which are less inhibited by carbon black than are diaroyl peroxide cures.

Acceleration. Polyester cures catalyzed with benzoyl and chlorine-substituted benzoyl peroxides (diaroyl peroxides), in combination with aromatic amines or resorcinol, are accelerated by carbon black. Increasing the carbon black concentration increases rate of cure in these systems. *tert*-Butyl perbenzoate (an aroyl-alkyl peroxide) cures, which are slightly inhibited by carbon black in systems without promoters, are also inhibited by carbon black in mixtures promoted by aromatic amines. Increasing the carbon loading in these cures, with or without aromatic amines as promoters, decreases cure rate. Di-*tert*-butyl peroxide (a dialkyl peroxide) is very strongly inhibited by carbon black in promoted systems, with the inhibition increasing with higher carbon loading.

These accelerating and inhibiting effects may be due to the peroxides being adsorbed in varying degrees on the carbon surface. Aromatic peroxides would be expected to be adsorbed to a greater extent than alkyl peroxides. In a diaroyl peroxide-aromatic amine–carbon black system both the peroxide and amine, therefore, are strongly adsorbed on the carbon surface. The high adsorption of peroxide and amine on the carbon surface produces decomposition at an extremely rapid rate which is far beyond the rate at which the carbon surface can inactivate the radicals formed. In addition, the adsorbed amine may decrease the termination reaction by blocking reactive sites on the carbon surface—the net effect is an accelerated cure. If lauryl mercaptan, an aliphatic promoter, is added to resin-carbon–aroyl peroxide mixtures, inhibition is severe indicating that adsorption of promoter as well as peroxide is essential for acceleration with carbon black.

With *tert*-butyl perbenzoate and particularly di-*tert*-butyl peroxide the specific adsorption of the peroxide is much lower. The aromatic amine is, nevertheless, adsorbed on the carbon surface which effectively reduces the concentration of amine in the system. Increasing the carbon black loading at constant amine concentration decreases the effective concentration of amine. The rate of free radical formation is, therefore, much lower than in the benzoyl peroxide systems. The rate of termination on the carbon surface of the free radicals formed by thermal decomposition and the amine reaction is still sufficient to inhibit cure. In such cases cure rate decreases as carbon black loading increases.

CONCLUSIONS

1. Practical curing systems are described for carbon black–polyester resin mixtures.
2. Carbon black in these systems prolongs the shelf life of catalyzed resins but accelerates the polymerization when promoter is added. This combination of properties, should interest the fabricators of these resins.
3. Qualitative mechanisms of these carbon black–peroxide interactions are presented.

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Isobaric Heat Capacities at Bubble Point

Two Trimethylbenzenes and *n*-Heptane

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LIMITED experimental data are available for the heat capacity of 1,3,5-trimethylbenzene (*10, 19, 21*), but there do not appear to be any recent heat capacity measurements relating to 1,2,4-trimethylbenzene at temperatures above 70° F. (*19*). However, as part of an early investigation, Schiff (*19*) reported heat capacities for this compound at temperatures below 70° F. The critical constants of both the trimethylbenzenes were measured by Altschul (*1*). In addition, the critical temperature of 1,3,5-trimethylbenzene was determined by Prud'homme (*16*). Mair (*11*) reported the index of refraction and density of these trimethylbenzenes, and Smith and coworkers (*24, 25*) determined the vapor pressure and the index of refraction of 1,2,4-trimethylbenzene at relatively lower temperatures.

Because of the absence or limited availability of heat capacity data above room temperature for these trimethylbenzenes, the isobaric heat capacities of these compounds were measured at temperatures from 80° to 220° F. In addition, measurements were made at temperatures from 70° to 220° F. of the heat capacity of *n*-heptane, which has been selected by the Fourth Conference on Calorimetry (*4*) as one of the reference substances

for calorimetric work. The heat capacity of *n*-heptane was studied by Parks (*13*), and critically chosen values were reported by Ginnings (*7*). Beattie and coworkers (*23*) determined the critical constants and Smith (*22*) the vapor pressure of this compound. Rossini (*17*) summarized the properties of these three hydrocarbons and his values were used in establishing a measure of the purity of these compounds.

