

## SUMMARY.

The results incorporated in this investigation warrant the statement that pinene possesses an absorptive capacity for certain gases, in some instances to a very high degree. Whatever fact of chemical significance may be attached to this phenomenon remains to be investigated.

This investigation is to be regarded as a preliminary one for it is the intention to pursue the investigation further, using such gases as HCN, H<sub>2</sub>S, N<sub>2</sub>, NH<sub>2</sub>OH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CO, etc., in order to obtain true physical and chemical constants.

## REFERENCES.

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3. Semmler, *Die Aetherischen Oele, Bd., 2*, p. 252.
4. Kingzett, *J. Chem. Soc.*, 1876, p. 261.
5. Papasogli, *Gaz. chim. ital.*, 6, p. 538.
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## DIETHYLPHTHALATE.\*

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## I. SUMMARY OF AVAILABLE SCIENTIFIC DATA IN THE LITERATURE.

Of the three possible isomeric diethyl esters of phthalic acid, the one of the present commercial importance is the diethyl ester of ordinary or orthophthalic acid. This ester was first prepared by Laurent<sup>1</sup> in 1836, who was also the first chemist to prepare phthalic acid by the oxidation of naphthalene. Laurent states:

"When one boils a mixture of alcohol ('wine spirit'), hydrochloric acid and phthalic acid (called by him 'naphthalene acid') in a retort there is obtained at the end of the distillation an oily material which remains behind in the retort. This oily material is heavier than water and I believe it to be the ester of phthalic acid, without, however, having obtained a sufficient quantity to make further investigation of it."

There is no question that Laurent actually made the ester, as the procedure he used is a standard laboratory method for ester formation.

Von Graebe and Born<sup>2</sup> in 1867 state that the only existing data regarding this ester are those of Laurent. Von Graebe and Born prepared the ester by the same process as used by Laurent, and, after carefully purifying it, found it to be a colorless and odorless oil, boiling at 295° C. (cor.), and having the elementary composition of C<sub>8</sub>H<sub>8</sub>(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. It may be noted in passing that this b. p. of 295° C., as determined by these chemists over 50 years ago, checks exactly with that of the commercial product on the market to-day.

Michael<sup>3</sup> in 1879 accidentally prepared diethylphthalate by the action of phosphorus trichloride on monoethylphthalate which he was studying at the time. (The monoethyl ester is described by Michael as an oil, moderately soluble in water and unstable towards heat, decomposing on distillation into ethyl alcohol and phthalic anhydride.) Michael gives no data on the constants of the diethyl ester.

Von Graebe and Born<sup>4</sup> in 1883 studied further the ethyl and methyl esters of phthalic acid. They prepared the diethyl ester by three methods: (a) Ethyl iodide and silver phthalate, (b) sodium alcoholate and phthalyl chloride, and (c) phthalic anhydride and ethyl alcohol saturated with HCl gas. The esters obtained by these three methods showed the same b. p. of 294° C. at 734 mm., with the thermometer entirely in the vapor, and the sp. gr. (values not stated) differed only in the fourth decimal.

\* Read before Scientific Section, A. Ph. A., Cleveland meeting, 1922.

Brühl<sup>6</sup> in 1894 gives the physical properties of the diethyl ester, which he obtained from Kahlbaum. After drying over calcium chloride, and submitting it to fractional distillation, he found the great bulk of it to distil over sharply at 172° C. under 12 mm. pressure. At 752.5 mm. the ester distilled at 289° C. He also determined its density and refractive index for monochromatic light of different wave lengths as follows:

Sp. gr. $\frac{4.3^\circ}{4^\circ} = 1.1232$	Refractive index, $n$ , at 14.3° C.
	Li—1.49999
Sp. gr. $\frac{20^\circ}{4^\circ} = 1.1175$	H $\alpha$ —1.50070
	Na—1.50490
	Tl—1.50960
	H $\gamma$ —1.52498

W. H. Perkin<sup>8</sup> in 1896 found diethylphthalate to have a boiling point of 298–299° C. cor., to 760 mm. He determined its relative density at several temperatures, as follows:

$\frac{4^\circ}{4^\circ}$ C.—1.1358	$\frac{20^\circ}{20^\circ}$ C.—1.1234
$\frac{10^\circ}{10^\circ}$ C.—1.1306	$\frac{25^\circ}{25^\circ}$ C.—1.1205
$\frac{15^\circ}{15^\circ}$ C.—1.1268	$\frac{30^\circ}{30^\circ}$ C.—1.1178

In this same article, it might be of interest to note W. H. Perkin's<sup>8</sup> description of the other two isomeric diethylphthalates as follows:

"Diethyl ester of isophthalic acid, obtained by boiling the acid, alcohol, and ten percent of H<sub>2</sub>SO<sub>4</sub> for seven hours is an oily liquid, b. p. 302° C. at 760 mm., m. p. 11.5° C., sp. gr.  $\frac{15^\circ}{15^\circ}$  C. = 1.1289."

