,8543	1,4636	+48°,1
3	0,8547	1,4633	+47°,4
4	0,8548	1,4638	+48°,7
5	0,8550	1,4638	+48°,7
6	0,8545	1,4639	+48°,5
7	0,8541	1,4636	+47°,8
8	0,8547	1,4637	+47°,9
9	0,8541	1,4639	+47°,8
10	0,8542	1,4634	+48°,4
11	0,8545	1,4638	+48°,0

Comme nous l'avons montré en 1909<sup>1</sup>, ces données correspondent sensiblement à celles du pinène pur, pour lequel on a (mesures faites sur des échantillons de pinène inactif régénéré de son nitroschlorure):

Auteur	Ebullition sous 760 mm.	$d_{25}^{\circ}$	$n_D$ à 25°
Wallach <sup>2</sup> . . . . .	155° -156°	0,8540	1,4635
Schimmel <sup>3</sup> . . . . .	154°,5-155°	0,8554	1,4639

et pour lequel le pouvoir rotatoire le plus fort observé dans des échantillons gauches a été<sup>4</sup>

$$(\alpha)_D = -48^{\circ},63,$$

nombre presque indentique, au signe près, au maximum (+48°,7) obtenu par nous dans le fractionnement de nos échantillons 4 et 5.

Ces résultats sont d'accord avec ceux qu'a récemment obtenus

<sup>1</sup> Loc. cit., p. 932-933.

<sup>2</sup> Wallach, Liebigs Annalen, t. 258, p. 344; 1890. L'indice, mesuré à 21°, a été ramené à 25° au moyen du coefficient de température 0,0005.

<sup>3</sup> Gildemeister, Die Aetherische Oele, 2° Auflage, t. 1, p. 308; 1910. La densité et l'indice, mesurés à 15° et 20°, ont été ramenés à 25° au moyen des coefficients de température 0,0008 et 0,00055.

<sup>4</sup> Smith, in Bericht von Schimmel & Co., avril 1899, p. 24.

M. Darmois,<sup>1</sup> au cours de ses recherches sur la dispersion rotatoire des corps actifs.

Partant de ce principe, conséquence de la règle de Biot, que "la caractéristique d'une espèce chimique est, non pas le pouvoir rotatoire pour telle ou telle couleur, mais la dispersion rotatoire,"<sup>2</sup>

M. Darmois a déterminé la dispersion rotatoire du pinène pour les principales raies du spectre du mercure, c'est à dire les rapports de la rotation observée pour chacune de ces raies (raie jaune,  $\lambda = 578\mu\mu$ ; raie verte,  $\lambda = 546\mu\mu$ ; raie bleue,  $\lambda = 436\mu\mu$ ) à la rotation donnée, toutes choses égales d'ailleurs, par la raie jaune du sodium ( $\lambda = 589\mu\mu$ ). Il a obtenu ainsi, au moyen de pinène pur extrait de l'essence de pin d'Alep, les nombres suivants,<sup>3</sup> qui caractérisent le pinène, indépendamment de son pouvoir rotatoire, aussi bien que son point d'ébullition, sa densité ou son indice de réfraction:

$\lambda = 589\mu\mu$	$578\mu\mu$	$546\mu\mu$	$436\mu\mu$
Dispersion rotatoire: 1	1,043	1,185	2,017

Nous avons déterminé, relativement aux mêmes lumières monochromatiques, la dispersion rotatoire de quelques uns de nos échantillons d'essence de pin d'Alep; le tableau suivant donne les résultats de ces mesures.

Echant. n°	( $\alpha$ ) <sub>D</sub>	$\lambda = 589\mu\mu$	$578\mu\mu$	$546\mu\mu$	$436\mu\mu$
4	+47°,8	1	1,042	1,184	2,016
5	+47,4	1	1,042	1,183	2,006
6	+47,6	1	1,046	1,188	2,016
7	+47,3	1	1,044	1,182	2,015
8	+47,6	1	1,040	1,181	2,004
10	+47,6	1	1,045	1,188	2,010
11	+46,5	1	1,044	1,185	2,009

De ces résultats comme de ceux qui précèdent, il paraît légitime de conclure que l'essence de térébenthine extraite par distillation aqueuse de la gemme de Pin d'Alep est constituée presque exclusivement par du pinène droit.

<sup>1</sup> Darmois, Thèse Paris 1910, p. 63.

<sup>2</sup> Loc. cit., p. 45.

<sup>3</sup> Loc. cit., p. 66.

II—Nous avons eu entre les mains deux échantillons de gemme provenant du *Pinus Massoniana* Sieb. & Zucc., arbre qui croît sur les hauts plateaux de l'Inde anglaise et de la Birmanie. La composition immédiate de ces deux échantillons était la suivante:

Echant. n°	Essence	Produit sec.	Impuretés solides, eau et perte.
1	20,3%	78,1%	1,6%
2	22,1	77,8	0,1

Le premier, récolté dans d'assez mauvaises conditions, paraissait assez altéré; le deuxième au contraire paraissait récolté avec beaucoup de soin: il ne contenait sensiblement pas d'eau ni d'impuretés solides.

