

and heated from time to time to decolorize the permanganate. When 400 cc. had been used and the suspension in the flask was at the boiling point, the further addition was continued until the brown color no longer could be discharged by boiling. This required an additional 200 cc. together with 1 cc. of concentrated sulfuric acid. When the suspension was cool, the brown solid was collected on a Büchner funnel, well washed with water and dried; yield 8.4 g. The filtrate and washings were combined and concentrated to 50 cc. On cooling, crystals of crude isoamyldialuric acid were obtained; yield 4.4 g. The acid was purified by boiling an aqueous solution with norite, filtration and crystallization: yield 3.4 g., m. p. 179.5°. The melting point of a mixture of the isoamyldialuric acid obtained by this procedure with that obtained by the peroxide oxidation showed no depression.

Anal. Calcd. for $C_9H_{14}O_4N_2 \cdot 2H_2O$: H_2O , 14.40. Found: H_2O , 14.12. Calcd. for $C_9H_{14}O_4N_2$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.56; H, 6.36; N, 12.86.

Hydrolysis of 5-Isoamyldialuric Acid.—One-half gram of the acid was added to a solution of 2 g. of sodium hydroxide in 4 cc. of water. Foaming and vigorous evolution of ammonia resulted, and the flask was placed in a steam oven overnight. The residue was dissolved in water, the solution made acid to congo red paper with hydrochloric acid and extracted with ether. The ether extract was concentrated to a small volume, a few cc. of benzene added, and the solution boiled to remove the ether. On cooling, 0.22 g. of isoamyltartronic acid was obtained, which melted with evolution of gas at 134.5°. The melting point of a mixture of this acid and isoamyltartronic acid prepared by the hydrolysis of bromo-isoamylmalonic diethyl ester, method of Braun and Nelles,⁹ showed no depression.

5-Benzoyl-5-isoamyldialuric Acid.—One-half gram of 5-isoamyldialuric acid was added to 5 cc. of benzoyl chloride and the mixture was heated slowly to 200–210° in an oil-bath. Solution was almost immediate, followed

(9) Braun and Nelles, *Ber.*, **66B**, 1466 (1933).

by gradual evolution of hydrogen chloride. On cooling, crystals were obtained by scratching the walls of the flask with a stirring-rod. The reaction mixture was transferred to a centrifuge tube with ligroin and the crystals were washed several times with this solvent. The slightly brown crystals were dissolved in alcohol, boiled with norite, filtered, and the filtrate diluted with water. After standing for several days the crystals which formed were collected; yield 0.5 g. and m. p. 210.5–216°.

Anal. Calcd. for $C_{16}H_{18}O_6N_2$: N, 8.80. Found: N, 8.88.

5,5'-Diisoamylhydrilic Acid.—This acid which was present in the insoluble residue from the preparation of 5-isoamyldialuric acid by the permanganate method was dissolved in acetone and filtered from the manganese oxide. The acetone was diluted with water and the crystals which formed on standing were collected and air-dried; yield 5.3 g. The acid darkened and melted with decomposition at 290°.

Anal. Calcd. for $C_{18}H_{26}O_6N_4 \cdot 2H_2O$: H_2O , 8.37. Found: H_2O , 8.34. Calcd. for $C_{18}H_{26}O_6N_4$: C, 54.81; H, 6.65; N, 14.21. Found: C, 54.82; H, 6.52; N, 14.06.

We wish to thank Dr. Carl Pfeiffer for the pharmacological testing of our compounds, and Dr. H. A. Shonle, of Eli Lilly and Company, for the gift of certain chemicals which were used in the course of this work.

Summary

A new bibarbituric acid derivative, 5,5'-diisoamylhydrilic acid, and a new 5-hydroxybarbituric acid, isoamyldialuric acid, have been prepared. Solutions of the sodium salts of these compounds and of the corresponding ethyl compounds have no appreciable effect when injected into rats.