MATERIALS

The 1,2 4-trimethylbenzene was obtained from Project 44 of the American Petroleum Institute at the Ohio State University and was reported to contain less than 0.006 mole % of impurities. The specific weight was 54.4263 pounds per cubic foot at 77° F., and the refractive index as measured with the D-lines of sodium at 77° F. was 1.5024. These values may be compared with a specific weight of 54.4250 pounds per cubic foot and an index of refraction of 1.50237 under the same conditions reported by Rossini (*17*). The 1,3,5-trimethylbenzene was reported by Project 44 to contain 0.0022 mole fraction of impurities. The
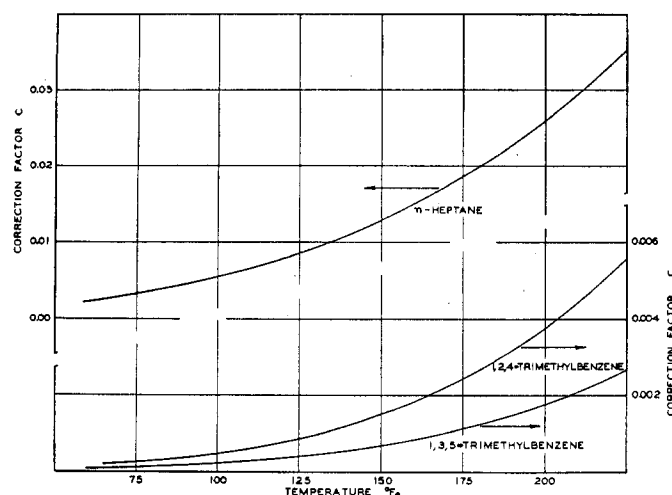
Figure 1. Volumetric corrections

Figure 2. Comparison of experimental results for n-heptane

small size of the sample available precluded confirming measurements of physical properties of this sample.

The n-heptane used in this work was supplied by the National Bureau of Standards which determined its purity by freezing-point experiments and found it to contain 0.013 mole fraction of material other than n-heptane. After deaeration this material had a specific weight of 42.4194 pounds per cubic foot at 77° F. and an index of refraction at that temperature of 1.3852 relative to the D-lines of sodium. These values compare with 42.4207 cubic feet per pound for the specific weight and an index of refraction of 1.38511 under the same conditions reported by Rossini (17) for an air saturated sample.
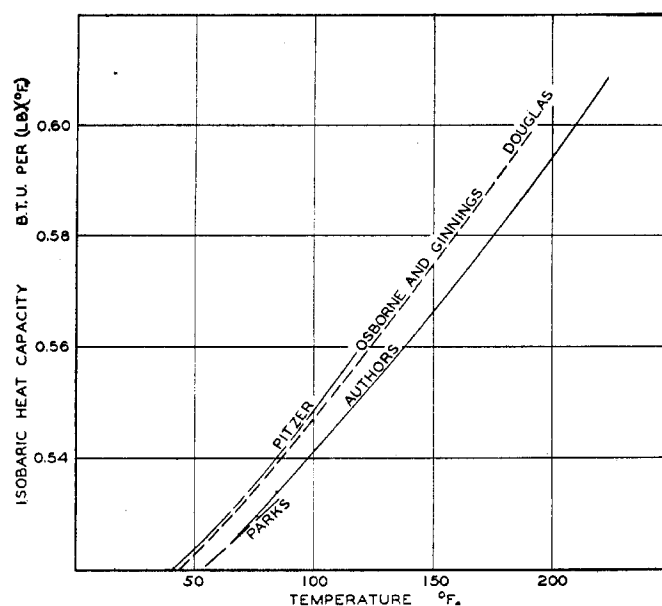
METHODS AND APPARATUS

Experimental measurements of the heat capacity were made under isochoric conditions in the two-phase gas-liquid region in a calorimeter which has been described in some detail (2, 3, 5, 18, 20). A known quantity of energy was added electrically to the calorimeter and contents, and the resulting change in temperature of the system after the attainment of equilibrium was determined. This procedure was repeated throughout the temperature interval of the investigation. No changes were made from the experimental techniques that were used in the study of other hydrocarbons (2, 5).