"Diethyl ester of terephthalic acid, obtained by adding absolute ethyl alcohol, a little at a time, to phthalyl chloride made by the action of PCl<sub>5</sub> on terephthalic acid, has a m. p. 43.2° C. and b. p. 302° C. at 760 mm."

Bogojawlenski and Narbutt<sup>7</sup> in 1905 prepared diethylphthalate by a rather unusual procedure of esterification in which they employed anhydrous copper sulphate as the condensing agent and claimed to have obtained a 67 percent yield of the ester from phthalic anhydride and ethyl alcohol.

No experimental data regarding the pharmacodynamics of diethylphthalate were found other than the general statements given in U. S. Patents 969,636 and 1,017,669, and in recent articles on specially denatured alcohol formula 39B in perfumery trade journals, stating that esters of orthophthalic acid are non-irritating and non-poisonous.

About twelve years ago, a German concern under the name of Dralle began manufacturing perfumes with diethylphthalate as a vehicle, instead of alcohol. This line met with considerable success at the time, and resulted in much experimental work along the same line here in America.

Shortly after this, a perfumer by the name of Rieger of California put on the market a line of perfumes known as "Rieger's Flower Drops," in which he used diethylphthalate as a vehicle, instead of alcohol.

About this time, Larkin Co. started its experimental researches on the use of this ester in obtaining colorless, non-alcoholic perfumes. The samples made at that time, and which we still have, show no signs of deterioration as to color, odor, etc.; however, this method was found to be very expensive and not as satisfactory, both from the standpoint of production and quality of product, as perfumes made with alcohol as a vehicle.

Long before this ester came into known use in this country, it was being used secretly under different trade names in synthetic perfumery compounds as an

adjusting agent for strength. One of its early specific uses was as a solvent for musk, in place of benzyl benzoate.

## II. PATENTS ON THE USE OF DIETHYLPHTHALATE.

The importance and possible uses of diethylphthalate appear to have been realized in Germany over a decade ago.

On June 15, 1909, Hesse took out German Patent 227,667,<sup>9</sup> covering the use of the alkyl and aryl esters of phthalic acid, or their mixture, as solvents for fatty acids and ethereal oils, perfumes, etc., but especially for rosin and varnish gums, it being claimed the use of 30 parts by weight of diethylphthalate would give a perfect solution with 100 parts of rosin.

On May 19, 1911, Hesse took out German Patent 251,237,<sup>10</sup> an addition to the preceding patent, and patented the use of the "phthalic acid esters" as solvents for obtaining the natural perfumes by extraction, maceration, or diffusion, obtaining thereby perfume products which do not contain objectionable constituents and which dissolve completely and directly in alcohol even when diluted.

On February 20, 1912, U. S. Patent 1,017,669<sup>11</sup> was granted Albert Hesse of Wilmersdorf, Germany, as a new composition of matter, a solution of an organic perfume containing a phthalic acid ethyl ester, alcohol, and water as solvents. You can read the original application on page 61 of the *American Perfumer* for 1912. Although he used dimethylphthalate, as well as the ethylphthalates, he brings out that the phthalates are excellent solvents and act as fixatives in the prevention of irregular evaporation of perfume materials. This patent is now owned by the Chemical Foundation.

On September 6, 1910, U. S. Patent 969,636<sup>8</sup> was granted Dr. Kleber, now of Fritzsche Bros., on the use of the esters of orthophthalic acid as improved perfume bases in the manufacture of perfumery. This specifically set forth that the neutral ethyl esters of orthophthalic acid, including the diethyl ester, are colorless, practically odorless, have a low freezing point, are not readily inflammable, do not irritate the skin, and are non-poisonous; that they are miscible with alcohol, ether, chloroform, and glycerine in all proportions; that they are excellent solvents of various essential oils, balsams, synthetic compounds such as artificial musk, coumarin, and other substances used in the manufacture of perfumery; that they possess the properties of blending the various odoriferous materials in a satisfactory manner, as well as acting more or less as fixatives; that they are stable and without chemical action on the substances dissolved. On account of their high boiling points (275–325° C.), they volatilize very slowly but finally completely without leaving any stain on fabrics. This patent is now owned by Fritzsche Bros. Inc., New York City.

The *American Perfumer* for January 1922 published signed statements by both the Chemical Foundation and Fritzsche Bros., in which they generously waive any infringement under their respective patents, for the use of diethylphthalate as a denaturant in specially denatured alcohol formula 39B.

German Patent No. 313,059<sup>12</sup> covers the use of the ester salts of phthalic acid as glycerine substitutes.

In 1917, German Patent 302,581<sup>13</sup> was taken out, covering the use of the neutral esters of phthalic acid as heat-transmitting media, it being specified that these esters were mobile liquids, stable, non-inflammable, with a high boiling point (280–290° C.) and a flash point above 160° C.