CHICAGO, ILLINOIS

RECEIVED JUNE 9, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Vapor Pressures and Accommodation Coefficients of Four Non-Volatile Compounds. The Vapor Pressure of Tri-*m*-cresyl Phosphate over Polyvinyl Chloride Plastics

BY FRANK H. VERHOEK AND A. L. MARSHALL

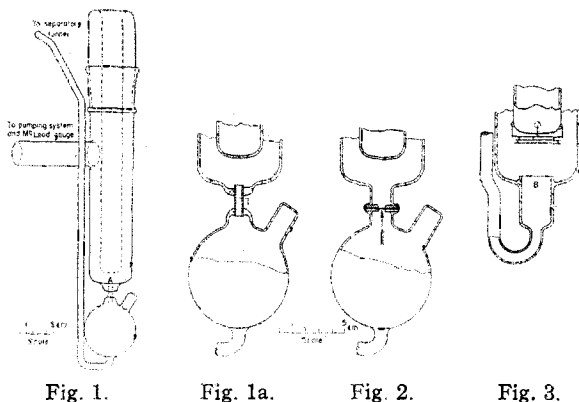
The vapor pressures and accommodation coefficients of the non-volatile organic compounds useful as plasticizers are data of fundamental importance in interpreting the losses of plasticizers which occur from plastics under certain conditions. Such data are given below for pure samples of di-*n*-butyl phthalate, tri-*m*-cresyl phosphate, tri-*p*-cresyl phosphate, and dibenzyl sebacate. The experimental methods employed were: measurements of the rate of effusion of

saturated vapor through various tubes and through a small hole in a thin plate; measurements of the rate of evaporation from a free surface; measurements of the vapor pressure by a static method similar to that of Hickman, Hecker and Embree.¹ The vapor pressures of tri-*m*-cresyl phosphate over polyvinyl chloride plastics in which it served as plasticizer were determined by the static method.

(1) Hickman, Hecker and Embree, *Ind. Eng. Chem., Anal. Ed.*, **9**, 264 (1937).

Experimental Details

Method I. (Figs. 1 and 1a).—The saturated vapor effused through the Fernico tube T (length 2.00 cm., diameter 0.498 cm.). The apparatus was immersed up to the vacuum side-arm in a constant-temperature bath.



After the bath had been heated to a temperature in the region where measurements were to be made, the apparatus was evacuated, liquid air was placed in the condensing tube and the liquid (whose flow was controlled by the stopcock of a separatory funnel) was run slowly into the 300-cc. reservoir bulb. When the bulb was one-third full, giving an evaporating surface about 30 sq. cm. in area, the separatory funnel was sealed off below the stopcock. After further evacuation to remove any residual air that may have remained in the liquid, the vacuum was broken behind the liquid air trap and the liquid air sucked out of the condensing tube. When the latter had come to room temperature it was removed, washed with ether and replaced. The apparatus was then quickly exhausted; when the pressure had fallen below 10 microns, the condensing tube was refilled with liquid air, the time of this filling being taken as zero time for the experiment. When effusion had proceeded long enough for a suitable quantity of vapor—usually about 30 mg.—to condense on the liquid air tube, the experiment was stopped by breaking the vacuum. The condensate was then washed into a weighed platinum dish with 15–20 cc. of ether, which subsequently was evaporated so that the weight of condensate could be determined. Three or more experiments were made at each temperature and the average taken in calculating the vapor pressure; individual experiments agreed with each other to within 2 or 3%. The temperatures of the individual experiments conformed to no sequence; the last experiment on each substance was always carried out at the temperature of the first; these measures were taken to detect any change in the nature of the material under investigation. No evidence of any such change was observed with the four compounds in question. In certain cases, the reproducibility of the method was tested by making duplicate runs on separate charges of material; these results, which are in satisfactory agreement, are given under Method I, in Columns A and B of the tables below. The refractive index of the distillate was the same as that of the liquid being studied and in the case of trimethyl phosphite the distillate gave the correct percentage of phosphorus by analysis.