A series of measurements such as has been described was made with two different quantities of the sample of each of the three compounds investigated. The isobaric heat capacity was related to the quantities measured by means of the following equation:

$$C_{P,b} = \frac{\dfrac{q_1}{dT} - \dfrac{q_2}{dT}}{m_1 - m_2} \left(\frac{V_d - V_b}{V_d} \right) + T$$

$$\left(\frac{\partial V}{\partial T} \right)_{P,b} \frac{dP''}{dT} + T \frac{dP''}{dT} \left(\frac{V_d \dfrac{dV_b}{dT} - V_b \dfrac{dV_d}{dT}}{V_d} \right) \quad (1)$$

$$\frac{V_b}{V_d} \left[C_{P,d} - T \left(\frac{\partial V}{\partial T} \right)_{P,d} \frac{dP''}{dT} \right] = \frac{\dfrac{q_1}{dT} - \dfrac{q_2}{dT}}{(m_1 - m_2)(1 - c)}$$

In the second equality of Equation 1, the volumetric corrections were reduced to a single quantity, c. This correction term was established from the volumetric data available by the methods outlined by Auerbach (2) and Connolly (5). The magnitude of this correction term is shown in Figure 1. In most of the meas-

urements except those on n-heptane the volumetric correction was less than 0.3% of isochoric heat capacity. As a result of the small magnitude of the volumetric correction term it was not necessary to establish these quantities with high accuracy. The law of corresponding states was employed in most cases to establish the volumetric behavior of the gas phase whereas the available experimental data were used to determine the vapor pressure and the specific volume of the liquid phase as a function of temperature. The heat capacity of the gas phase was established from the Rossini values (17) for the heat capacity of the ideal gas. Uncertainties in the determination of the volumetric correction shown in Figure 1 for each compound introduced less than 0.1% uncertainty in the reported values of the heat capacities.

RESULTS

Measurements were made on n-heptane as a reference substance and data were obtained from two different quantities of this compound. From these measurements, quadratic equations were fitted to the experimental data (8) by least squares techniques. The results of these calculations indicated a standard deviation of about 2.1% of the average difference between the heat capacities of the calorimeter and contents in each set of measurements. This large an uncertainty resulted from the relatively small sample of n-heptane available for measurement.

A summary of the experimental data obtained for n-heptane is recorded in a part of Table I. The results are in good agreement with the measurements of Parks and coworkers (14) at lower temperatures. The values are about 1% below the data reported by Ginnings (7, 12) for n-heptane at the lower temperatures and nearly 2% below at the higher temperatures. They also are below the critically chosen values reported by Douglas and coworkers (6). The results of the measurements on n-heptane are shown in Figure 2. For comparison the data of Parks (14) and Pitzer (15) and the critically chosen values of Douglas (6) were included. These comparative measurements for n-heptane indicate that the heat capacity studies that have been made with the instrument used in this investigation may have yielded results as much as 1% below the most probable value. Throughout this series of measurements (5, 20) good agreement was obtained with the earlier studies of Parks and
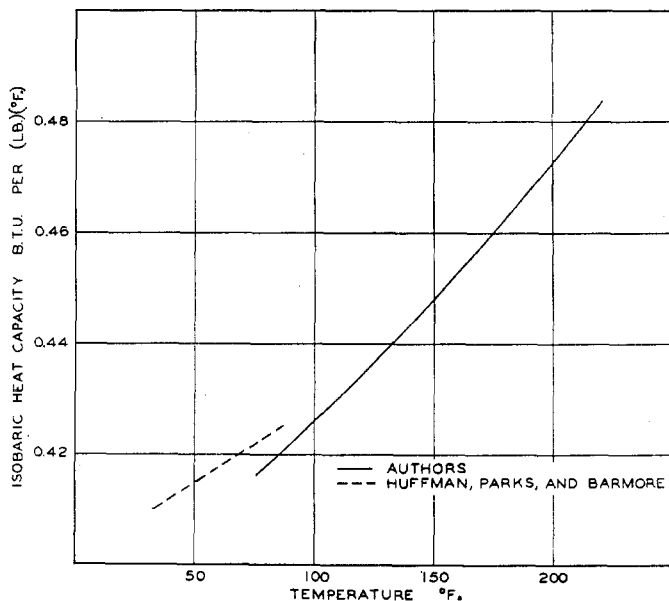
Table I. Isobaric Heat Capacities at Bubble Point for Two Trimethylbenzenes and n-Heptane