L'essence retirée de ces gemmes par distillation aqueuse présentait les caractères suivants:

Echant. n°	d <sub>20</sub> °	n <sub>D</sub> à 25°	(α) <sub>D</sub>	Dispersion rotatoire			
				λ = 589μμ 578μμ 546μμ 436μμ			
1	0,8538	1,4645	+36°,4	1	"	"	"
2	0,8532	1,4650	+31°,6	1	1,040	1,180	2,021
3	0,8541	1,4647	+42°,4	1	1,042	1,180	"

Les échantillons 1 et 2 ont été recueillis au cours de la distillation de la gemme n° 1; l'échantillon n° 3 est le produit total de celle de la gemme n° 2. On voit que ces essences, très comparables en ce qui concerne la densité, l'indice de réfraction et la dispersion rotatoire, diffèrent cependant notablement par la valeur de leur pouvoir rotatoire.

Soumis au fractionnement, ces échantillons se sont montrés très homogènes: sous la pression atmosphérique normale, la majeure partie passe entre 154° et 156°, et les fractions recueillies dans cet intervalle diffèrent fort peu les unes des autres en ce qui concerne la densité et l'indice, comme le montre le tableau suivant:

	Echant. n° 1		Echant. n° 2		Echant. n° 3	
	$d_{20}^{\circ}$	$n_D$ à 25°	$d_{20}^{\circ}$	$n_D$ à 25°	$d_{20}^{\circ}$	$n_D$ à 25°
Fraction 1	0,8539	1,4640	0,8536	1,4643	0,8542	1,4640
2	0,8539	1,4640	0,8537	1,4643	0,8542	1,4641
3	0,8541	1,4641	0,8538	1,4644	0,8543	1,4642
4	0,8537	1,4642	0,8535	1,4648	0,8541	1,4646
Residu	0,8530	1,4658	0,8530	1,4669	0,8555	1,4661

En revanche, la rotation (mesurée dans un tube de 100 millim. et pour la raie D) subit une décroissance sensible de la première fraction à la cinquième: la densité des fractions étant très voisine, leur pouvoir rotatoire décroît évidemment de la même façon. Mais si l'on mesure, comme nous l'avons fait pour l'échantillon n° 3, les rotations pour les raies jaune et verte du mercure, on trouve pour les dispersions correspondantes des valeurs sensiblement constantes:

	Echant n°1 $\alpha_D$	Echant. n°2 $\alpha_D$	Echant. n°3 $\alpha_D$	$\lambda=589\mu\mu$	578 $\mu\mu$	546 $\mu\mu$
Fraction 1	+35°,00	+33°,00	+38°,27	1	1,043	1,184
2	+34°,37	+31°,90	+37°,87	1	1,042	1,181
3	+33°,10	+30°,10	+37°,43	1	1,038	1,180
4	+30°,90	+26°,81	+36°,33	1	1,041	1,181
Résidu	+20°,76	+12°,57	+31°,30	1	1,045	1,188

Ces dispersions, comme celles des essences elles-mêmes, se trouvent être sensiblement égales à celles du pinène pur, qui comme nous l'avons vu plus haut, donne pour les mêmes radiations les valeurs.

$$1 \quad 1,043 \quad 1,185.$$

Comme on vient de voir d'autre part que le point d'ébullition, la densité et l'indice de réfraction des fractions distillées s'écartent peu de ceux du pinène pur, qui ont été donnés plus haut, on est

en droit d'en conclure que l'essence de térébenthine extraite par distillation aqueuse de la gemme du *Pinus Massoniana* est constituée presque exclusivement par du pinène (pinène droit mélangé d'un peu de pinène gauche, ou pinène droit partiellement racémisé).









GENERAL INDEX  
TO THE TWENTY-FOUR VOLUMES OF  
ORIGINAL COMMUNICATIONS

Volume	Section	
1	I.	Analytical Chemistry.
2	II	Inorganic Chemistry.
3	IIIa	Metallurgy and Mining.
4	IIIb	Explosives.
5	IIIc	Silicate Industries.
6	IV	Organic Chemistry.
7	IVa	Coal Tar Colors and Dyestuffs.
8	Va	Industry and Chemistry of Sugar.
9	Vb	India Rubber and other Plastics.
10	Vc	Fuels and Asphalt.
11	Vd	Fats, Fatty Oils and Soaps.
12	Ve	Paints, Drying Oils and Varnishes.
13	VIa	Starch, Cellulose and Paper.
14	VIb	Fermentation.
15	VII	Agricultural Chemistry.
16	VIIIa	Hygiene.
17	VIIIb	Pharmaceutical Chemistry.
18	VIIIc	Bromatology.
19	VIII d	Biochemistry including Pharmacology.
20	IX	Photochemistry.
21	Xa	Electrochemistry.
22	Xb	Physical Chemistry.
23	XIa	Law and Legislation Affecting Chemical Industry.
24	XIb	Political Economy and Conservation of Natural Resources.









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