## III. RECENT ARTICLES AND EDITORIALS ON USE OF DIETHYLPHTHALATE AS A DENATURANT.

Within the past year numerous editorials and general statements have appeared in the journals of the Perfumery and Essential Oil trade.

In the special May 12, 1921, edition of the *Perfumers' Journal and Essential Oil Recorder*,<sup>14</sup> diethylphthalate is discussed as a denaturant for alcohol that would meet with universal satisfaction.

An article in the June 1921 edition (Vol. 1, No. 10, pp. 32-33)<sup>15</sup> of the same journal warmly supports the use of diethylphthalate, and quotes Dr. I. V. Stanley Stanislaus and Mr. Fries of Fries and Fries Co., manufacturing chemists, Cincinnati, as endorsing a two to three per cent solution of diethylphthalate in alcohol as a substitute for pure alcohol in the manufacture of perfumes and toilet waters. Dr. Stanislaus further stated:

"If the Department should adopt this new denaturant, it could regulate so that all of the U. S. P. and all the N. F. fluidextracts, tinctures and spirits could be made with the alcohol, because their doses range between 5 and 60 drops (about a teaspoonful is the major dose of a majority of these), and 5 to 30 drops dose of these preparations largely diluted with sweetened water could be taken without any injury to the patient, and without much inconvenience, whereas larger doses, of, say, half a wine glass full, would make the drinker sick."

A large amount of research work was carried on under the auspices of the Alcohol and Research Committee of the Manufacturing Perfumers' Association in collaboration with the Industrial Alcohol and Chemical Division of the Internal Revenue Dept., which finally resulted in the issuance by the Treasury Department of Pro-Mimeograph, Coll. No. 2840, on September 23, 1921, authorizing the use of specially denatured alcohol formula 39B, to wit:

"To every 100 gallons of pure ethyl alcohol add 2 $\frac{1}{2}$  gallons of diethylphthalate, for use in the manufacture of perfumes, toilet waters, alcoholic barber supplies, and lotions." The specifications for the diethylphthalate to be used in this formula are as follows: "Diethylphthalate is colorless, practically without odor and is miscible with alcohol. Boiling point 290-297° C. The ester content should be not less than 99 percent determined by the usual saponification method."

*The American Perfumer*, October 1921, p. 328,<sup>16</sup> carries an editorial which includes a reprint of the authorization by prohibition enforcement authorities of the new 39B alcohol, and a statement from Dr. I. V. Stanley Stanislaus that "the new alcohol when used in perfumes will not irritate the most sensitive and delicate skin. Its non-irritating qualities have been amply demonstrated." Dr. Stanislaus further states that it is a fact that for years the floral oils of Europe have been standardized by the use of diethylphthalate (much as dyes are standardized by the manufacturer with salt or Glauber salt). In this connection it is of interest to note that in 1920 there appeared an anonymous article<sup>17</sup> printed in the *Deut. Parfümerie Ztg.* in which it is claimed that diethylphthalate is extensively used as an adulterant of essential oils and mentions particularly the adulterations of the essential oils of anise, bergamot, cassia, violet, lavender, mint, and cinnamon. It is possible that in these cases diethylphthalate, if not present in an excessive quantity, was used for purposes of standardization rather than adulteration.

In the *Perfumers' Journal and Essential Oil Recorder* for January 1922, there is an article by F. H. Lowenfels.<sup>18</sup> The author states that there is a general impression in the trade that 39B alcohol cannot be used in foaming hair tonics where it is believed the ester will saponify in the alkaline solution used. Lowenfels states that as a matter of fact the ester is remarkably stable and will not saponify in a solution of the degree of alkalinity employed in hair tonics. Lowenfels claims, however, that 39B alcohol reduces the foaming power because of the effect of diethylphthalate on the surface tension of alcohol. He neglected to state, however, whether it increased or decreased the surface tension of the alcohol or the tonic.

Geo. A. Witmer, in *Ungerer's Bulletin*,<sup>19</sup> states that specially denatured alcohol formula 39B is the only denaturing alcohol up to the present time (April 1922) which has met with anything like general approval. However, he questions whether diethylphthalate in 2½ percent solution in alcohol is a suitable denaturant for all perfumes, especially those composed of delicate floral ingredients.

A. B. Lyons, in his excellent article<sup>20</sup> on the "Detection of Diethylphthalate in Whisky," describes both a qualitative and quantitative method for diethylphthalate. Lyons' qualitative method involves an extraction of the ester by means of petroleum ether and its subsequent conversion into fluorescein by a procedure practically identical with the method which we have used and which is subsequently described in our paper as the modified Mulliken Test for Fluorescein.

ANALYTICAL DATA SHOWING COMPARISON OF STANDARD DOMESTIC DIETHYLPHTHALATES WITH TWO SAMPLES OF FOREIGN MANUFACTURE.