Method I'.—In the hope of measuring the rate of evaporation from a free surface, the Fernico tube and reservoir bulb in the above apparatus were replaced by a glass tube, 2.24 cm. in diameter, joined at A in Fig. 1. The smaller tube was filled to within a few centimeters of its top, and measurements were carried out as in Method I. Metal disks attached to the condensing tube (*cf.* Fig. 3) were used to minimize radiation losses from the surface of the liquid. (An attempt to reduce these losses by replacing the liquid air with 15° water had to be abandoned because of incomplete condensation.) Identical experimental results were obtained with the following systems of baffles, connected so as to make heat flow as difficult as possible: 7 nickel disks, 0.013 cm. thick; 3 such disks; and 3 disks with a nickel oxide or a silver surface facing the liquid.

The rates of evaporation measured in this apparatus increased as the level of the material approached A (Fig. 1), indicating that the 2.24-cm. tube was narrow enough to reduce the rate of evaporation to a value below that for a free surface.

A new apparatus (Fig. 3) was then constructed in which the position of the liquid meniscus could be accurately measured with a cathetometer in order to establish the length of narrow tube through which the vapor was effusing. The tube B (diameter 2.133 cm.) extends about 1 cm. into the larger tube, has its top carefully ground level, was sealed in without being distorted, and bears a reference mark to facilitate the cathetometer measurements. The baffle system consists of 3 nickel disks, 0.013 cm. thick.

Method II. (Fig. 3).—The rate of evaporation from a free surface was measured directly by raising the level of the liquid to the top of B.

Method III. (Fig. 2).—The rate of effusion of saturated vapor through a circular hole (diameter 0.1078 cm.) in a nickel disk 0.013 cm. thick held in a Fernico seal was measured. The diameter of the hole was measured after the seal had been made by projecting the image of the hole and a millimeter scale on a large screen.

Method IV. (Fig. 4).—A static method can yield reliable vapor pressure results for substances (*e. g.*, plastics) for which dynamic methods may involve undesired changes in composition during the measurements. The apparatus of Hickman, Hecker and Embree¹ was modified by the addition of the condensing tube C (filled with liquid air) intended to eliminate possible back pressure on the disk D, and by the addition of a platinum resistance heater at 0. One or two watts output by the heater for a few minutes drove any material condensed near 0 back into the boiler; the presence of the condensate did not affect the experimental results, but it did introduce the hazard of having D held to the glass by the surface tension of the liquid. The vapor pressure is measured by turning the entire apparatus through an angle θ that will just suffice to close the orifice. To measure θ , the turning motion was carried through a worm gear to a disk 15.0 cm. in diameter divided on its circumference into 216 divisions, each of which corresponded to a deflection of one minute of arc. Consecutive readings at a given temperature could easily be reproduced to within one minute of arc. The pendulum consists of a duralumin disk D, 0.013 cm. thick, suspended by means of duralumin wire, 0.05 cm. in diame-

ter, from a shaft riding in jeweled bearings. The circular corrugation (dd' , Fig. 4) in the disk serves to stiffen and hold it perfectly flat. The effective weight of the assembled pendulum, carefully determined on an analytical balance, was 0.787 g. The vapor pressure is obviously given by

$$P \text{ (microns)} = \frac{0.787 \sin \theta}{0.00136(1.567)^2\pi} \quad (1)$$

where the factor 0.00136 converts the pressure from grams per square centimeter into microns, and 1.567 cm. is the radius of the orifice at 0. The results of duplicate measurements on the same materials are given under Method IV, Columns A, B and C in the tables.

Materials.—A colorless sample of tri-*m*-cresyl phosphate was obtained from the Celluloid Corporation, and a slightly yellowish one from the Eastman Kodak Company. Neither sample was treated further.

The tri-*p*-cresyl phosphate was a Celluloid Corporation product melting at 76.4–76.7° (stem correction included). Five recrystallizations from a five-to-one mixture of absolute ethanol and water did not change this melting point, and made only a slight difference in the shape of the cooling curve.

The dibutyl phthalate was purified by vacuum distillation through a 1.25-meter column. The middle fraction, which was used, was colorless, neutral, with the theoretical saponification value, and n_D^{20} equal to 1.4933. Further distillation did not change the refractive index.