Temperature, °F.	n-Heptane		1,2,4-Trimethylbenzene		1,3,5-Trimethylbenzene	
	$\dfrac{q_1}{dT} - \dfrac{q_2}{dT}$ $\overline{m_1 - m_2}$	$C_{P,b}$ B.t.u./(lb.) (° F.)	$\dfrac{q_1}{dT} - \dfrac{q_2}{dT}$ $\overline{m_1 - m_2}$	$C_{P,b}$ B.t.u./(lb.) (° F.)	$\dfrac{q_1}{dT} - \dfrac{q_2}{dT}$ $\overline{m_1 - m_2}$	$C_{P,b}$ B.t.u./(lb.) (° F.)
70	0.5256	0.5271	0.4140	0.4141	0.3941	0.3941
80	0.5299	0.5318	0.4180	0.4181	0.4002	0.4003
90	0.5342	0.5366	0.4219	0.4221	0.4064	0.4065
100	0.5385	0.5414	0.4260	0.4262	0.4126	0.4126
110	0.5427	0.5463	0.4301	0.4304	0.4187	0.4188
120	0.5469	0.5512	0.4343	0.4347	0.4249	0.4250
130	0.5511	0.5562	0.4386	0.4391	0.4310	0.4312
140	0.5552	0.5613	0.4430	0.4436	0.4372	0.4374
150	0.5592	0.5665	0.4475	0.4482	0.4433	0.4436
160	0.5633	0.5718	0.4520	0.4529	0.4495	0.4499
170	0.5673	0.5773	0.4567	0.4577	0.4557	0.4561
180	0.5712	0.5828	0.4614	0.4626	0.4618	0.4624
190	0.5751	0.5886	0.4662	0.4677	0.4680	0.4687
200	0.5790	0.5945	0.4711	0.4728	0.4741	0.4750
210	0.5829	0.6006	0.4760	0.4781	0.4803	0.4813
220	0.5867	0.6069	0.4811	0.4836	0.4864	0.4877

coworkers (13, 14). The results for all compounds reported are based on experimental measurements and did not involve any correction associated with calibration of the calorimeter with material of known heat capacities.

Similar measurements (8) were made for the two trimethylbenzenes. In the case of 1,2,4-trimethylbenzene a standard deviation of 0.00242 B.t.u. per ° F. was found in the experimental measurements on the two samples. This deviation corresponded to 1.2% of the heat capacity of this compound. These measurements are recorded in a part of Table I. Similar information is presented in a part of this table for 1,3,5-trimethylbenzene. In this instance the standard deviation corresponded to 0.006 B.t.u. per ° F. which was equivalent to approximately 2.5% of the heat capacity of 1,3,5-trimethylbenzene. The larger uncertainty for the latter compound resulted from the smaller sample available.

A comparison of the experimental measurements for 1,2,4-trimethylbenzene with the measurements of Huffman (9) is shown in Figure 3. In this instance, the heat capacities reported here are approximately 0.9% below the values reported by Huffman (9) at the lower temperatures. Since this deviation is of the same order as the standard deviation of the present data this discrepancy is not significant. A similar comparison is shown in Figure 4 for 1,3,5-trimethylbenzene. The early values of

Schiff (19) and Kurbatov (10) have been included. Here again the present data are somewhat below the Schiff and the Kurbatov measurements.

NOMENCLATURE

c = volumetric correction factor
C_p = isobaric heat capacity, B.t.u. per (pound) (° F.)
d = differential operator
m = weight of material in calorimeter, pounds
P = pressure, pounds per square inch absolute
q = heat associated with infinitesimal change in state, B.t.u.
T = thermodynamic temperature, ° R.
V = specific volume, cubic feet per pound
∂ = partial differential operator

Subscripts

b = bubble point
d = dew point
$1, 2$ = conditions with different quantities of sample in calorimeter