Manufacturer.	Sp. gr. 15.6° C.	Refractive index 20° C.	Opt. act. 20° C.	Free acidity as phthalic acid, %	Saponification number. Mgm. KOH per Gm.	Corrected for free acidity.
1. Van Dyk.....	1.1236	1.5008	(-)0°, 26.4'	0.105	503.35 99.66% ester	502.54 99.50% ester
2. A. Chiris.....	1.1232	1.5013	(-)0°, 2.0'	0.048	502.98 99.58% ester	502.63 99.51% ester
3. Fritzsche Bros..	1.1261	1.5018	(+)0°, 3.6'	0.103	503.58 99.70% ester	502.96 99.58% ester
4. C. E. Ising.....	1.1229	1.5020	(+)0°, 4.1'	0.049	500.82 99.16% ester	500.49 99.09% ester
5. U. S. Ind. Al- cohol Co.....	1.1222	1.5008	(+)0°, 5.1'	0.025	504.16 99.82% ester	503.99 99.78% ester
6. The Rossville Company.... <i>Foreign</i>	1.1220	1.5008	(+)0°, 1.2'	0.017	503.92 99.77% ester	503.81 99.75% ester
7. Morana Inc. (German)....	1.1239	1.5019	(+)0°, 6.2'	0.105	502.54 99.50% ester	501.74 99.34% ester
8. Muhlethaler Co. (Swiss).....	1.1218	1.5014	(-)0°, 5.2'	0.020	501.30 99.25% ester	501.10 99.21% ester

Since the authorization of specially denatured alcohol formula 39B by the U. S. Treasury Dept. in September 1921, the Alcohol Committee of the American Manufacturers of Toilet Articles has been accumulating practical information on the efficiency of this formula in the manufacture of high-grade perfumes and toilet waters. It having been demonstrated that high-grade perfumes and toilet waters contain sufficient denaturing agents in the form of essential oils and other non-potable perfume bodies to render the alcohol unfit for beverage purposes when there in proportions of two percent and over, and whereas the diethylphthalate because of its viscosity and fixative properties tended to flatten somewhat the more delicate floral odors, and when used on the skin in the strength of 2½ percent solution tended to hold the alcohol and certain perfume materials on the skin long enough to cause slight burning and irritating effect, especially with those who might have a sensitive skin, it was deemed advisable to obtain a reduction in the

amount of diethylphthalate from 2½ percent to 1 percent as authorized in specially denatured alcohol formula 39C under Pro-Mimeograph Coll. No. 2993, issued by the U. S. Treasury Department on August 2, 1922, to wit:

"To every 100 gallons of pure ethyl alcohol add 1 gallon of diethylphthalate, for use in the manufacture of high-grade perfumes and toilet waters containing not less than 2 percent by weight of essential oils or their equivalent in perfume materials. The diethylphthalate used in this formula shall be of the same quality as that specified for use in formula 39B, and shall be free from chlorine."

"The Department will only permit the use of this formula by manufacturers who are properly equipped by reason of experience and manufacturing facilities to effectively control their manufacturing operations in accordance with the limitations governing the use of this formula."

ANALYTICAL DATA SHOWING RANGE OF THE MORE IMPORTANT PHYSICAL AND CHEMICAL  
CONSTANTS FOR ALL THE DIFFERENT SAMPLES.

Specific gravity/15.6° C.....	1.1218 to 1.1261
Refractive index/20° C.....	1.5008 to 1.5020
Optical activity/20° C.....	(- )0°, 26.4' to (+)0°, 6.2'
Free acidity as phthalic acid.....	0.017 to 0.105%
Saponification number mgm. KOH per Gm.....	500.82 to 504.16
	99.16 to 99.82% ester
Saponification number corrected for free acidity.....	500.49 to 503.99
	99.09 to 99.78% ester
Boiling point at 734 mm. pressure.....	295° C. average temp.
Boiling point at 30 mm. pressure.....	182° C. average temp.
Boiling point at 14 mm. pressure.....	163° C. average temp.
Surface tension (Sample 2), static, dynes per cm./25° C.....	42.5
Flash point (Sample 2). (Cleveland Open Cup Tester, A. S. T. M. model).....	153.3° C.

DETAILED DESCRIPTION OF TECHNIQUE EMPLOYED IN OBTAINING  
FOREGOING CONSTANTS.

*Specific Gravity.*—Determined at  $\frac{15.6^\circ}{15.6^\circ}$  C. by means of calibrated pycnometer provided with thermometer.

*Refractive Index.*—Determined at 20° C. on Zeiss refractometer. Refractometer calibrated with distilled H<sub>2</sub>O and cedar oil, and corrections applied to readings of the samples.