The dibenzyl sebacate was prepared and carefully purified in this Laboratory by Burnett and Russell.^{1a}

The plastics were prepared by weighing out the required quantities of polyvinyl chloride and the Celluloid Corporation tri-*m*-cresyl phosphate, mixing by milling at 100°, and pressing into a thin sheet at 500 lb./sq. in. (33 atm.) for five minutes at 140°. Loss in the milling and pressing operations amounted to 0.2–0.4%. The pressed sheets were cut into strips weighing from 7 to 10 g., on which the measurements were made.

Calculations for the Dynamic Methods.—The number of molecules per second, Z , colliding with (hence entering) a uniform circular tube of radius a is

$$Z = a^2 p N \sqrt{\pi/2RTM} \quad (2)$$

where p is the pressure; N , R and T have their usual meanings; M is the molecular weight; and c. g. s. units are employed. The experimental results give the rates of effusion, Q , in grams/sec., through tubes of varying length, when the pressure is equal to the vapor pressure of the liquid at one end and virtually zero at the other. To obtain the rate at which matter will leave such a tube, Z must be multiplied by the weight of a molecule and by the probability, W , that a molecule entering the tube will leave it; or

$$Q = WZM/N = Wa^2P \sqrt{M\pi/2RT} \quad (3)$$

For a hole in an infinitely thin sheet, W is equal

(1a) Burnett and Russell, *THIS JOURNAL*, **61**, 2246 (1939).

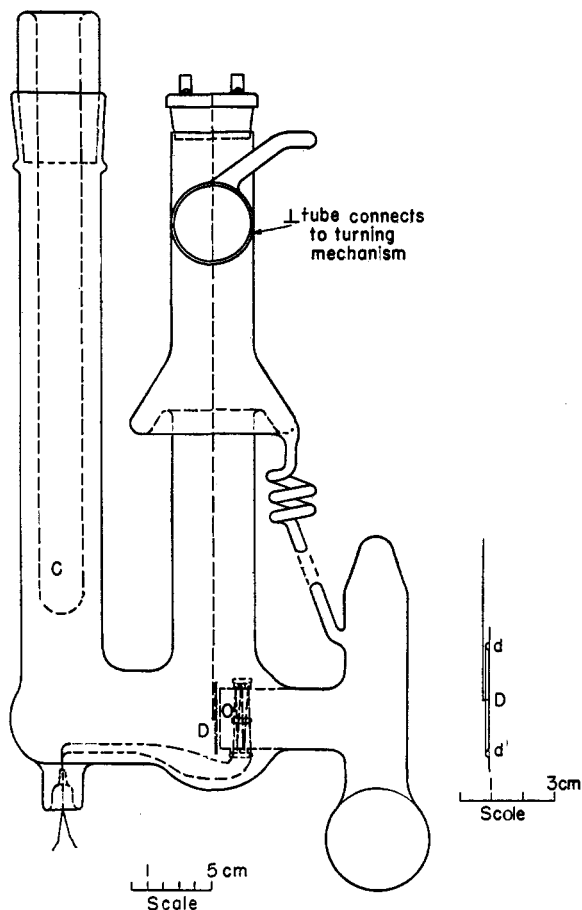


Fig. 4.

to unity; for a cylindrical tube with perfectly diffusing walls of length l such that $l \gg a$, at pressures such that the mean free path is much larger than the diameter of the tube, W equals $8a/3l$. For cylindrical tubes of intermediate length, Clausing² gives a table of values of W for various values of l/a , which represent close approximations that he made because he was unsuccessful in deriving an accurate expression for W in terms of known functions. The values of W used in calculating our values were obtained when necessary by interpolating in this table; for example, when $l/a = 8.025$ (Method I), $W = 0.2310$ so that

$$p = \frac{Q}{0.2310 a^2} \sqrt{\frac{2RT}{\pi M}} \quad (4)$$

In the actual calculations, $R = 83.15(10^6)$ ergs/degree was used, and the right-hand side of Eq. 4 was multiplied by 0.75 to give the pressures in microns.