Superscript

$''$ = two-phase state

Figure 3. Heat capacities of 1,2,4-trimethylbenzene
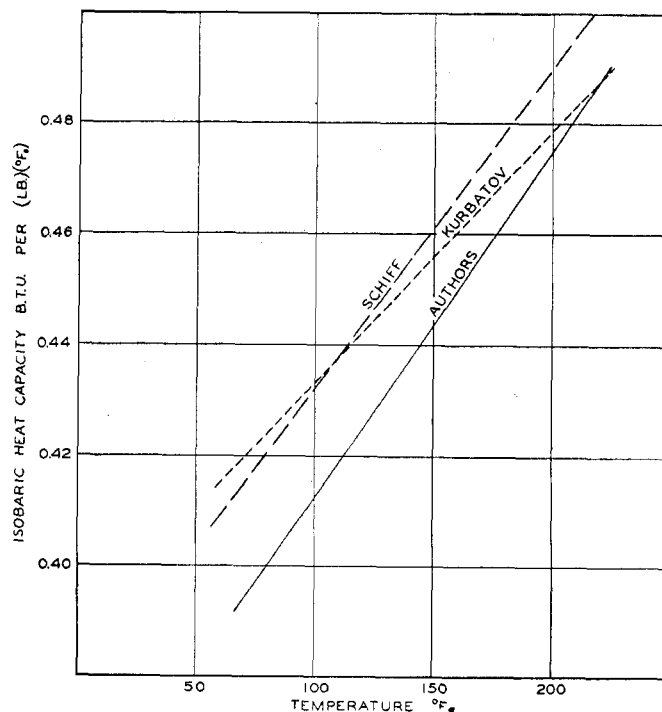
Figure 4. Heat capacities of 1,3,5-trimethylbenzene

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Effects of Radiation on Organopolysiloxanes

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THE original purpose of this study was to evaluate organopolysiloxane elastomers and resins as materials of construction around radiation sources of high intensity. It soon was clear that vulcanization of organopolysiloxane elastomers by radiation gave rubbers of superior high temperature performance. Ultimately the effects of radiation from four different sources were noted. In most respects the results were parallel to those reported recently for a number of organic polymers (*8, 10*); the greatest differences were in the precise nature of the chemical effects. However, the same equivalence of energy, regardless of source, was observed with dimethylpolysiloxanes as with organic polymers. The few phenomena already observed on radiating dimethylpolysiloxanes (*2, 9*) with two types of source were confirmed.

The radiation used in this work was secondary radiation including neutrons produced from cyclotron-accelerated deuterons, gamma rays from cobalt-60, electrons from a high voltage electrostatic source, and x-rays from conventional targets.

Samples were placed inside a water cooled copper cup in the primary cyclotron beam, where the 14.5 m.e.v. deuterons produced secondary radiation from the cup. A. J. Allen, director of the cyclotron at the University of Pittsburgh, cooperated in making these exposures.

The samples which received gamma radiation from cobalt-60 were exposed within a cylindrical source of 1470 curies, where they received 500,000 roentgens per hour as certified by the agency making the exposures. The exposures were made by S. I. Taimuty of the Stanford Research Institute using a cobalt-60 source provided by the United States Atomic Energy Commission under contract No. AT (04-3)-52.

The electron-irradiated samples were exposed to 2-m.e.v. electrons from a van der Graaf generator operating at 246-μa. current to yield 2 Mrep (million roentgen equivalent physical) per pass under the beam. Some of the radiation exposures carried out at the plant of the High Voltage Engineering Corp., Boston, Mass., were facilitated by arrangements made by the Westinghouse Electric and Manufacturing Corp. for the use of the radiation source.

Samples receiving x-ray exposure were subject to the full beam no more than 2 inches from the tube. In this case a number of different targets were used through the courtesy of L. E. Alexander and Alvin Cohen, Departments of Chemical Physics and Glass Science, Mellon Institute.

CYCLOTRON RADIATION

Experiments with the secondary radiation produced by the 14.5-m.e.v. deuteron beam within the water-cooled copper cup were less satisfying quantitatively than all the other experiments. It was impossible to make any reasonable measurement or even any estimate of the intensity of the radiation used. However, these experiments were first, chronologically, and demonstrated two points clearly.

Comparative measures of the effects of the secondary radiation, gamma, electrons, and neutrons, on a number of commercial silicone rubbers showed the phenomenon to be similar to aging at high temperatures. Moreover, the nature of the process was shown to be one of cross linking equivalent to a normal vulcanization.

Samples of Silastic 152 (Dow Corning Corp.), a simple formulation of dimethylpolysiloxane, roughly 20 volume % of a finely divided silica as the major filler (25 to 30 mμ), and an organic peroxide as vulcanizing agent, both as press vulcanized and after oven aging 24 hours at 250° C., were exposed in the water-cooled

Table I. Effect of Cyclotron Radiation on Elongation

	% Elongation	
	As cured	Aged
Before radiation	587	309
Radiated stack		
Top	225	165
Second	315	185
Third	350	200
Bottom	350	165