*Optical Activity.*—Reported as degrees and minutes of angular rotation of a 2 dcm. column of the substance at 20° C., using sodium flame as a source of illumination. Instrument used was a Schmidt and Haensch polariscope, calibrated by the Bureau of Standards and certified to have an error of +0.7' at 0° rotation. The 200-mm. tube used was No. 252, certified by the Bureau of Standards to have a length of 200.02 mm. at 20° C. The reported values for optical activity are the means of eight closely agreeing observations. The instrument was so adjusted that its observed correction at 0° was zero. The Bureau of Standards correction of +0.7' (inherent error of the instrument) was applied to the observed readings.

*Free Acidity.*—Determined by dissolving weighed samples of about 3 Gm. in hot neutral alcohol, and titrating to a faint, permanent pink with N/10 NaOH, using phenolphthalein as indicator. Acidity is reported as phthalic acid, of which 1 cc N/10 NaOH = 0.0083044 Gm., on the basis of the 1921 atomic weights.

Phthalic acid, C<sub>8</sub>H<sub>6</sub>O<sub>4</sub> = Molecular wt. of 166.088

(Dibasic acid, equivalent weight = 83.044)

*Saponification Number.*—Mgm. KOH required to saponify 1 Gm. of the ester.

Diethylphthalate = C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>.

Atomic weights for 1921. *Jour. Am. Chem. Soc.*, August 1921, p. 1752.

C = 12.005                      H = 1.008                      O = 16.00                      K = 39.10

Molecular weight of diethylphthalate = 222.172

Molecular weight of 2KOH = 112.216

Saponification number of 100.00 per cent diethylphthalate =  $\frac{112.216}{222.172} \times 1000 = 505.086$

Saponification number of 99 percent diethylphthalate would be . . . . . 500.03

Saponification number of the ester was determined, in duplicate, by accurately weighing about 2 Gm. into a flask from an acetylation apparatus, adding 50 cc *N*/2 alcoholic KOH from a calibrated pipette, boiling under reflux for one hour, rinsing apparatus with hot, neutral alcohol, and titrating while hot with *N*/1 H<sub>2</sub>SO<sub>4</sub>, using phenolphthalein as indicator, until the pink color was barely discharged. Duplicate blanks were run in exactly the same manner.

The *N*/2 alcoholic KOH was prepared according to U. S. P. IX, page 567, using Cologne Spirit. The final reagent resulting was water-white, which enabled the very accurate determination of the end-point in titrations, because of absence of any interfering colors.

The *N*/2 KOH was standardized with Merck's C. P. Potassium Bitartrate, dried at 120° C. 2.3518 Gm. of KHC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> should require 25 cc exactly *N*/2 KOH to neutralize. Duplicate standardizations required 23.45 and 23.46 cc, respectively. Normality of the *N*/2 alcoholic KOH is, therefore, 0.53295 or 1.0659 *N*/2.

The *N*/1 H<sub>2</sub>SO<sub>4</sub> used for back titration was standardized against the *N*/2 alcoholic KOH and its normality in very closely agreeing duplicate standardizations was found to be 1.0437 *N*. This standardization was also further verified by titration against an aqueous *N*/2 KOH standardized against benzoic acid purified according to directions of the Bureau of Standards.

Calibrated burettes were used, and the proper corrections to observed readings were applied.

Owing to its very high numerical value, the accuracy with which the saponification number of diethylphthalate may be determined, even when extreme care is used at every step, may be placed at about 1/10 of 1 percent (numerically about 0.50 on a value of 505). To obtain values which would check to within 0.25 in duplicate determinations, using the same weight of sample (about 2 Gm.) it is necessary that the titrations check to within 0.01 cc *N*/1 H<sub>2</sub>SO<sub>4</sub>, or about 1/3 of a drop. Since this is the ultimate limit of accuracy in reading a burette, it will be clear that the degree of accuracy stated above, *i. e.*, 0.1 percent, is about what may be expected and attained by working with great care.

NOTE: It is believed that no appreciably greater accuracy would result if the back titrations were made with a weaker acid, *i. e.*, *N*/2 or even *N*/4, on account of the fact that the end-point is the disappearance of a faint pink in a milky white solution (due to the insolubility of potassium phthalate in alcohol). In such a solution, the end-point is not quite so sharp or sensitive as in a water-white solution. A fraction of a drop of *N*/1 acid would, it is believed, enable the operator to secure a sharper end-point than could be obtained from the very gradual transition at the end-point which would result from the addition of fractions of drops of *N*/2 or *N*/4 acid.

Example of saponification number determination: 50 cc *N*/2 alcoholic KOH from the same calibrated pipette used in every case.

Cc <i>N</i> /1 H <sub>2</sub> SO <sub>4</sub> (1.0437 <i>N</i> ) for				
back titration . . . . .	Blank No. 1 25.31 cc	No. 2 25.29 cc	Average, 25.30 cc	
Sample diethylphthalate . . . . .	Detn. No. 1 6.37	No. 2 6.11		
Difference: Blank minus				
back titration . . . . .	No. 1 18.93 cc.	No. 2 19.19 cc		
Weight of samples . . . . .	No. 1 2.1950 Gm.	No. 2 2.2275 Gm.		