For Method I', W was obtained as for Method I. For Method II, W is obviously unity, and the

(2) Clausing, *Ann. Physik*, **12**, 961 (1932).

TABLE I
THE VAPOR PRESSURE OF TRI-*m*-CRESYL PHOSPHATE
a. Celluloid Corporation Samples

l/a $T, ^\circ\text{C.}$	Method I		Vapor pressure in microns Method I'		Method II	Method IV		
	8.035 A ⊙	8.035 B ⊗	2.850 □	1.669 ⊠	⊗	A △	B ▽	C ▽
80.0			0.0459	0.0453	0.0387			
90.0	0.133							
100.2	.346							
109.9		0.925						
110.5	.957							
114.0						1.59	1.56	1.60
119.0						2.42		
120.0		2.36						
120.7	2.37							
124.0						3.69	3.78	
125.9	3.82							
128.8						5.54		
129.0							5.89	5.83
130.0		5.83						
131.0	6.07							
136.2	10.14							

b. Eastman Kodak Company Sample

Temp., $^\circ\text{C.}$	85.2	95.4	105.6	115.8	126.0
p , microns	0.0993	0.250	0.562	1.33	3.36

Method I was used. $l/a = 8.035$.

pressures were calculated on the assumption that the area of the liquid surface was equal to the cross-sectional area of B (Fig. 3). For Method III, W is unity and a is the area of the hole in the nickel disk.

In all these calculations, an accommodation coefficient of unity is assumed.

Results and Discussion

The Pure Substances.—The detailed results for the pure substances are given in Tables I–IV and in Fig. 5, in which the values of Hickman, Hecker and Embree¹ for dibutyl phthalate have also been plotted. The constants derived from

these detailed results are given in Table V. With a single exception, there is no systematic departure from the straight lines in Fig. 5 for any one method of measurement on any one sample. The exception, tri-*p*-cresyl phosphate, shows results by method IV that are definitely larger than those by method I; a slight decomposition of the material to give volatile products is one reasonable explanation of this discrepancy. Our failure to check the measurements of Hickman, Hecker and Embree exactly is not surprising in view of the differences which we found in the vapor pressures of the tri-*m*-cresyl phosphates from two different sources.

TABLE II
THE VAPOR PRESSURE OF TRI-*p*-CRESYL PHOSPHATE

l/a $T, ^\circ\text{C.}$	Vapor pressure in microns		
	Method I 8.035 ⊙	Method IV A △	B ▽
92.0	0.0848		
100.0	.200		
110.0	.490		
119.0		1.35	1.42
123.5			2.11
124.0		2.12	
125.0	1.87		
129.0		3.31	3.36
134.0		5.01	
134.5			5.22
135.0	4.50		
145.0	11.7		

TABLE III
VAPOR PRESSURE OF DIBUTYL PHTHALATE

l/a $T, ^\circ\text{C.}$	Vapor pressure in microns				
	Method I 8.035 A ⊙	Method I' 8.035 B ⊗	Method I' 2.765 □	Method III ●	Method IV △
40.0			0.167		
55.0	1.03	0.816			
59.7					1.78
64.7					2.95
65.0	3.07				
69.7					4.59
70.0	4.51				
74.6					7.36
75.0	8.07			6.78	
85.0	21.6	18.9		18.9	
95.0				45.3	

