The dielectric constants and dissipation factors of all five new liquids are independent of frequency over a very wide range in contrast with pentachlorodiphenyl. The 250-cs. fluorosilicone is the most outstanding; frequency has little effect on the magnitude of the dielectric constant below 6 Mc.

Studies of the electrical properties at elevated temperatures show that those compounds containing propyl groups are not sufficiently stable to justify consideration for high temperature applications. Pentachlorodiphenyl withstands exposure to elevated temperatures with less change in electrical characteristics than any of the new liquids studied. The electrical properties of the 250-cs. fluorosilicone at elevated temperatures are in general superior to those of the other new liquids under the same conditions.

Capacitors impregnated with the bis(ψ'-amyl)2,2′-diphenate or one of the fluorosilicones would be capable of storing more electrical energy for a given size and would give better performance at low temperatures than those impregnated with the chlorodiphenyls recommended for this purpose. Further studies are needed to determine the performance characteristics of such capacitors under all operating conditions and to learn whether improvements might be obtained through the use of stabilizing additives.

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Solubility Measurements Using a Sealed Ampoule

Dynamic *vs.* Static Method

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The solubility of several organic solids in a volatile solvent using a sealed ampoule was determined using different rates of heating. Even the slowest rate of heating gave a significant overshoot of the true solubility temperature, and use of the static method of holding the temperature constant for at least three hours was recommended.

TWO METHODS, each utilizing a sealed ampoule, are in common use for determining the solubility of a solid in a volatile solvent. In the dynamic method (*3*), a sealed glass ampoule containing a weighed amount of solute and solvent is shaken in a liquid bath while the temperature is raised at a constant rate. The bath temperature at which the last portion of solid phase disappears is taken to be the solubility temperature.

In the static method (*1*), the ampoule is shaken in a constant temperature bath for at least three hours. If the last portion of solid has not dissolved, the temperature is raised 0.1° C. and held there for another three hours (smaller temperature increments such as 0.05° can be used if greater accuracy is desired). This process is repeated until the last portion of solid disappears. The temperature at which this occurs is taken to be the solubility temperature. This paper reports the results on several ampoules using both methods and shows the desirability of using the static method for accurate work.

EXPERIMENTAL

Chemicals. Baker's reagent grade benzene (3 liters) was purified by agitation with C.P. sulfuric acid until the acid no

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longer turned yellow. The temperature was kept below 10° C. while the substances were being agitated to prevent sulfonation. The benzene was washed once with sodium bicarbonate solution, and then with distilled water. It was then dried with calcium chloride and passed through a 2-kg. column of 16- to 20-mesh silica gel. This benzene was used as the solvent in all the solubility measurements. Four hundred grams of Santowax M (95% *m*-terphenyl, 5% *p*-terphenyl) was distilled under a reduced pressure of 6 mm. of Hg at 208° C. through a column of approximately nine theoretical plates packed with stainless steel helices. Three middle fractions which showed the same melting point were combined, yielding a total weight of 145 grams. These fractions were recrystallized three times from ethanol, yielding 77 grams of pure *m*-terphenyl. Eastman Kodak biphenyl was used without further purification. Santowax P, a commercial grade of *p*-terphenyl, was recrystallized several times from trichlorobenzene and distilled at atmospheric pressure with a nitrogen sweep of the distillation flask.

The purity of all materials except *p*-terphenyl was determined by running cooling curves in an apparatus with five copper-constantan thermocouples. The thermocouples were not calibrated because only small temperature differences were measured. The purities of the samples were estimated from the difference between the temperature of the formation of the first crystal and the temperature at which the sample is half-frozen (estimated visually), using the method described by Rossini (*2*). The purity of the *p*-terphenyl was determined from a cooling curve using a platinum resistance thermometer.

The chemicals contained the following amounts of impurities: benzene 0.05 mole %, *m*-terphenyl 0.05 mole %, biphenyl 0.04 mole %, and *p*-terphenyl 0.2 mole %.