Saponification number =  $\frac{\text{Mgm. KOH consumed}}{\text{Wt. of sample in grams}}$

Saponification Sample No. 1  $\frac{18.93 \times 1.0437 \times 56.108}{2.1950} = 505.03$

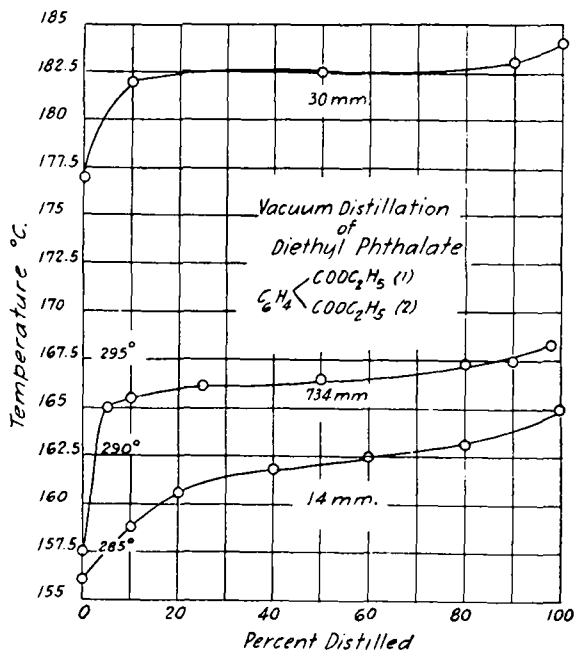
Saponification Sample No. 2  $\frac{19.19 \times 1.0437 \times 56.108}{2.2275} = 504.50$       Average, 504.760

$\frac{504.760}{505.086} \times 100 = 99.93$  percent diethyl ester

NOTE: A difference in titration of 0.01 cc N/1 H<sub>2</sub>SO<sub>4</sub> changes the value of the saponification number by 0.25.

**Boiling Point.**—Distillation test: 250-cc quantities of standard commercial diethylphthalate were distilled from a 500-cc Claisen distilling flask provided with a Tyco precision grade No. 360,771 nitrogen-filled thermometer in the side tubulation, and connected with a Graham water condenser. The entire flask was heavily lagged with asbestos and heat was supplied by an electric flask heater equipped with rheostat. A Cenco Rotary Vacuum Pump was used for the vacuum distillations, together with a special graduated Fuch's Vacuo receiving flask.

**Boiling Point.**—Distillation (a) at 734 mm. pressure: The actual barometric reading on the day the distillation was made. Rate of distillation—approximately 5 cc per minute. The first drop came over at 285° C. After 98 percent had distilled over, the temperature was 295.8° C., which was taken as the end-point. The average distillation range for the various samples tested was about 3° C., with about 65 percent of the sample distilling between 294° and 295° C., under the conditions prevailing at the time of this test. All samples turned yellow in the distilling flask during the boiling. Although the distillate was practically water-white, it had a pronounced still odor. There was about two percent of dark residue left in the flask at the end-point. In commercial practice, diethylphthalate is always distilled under vacuum as there is always some slight decomposition on prolonged boiling of compounds of this nature at high temperature.



Distillation (b) at 30 mm. pressure: About half an hour was required after starting vacuum and heat before the first drop came over. When a uniform heat had been established, distillation proceeded at the rate of 4 cc per minute. At this pressure, the boiling point over the bulk of the range of distillation was quite constant. The first drop came over at 177° C. and the last portion at 184° C. The bulk of the distillate between ten and ninety percent distilled within the range of 182° to 183° C.

Distillation (c) at 14 mm. pressure: The same degree of heat was applied as in distillation (b). There was a continual slight rise in distillation temperature, the first drop coming over at 156° C. and the last portion of the distillate at 165° C., the rate of distillation being 7 cc per min-



ute. The bulk of the distillate between 15 percent and 85 percent distilled within the range of 160–163° C. The foregoing curves show the distillations more clearly.

*Surface Tension.*—The static surface tension of diethylphthalate was determined with a Du Nouy Tensimeter which was standardized against redistilled water. The following values were found:

	Static surface tension dynes per cm./25° C.
1. Redistilled water.....	75.9 (note)
2. Diethylphthalate (lab. sample).....	42.5
3. Cologne Spirit (lab. sample).....	27.6
4. 39B alcohol made from (2) and (3).....	27.9
5. 39B alcohol, commercial sample.....	27.9
6. 39C alcohol, made from (2) and (3).....	27.7
7. 39C alcohol, commercial sample.....	27.7

NOTE: The value of 75.9 dynes per cm. for the surface tension of water at 25° C. (which was checked exactly on different days) is slightly lower than the value of 77 dynes per cm. at 25° C. reported by Du Nouy (*J. Gen. Physiology*, 1, 521, 1919). Dicks, in an unpublished thesis, working at M. I. T., found, however, the surface tension of conductivity water (specially purified distilled water) to be 79.5 dynes per cm. at 20° C. with the Du Nouy Tensimeter. This value is equivalent to 78.7 dynes per cm. at 25° C., or 1.7 dynes higher than the value found by Du Nouy. These variations may be due in part, at least, to slight variations in the circumference of the 4-cm. platinum wire rings supplied with the different tensimeters. Harkins (*J. Am. Chem. Soc.*, 49, 499, 1919), using different methods, arrived at a value of 73 dynes per cm. for the static surface tension of distilled water.