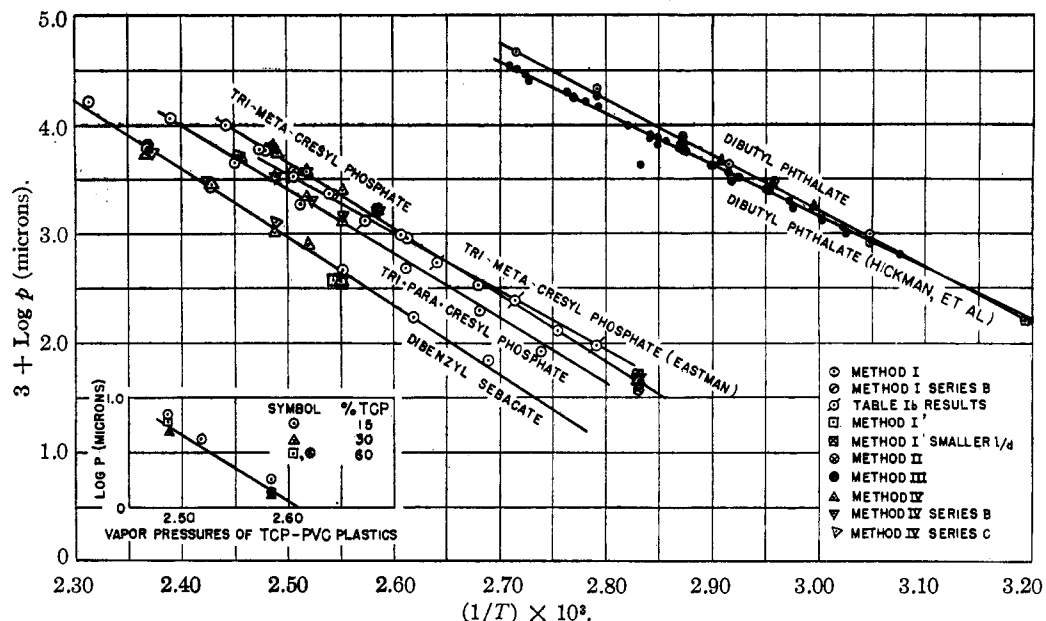


Fig. 5.—Vapor pressures of plasticizers.

TABLE IV
VAPOR PRESSURE OF DIBENZYL SEBACATE

1/a T, °C.	Vapor pressure in microns			Method IV	
	Method I 8.035 A	8.035 B	Method I' 2.658 □	A △	B ▷
99.0	0.0679				
100.0			0.0552		
109.0	.169				
118.9				0.365	
119.0	.451	0.398			
120.0			.366		
124.0					0.792
129.0	1.05			1.03	1.21
139.0	2.56			2.67	2.75
148.7					5.71
149.1	6.48	5.90		5.69	
159.1	16.6				

TABLE V
DERIVED CONSTANTS FOR THE PURE SUBSTANCES

	Observer or source of material			
	A	B	L	
Tri- <i>m</i> -cresyl phosphate	6088	15,886	27,850	Celluloid Corp.
	5373	13,982	24,580	Eastman
Tri- <i>p</i> -cresyl phosphate	5926	15,223	27,110	
Dibutyl phthalate	5122	15,589	23,440	Verhoek and Marshall
	4680	14,215	21,400	Hickman, Hecker and Embree
Dibenzyl sebacate	6320	15,775	28,910	

$\log p$ (microns) = $-(A/T) + B$ $L = 4.575 A$.

That the accommodation coefficients for all four substances are unity is shown by the agreement of the Method I' results with the others. If a vapor pressure is calculated from a rate of evaporation into a vacuum (Method I') on the assumption

that the accommodation coefficient is unity, this calculated pressure will be less than the true pressure (as measured, for example, by Method III or IV) if a fractional accommodation coefficient exists.³ Our results indicate that the accommodation coefficients will always be unity for substances of the type studied here.

Although it is true that the vapor pressure calculated from the rate of evaporation from a free surface (Method II) is somewhat lower than the others, this small discrepancy probably does not indicate the existence of a fractional accommodation coefficient. A difference of 1.1° between the temperature of the bath and the temperature of the liquid at the surface of Tube B, Fig. 3, is sufficient to account for the lower vapor pressure obtained by Method II. Since the apparatus is so constructed that the heat lost from the surface by evaporation is not readily replaced, such a temperature difference may well have existed.