All solubility measurements were made in a Thermonitor (E. H. Sargent and Co.) water bath. The temperature variation at a given place within the bath was measured by a Beckmann thermometer graduated in 0.01° and found to be ±0.01°. The temperature variation within the region of the bath occupied by the ampoule was also ±0.01°.

The solubility temperatures were measured on a mercury-in-glass thermometer graduated in 0.1° C. The thermometer was 460 mm. long. A reading lens was used. The thermometer was calculated against a similar thermometer with a National Bureau of Standards certificate. Stem corrections were made.

The ampoules were made from 13 × 100 mm. borosilicate glass test tubes which were drawn out to have narrow necks for easy sealing. The empty ampoule fitted with a cork was weighed. The solid solute was placed in the ampoule and weighed. Benzene was pipetted into the ampoule, the ampoule corked, and about 30 minutes were allowed for the benzene to drain into the bottom of the ampoule, and the ampoule was again weighed. The ampoule was surrounded by dry ice up to the level of the benzene. After the benzene was frozen, the neck of the ampoule was warmed with the fingers to drive the benzene that had condensed in the neck into the solution. The solid benzene crystals were readily visible inside the neck, and their disappearance was easily observed. Then the neck of the ampoule was rapidly sealed with a hand torch. The ampoules were 13 mm. in diameter and 50 to 75 mm. long. The size of the ampoule was chosen so that after sealing it would be about ¾ full.

Table I. Solubility Temperatures for Five Ampoules

	Solute				
	m-Terphenyl	*m*-Terphenyl	Biphenyl	*p*-Terphenyl	*p*-Terphenyl
	Mole Fraction Solute				
	0.2805	0.3841	0.6137	0.01047	0.00689
	Static Method, ° C.				
	37.85	48.81	45.40	48.81	37.05
Heating/ Rate, °/Min.	Dynamic Method,° C.				
0.02	37.90	49.01	45.45	48.97	37.19
0.03	38.15	...	45.48	...	37.26
0.04	38.19	...	45.50	...	37.46
0.05	...	...	45.60	49.16	37.60
0.10	...	50.01	45.60	49.61	37.95

The ampoule was placed in the bath on a rocker arm driven by a vacuum-operated windshield wiper motor. The ampoule was rocked about 45° from the horizontal, both up and down, about 60 times a minute. The solution covered all parts of the ampoule during a cycle.

The dissolution of the last crystal was observed visually with the aid of a lamp. The rocking was stopped for 5 to 10 seconds every minute to check for crystals during a run using the dynamic method.

First the static solubility temperature was determined as described previously. At the start of a dynamic run the bath temperature was held constant for three hours or more at a temperature 1.0° to 1.5° below the static solubility temperature. Then the fine calibrated ten-turn dial on the Thermonitor was turned up to give the desired rate of heating. With practice the desired heating rate can be exactly obtained. About 20 to 40 minutes elapsed from the time heating was begun to the time the last crystal was observed to dissolve. The reproducibility of the dissolution temperature in the dynamic experiments was about ±0.05° with a heating rate of 0.10° per minute.

At the conclusion of the run the ampoule was removed from the bath and allowed to recrystallize at room temperature. This rapid cooling produced fine crystals.

RESULTS AND DISCUSSION

The solubility temperatures for five ampoules as measured by the static method and the dynamic method with heating rates between 0.02° per minute and 0.10° per minute are given in Table I.

In every case the dynamic method overshot the true solubility temperature as determined by the static method. In the worst case, the *m*-terphenyl ampoule with mole fraction 0.3841, the dynamic method with a heating rate of 0.10° per minute overshot the true solubility temperature by 1.20°. In other words, crystals were present for 12 minutes above the true solubility temperature. The reproducibility of the dynamically determined solubility temperatures gives a false impression of the accuracy of the method. The static method should be used for the accurate determination of the solubility temperature.

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