*Flash Point.*—A commercial sample of diethylphthalate was tested for flash point in the Cleveland Open Cup Tester, latest American Society for Testing Materials model. When heated at the standard rate of 5° C. per minute, duplicate tests gave a flash point by this apparatus of 308° F. or 153.3° C.

#### 1. DETECTION OF DIETHYLPHthalate BY THE MODIFIED MULLIKEN TEST FOR FLUORESCIN.

Mulliken, in his "Identification of Pure Organic Compounds," Vol. 1, p. 84, gives the following directions for the detection of phthalic acid:

"Mix 0.05 Gm. of the powdered acid with an equal quantity of resorcin. Place in a dry test-tube and moisten with one drop of concentrated sulphuric acid. Stand the test-tube in a liquid bath at a temperature of 160° C. and heat for three minutes. Cool, treat the fused mass with 2 cc dilute sodium hydroxide solution; pour into 500 cc of cold water. The water will show a very intense yellow-green fluorescence due to fluorescein."

When tried out on phthalic anhydride, the above test gives an intense yellowish green fluorescence, unobscured by the reddish brown color so prevalent from the official caustic soda fusion.

It was possible to modify the test as described by Mulliken to cover the detection of minute amounts of diethylphthalate, by "fixing" the phthalic acid from the ester with caustic as in the Linder test, and then adding an excess of 1.84 H<sub>2</sub>SO<sub>4</sub>, 0.05 Gm. resorcin, and heating three minutes at 160° C.

This procedure is very similar to that of Lyons, except that in our method no preliminary extraction of the sample with petroleum ether was considered necessary. Experiments in our laboratory have shown that extraction of 39-B alcohol with petroleum ether, according to Lyons' procedure, is practically quantitative, as

claimed by Lyons. In samples containing carbohydrate material, this preliminary extraction of the diethylphthalate would be advisable.

In testing liquid products like denatured alcohol, perfumes, and whisky, the extraction process is merely an extra, unnecessary step. In the case of perfumes, the petroleum ether has been found to extract a large proportion of the perfume oils. The same results, however, are obtained by testing a sample of perfume directly, as when a petroleum ether extract of the sample is used.

In cases where a large amount of aromatic bodies, resins, or other organic extractive matter is present, the following procedure can be used to advantage: Extract the sample with petroleum ether, evaporate the solvent, and saponify the ether extract with an excess of  $N/2$  alcoholic KOH. If the diethylphthalate is present, there will be formed white needle-like crystals of potassium phthalate which can be filtered off and treated with resorcin and sulphuric acid as described below.

Full directions for the test are as follows:

"To 10 cc of 39B alcohol or 5 drops diethylphthalate in a small casserole or evaporating dish, add 5 cc of 10 percent NaOH solution, and evaporate virtually to dryness on the steam-bath. Remove the dish from the bath, cool, and cautiously add 2 cc 1.84  $H_2SO_4$ , a drop at a time, from a pipette, covering with a watch glass if necessary to avoid spattering. Pour the resulting solution at once into a dry test-tube containing 0.05 Gm. of resorcin, stand the test-tube in an oil-bath heated to 160° C. and maintain at that temperature for 3 minutes. Remove the test-tube from the bath, allow it to cool, and transfer a small portion of the contents to a large test-tube containing 50 cc  $H_2O$  made alkaline with 5 cc of 10 percent NaOH. The characteristic color of fluorescein develops at once, if the above quantities of 39B alcohol or the ester are used. A blank run in precisely the same manner should give a pale amber- or straw-colored solution free from fluorescence."

Caution: When the test is run on floral essences it frequently happens that a greenish blue or greenish red bloom appears when no diethylphthalate is present. Care should be observed not to confuse this bloom (or pseudo-fluorescence) with the intense yellowish green fluorescence of true fluorescein. It is well, in testing unknowns, to run a control test with a genuine sample of the ester, 39B alcohol, or phthalic anhydride, in order that one may have a sample of genuine fluorescein to compare with the colors given by unknowns.

When the test is being made to detect very small amounts of the ester, it is advisable to pour the entire melt into 500 cc of water containing 50 cc of 10 percent NaOH. Working with great care and using absolutely clean utensils it is possible to detect with certainty 0.1 mg. of diethylphthalate in alcohol when no interfering substances are present.