The Plastics.—The static vapor pressures obtained by Method IV on three different polyvinyl chloride-tri-*m*-cresyl phosphate plastics are summarized in Table VI and plotted in Fig. 5. The values of θ could not be determined as accurately here as for the pure substances because the disk closing the orifice continued to vibrate. This vibration, which could not be eliminated by prolonged evacuation at the temperatures of the

(3) Cf. Langmuir, *Phys. Rev.*, **11**, 329 (1913), or Knudsen, *Ann. Physik*, **47**, 697 (1915).

measurements, might have been caused either by a continued liberation of air occluded in the sample or by the steady production of a volatile decomposition product in small amount (that a slight decomposition did occur was indicated by a gradual darkening of the sample). This explanation gains in plausibility from the fact that the measured vapor pressures for two of the plastics exceed somewhat the vapor pressure of the pure plasticizer.

TABLE VI

VAPOR PRESSURES OF POLYVINYL CHLORIDE-TRI-*m*-CRESYL PHOSPHATE PLASTICS

% polyvinyl chloride..... ^a	40	40	70	85
T, °C.				
114	1.44	1.38	1.68	1.37
119	2.29			3.17
124	3.59		4.19	4.17
129	5.57		6.02	4.97
				7.02

^a Calculated values (cf. Table V).

It seems reasonable to conclude that the vapor pressure of the plasticizer in these plastics is independent of concentration over the range 15-100% plasticizer. More results will be needed with other plasticizers to confirm this conclusion. It is possible that the quantity being measured in these experiments is the vapor pressure of a film

of plasticizer on the surface of the plastics. Since the slope of the vapor pressure curve and also its absolute position is the same for the plastics and the pure plasticizer, it may be concluded from this type of experimentation that the heat involved on mixing polyvinyl chloride and tricresyl phosphate is practically zero. To confirm this conclusion it would be desirable to carry out calorimetric experiments on the heat of wetting at elevated temperatures of polyvinyl chloride by several plasticizers.

Summary

The vapor pressures of tri-*m*-cresyl phosphate, tri-*p*-cresyl phosphate, dibutyl phthalate and dibenzyl sebacate in the neighborhood of 100° have been measured by a static and by dynamic methods.

The accommodation coefficients for these liquids are unity.

The vapor pressure of the plasticizer in a polyvinyl chloride-tri-*m*-cresyl phosphate plastic containing at least 15% of the latter appears to be equal to the vapor pressure of the pure plasticizer and is independent of the composition of the plastic.

SCHENECTADY, N. Y.

RECEIVED JUNE 21, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI, AND THE NEW MEXICO NORMAL UNIVERSITY]

Pied des Monts Uraninite

BY O. B. MUENCH

A fine specimen of uraninite was collected from the Lac Pied des Monts district in Quebec and given to Mr. H. S. Spence,¹ who sent it by way of Dr. A. C. Lane² to the writer for an age determination by the lead-uranium method and for the extraction and preservation of the lead for an isotopic determination to be made later by A. O. Nier at Harvard University. This material is of interest since considerable work has been done by Ellsworth³ on samples from this district. He gives a description of the geological occurrence of minerals in this district, accompanied by a complete chemical analysis and age determination.

(1) Mining Engineer, Mines Branch, Department of Mines, Canada.

(2) Chairman of the "Committee on the Measurement of Geologic Time."

(3) Report of the Committee on the Measurement of Geologic Time, 1934; *Am. Min.*, **19**, 421-425 (1934).

Another interesting account of the location, with references, is given in *Le Naturaliste Canadien*.⁴ Material from this location has been called cleveite⁵ by some, but Ellsworth,³ Berman,⁶ and others prefer the term uraninite for this mineral.

The surface of the mineral did not show any indication or sign of secondary uranium minerals. Before beginning the analysis, several autoradiographs were made of various pieces of the specimen on different smoothly ground surfaces. Some sections were cut through the middle and autoradiographs made of these. The prints seem to in-

(4) Carl Faessler, "La Cote Nord." *Le Naturaliste Canadien*, April, 1932, pp. 100-102.

(5) *J. Can. Min. Inst.*, **7**, 245-256 (1904). Obalski first mentioned the location and found the large crystal from which Ellsworth determined the lead ratio on a small sample.

(6) Dr. Berman of the Harvard Department of Mineralogy in a private communication to Professor A. C. Lane.