The modified Mulliken test was applied to small amounts of 39B alcohol. One cc of the 39B with 9 cc Cologne Spirit gives the test with nearly the same intensity as the 10 cc quantity of 39B; 0.1 cc of 39B alcohol with 9.9 cc Cologne Spirit gives a very distinct positive test; and even 0.01 cc of 39B yields recognizable fluorescence by this test.

## 2. DETECTION OF DIETHYLPHTHALATE IN PERFUMES AND TOILET WATERS.

The modified Mulliken test was applied to several different standard types of odors, including Violet, Rose, Lilac, and Essfloral (Bouquet) Perfumes and Toilet Waters on samples with and without the diethylphthalate denaturant. In each case the test was either negative or positive, depending upon whether the diethyl-

phthalate was absent or present. The Violet and Rose products, however, contain substances which give rise to a reddish green fluorescence resembling the bloom of a mineral oil. This bloom is entirely different from, and of much less intensity than, the yellowish green fluorescence produced by these products when the diethylphthalate was present.

### 3. CONTRACTION OF ETHYL ALCOHOL AND DIETHYLPHTHALATE MIXTURES.

Solutions were made up by adding 1 percent and 2½ percent by volume of diethylphthalate to 250 cc of Cologne Spirit in a 250-cc volumetric flask provided with stem graduations of 1/10 cc from 250 cc to 280 cc. The flasks, alcohol, and ester were all at the same temperatures of 25° C., and the diethylphthalate was added by means of a calibrated graduated pipette. The following table shows the total contraction in volume:

Vol. of Cologne Spirit, cc.	Cc diethyl- phthalate.	Vol. of mixture, cc.	Contraction.	
			Cc.	Percent of total vol.
250	2.50	252.4	0.1	0.04%
250	6.25	256.0	0.25	0.10%

### 4. COMPARATIVE EFFECT OF COLOGNE SPIRIT AND 39B ALCOHOL ON THE FOAMING OR LATHERING POWER OF SOAP AND SAPONIN.

This was determined by means of a special graduated cylinder used in determining the comparative lathering power of soaps. The results tabulated in the following table show that while Cologne Spirit in low concentration causes an increase in lather, 39B alcohol has a marked inhibitory effect on the lathering or foaming power of soap and saponin solutions. This observation coincides with Lowenfels'<sup>18</sup> statement regarding the effects of 39B on foaming hair tonics.

(A) Soap. 1 cc of 20 percent liquid soap used in each test.

Total volume of liquid—100 cc used in each test.

Dist. H <sub>2</sub> O, cc.	Cologne Spt., cc.	39B, cc.	Vol. lather, cc.	Percent change.
99	0	0	405	....
89	10	0	455	12 percent increase
89	0	10	120	70 percent decrease
74	25	0	190	53 percent decrease
74	0	25	0	100 percent decrease

(B) Saponin. Ten cc of a solution of 0.2 Gm. saponin (Merck's purified) in 100 cc dist. H<sub>2</sub>O used in each test.

90	0	0	170	....
80	10	0	230	35 percent increase
80	0	10	0	100 percent decrease

### SUMMARY.

Of all the esters of phthalic acid, the diethyl has proven to be the most satisfactory, so far, for use as a denaturant for perfumes and toilet preparations for the following reasons:

1. Because of its stability and freedom from color and odor. (The ethyl and methyl phthalates are readily decomposed upon heating.) It acts as a fixative, giving more uniform evaporation and lasting quality to odors.

2. Its ready miscibility and sufficient volatility, as well as high boiling point,

enable it to serve as both a volatile and non-volatile key in establishing the identity of specially denatured alcohol 39B and 39C.

3. It possesses a bitter, acrid, and numbing taste which renders the spirit unfit for beverage purposes in one percent solution.

4. It leaves no sediment and is a natural constituent of many perfumes because of its presence as a solvent and adjusting agent in many of the synthetic perfume materials.

5. It is not poisonous or toxic when applied to the skin. It possesses the slight antiseptic quality of the phthalic group and takes off the drying and slightly caustic action which pure alcohol leaves on the skin.

6. Its chemical test of identity is positive and easily carried out.

7. Diethylphthalate of exceptionally high purity and standard quality is being produced commercially in this country by several reputable manufacturers, at a reasonable price.

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#### THE STATUS OF DRUG-PLANT GROWING IN THE UNITED STATES IN 1921.

BY W. W. STOCKBERGER.

In 1921 the commercial cultivation of drug plants occupied a much less favorable position than that reported for 1918. Following the renewal of imported supplies this industry promptly reacted to the general principle that the production of any article declines as the price drops. The medicinals which were successfully grown during the World War were

still produced in 1921 but in relatively unimportant quantities.

The drug gardens maintained by schools of pharmacy in various parts of this country which number 25 have continued to be centers of much popular interest, and, aside from their primary educational function, have rendered a distinct public service through the dissemination of practical information on drug-plant culture gained through experience.