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EPOXY ADHESIVE SURFACE ENERGIES VIA THE PENDANT DROP METHOD

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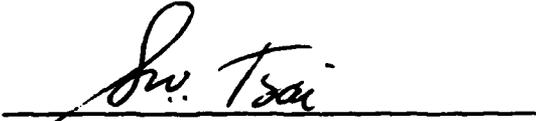
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The pendant drop method is used to determine the surface energy of epoxy resins and resin mixtures. Epon 828, a liquid bisphenol A-epichlorohydrin resin, affords a surface energy($\gamma$) of 42.89 $\pm$0.46 mNm$^{-1}$ at 75° with a temperature coefficient of -0.111 mNm$^{-1}$/°C. After heating, mixtures of Epon 828

**20. ABSTRACT (Continue on reverse side If necessary and Identify by block number)**

and its higher molecular weight homologue, Epon 1007F, yield surface energies which gradually decrease with time. Surface energies of amine-Epon 828 adhesives are reported as a function of temperature, cure time, and resin concentration.

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# INTRODUCTION

Polymer surface properties are of both practical and theoretical importance in adhesion and adhesive formulation, stabilization of colloidal systems and the use of polymers as surface active additives. Theoretically, the description of polymer surface properties is progressing along with improved methods of measuring polymer surface energies[1,2]. Therefore we set out to accurately measure the surface energy of epoxy resins and resin adhesive mixtures as part of an effort to optimize epoxy resin adhesive formulations.

Of the numerous methods used to measure polymer surface energies, the pendant drop method has several advantages. It is an absolute method, it is static, it can be used with viscous liquids and, with viscous liquids, it provides a way to monitor the attainment of hydrodynamic equilibrium in the pendant drop. Enlarged photographs of the pendant drop provide a permanent record of the drop dimensions from which surface energy, drop profile area, drop surface area and drop volume can be determined[3]. Roe[4] has refined the technique of Andreas, Hauser and Tucker[5] in the pendant drop determination of polymer surface energies. From the measurement of two drop dimensions, the maximum drop diameter ($d_e$), and the drop diameter at a distance $d_e$ above the drop apex ($d_s$), the surface energy was calculated from Equation 1 (see also Figure 1). Roe's refinement allows the calculation of 1/H from the measurement of several, independent drop dimensions. Constant 1/H values obtained from the same drop profile confirms that this profile obeys the

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EQUATION 1 $\qquad$ $\gamma = \Delta\rho g d_e^2 (1/H)$

$\gamma$ = SURFACE TENSION ( DYNES/CM )

$\Delta\rho$ = DENSITY DIFFERENCE BETWEEN TWO PHASES ( G/CM$^3$)

$g$ = ACCELERATION OF GRAVITY (CM/SEC$^2$)

$1/H$ = A CORRECTION FACTOR FROM TABLES OF $S_N$ VERSUS $1/H$

$$S_N = \frac{D_{S_N}}{D_E}$$  ( N= 8-12 )
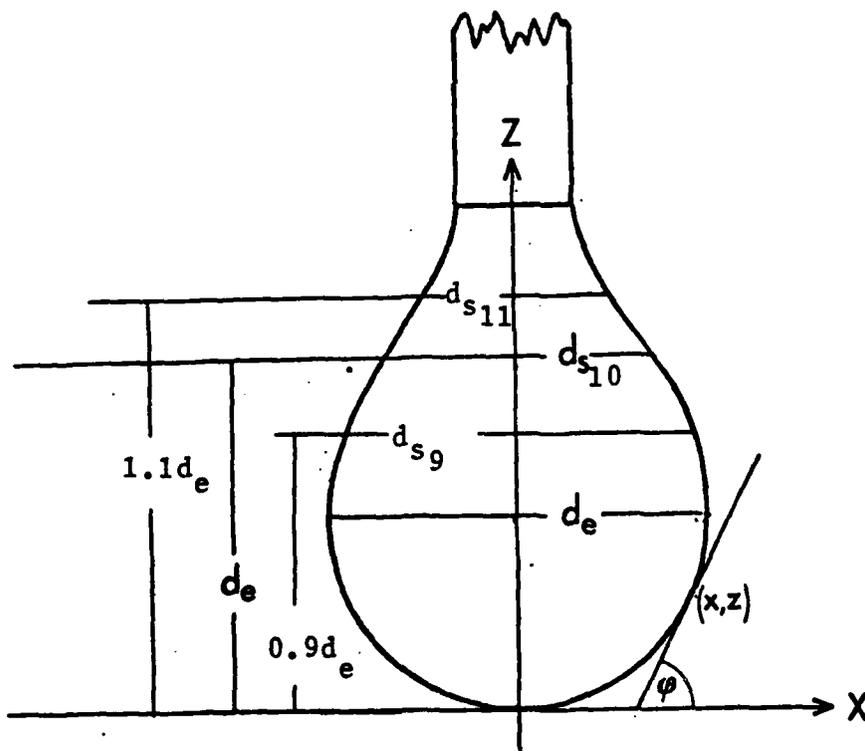


FIGURE 1. PENDANT DROP PROFILE AND DROP DIMENSIONS.

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known differential equation describing a hanging pendant drop, and is not being influenced by viscous flow effects (see Figure 1 and Appendix 1). For most polymer fluids, Roe[6] reports hydrodynamic equilibrium is reached within ten minutes and surface energies (reproducible to $\pm$ 0.3 dynes/cm) are constant over periods of 80 minutes.

Dearlove[7] has reported the surface energy, viscosity and density of epoxy resins and epoxy resin adhesive mixtures. When a bisphenol A-epichlorohydrin resin of 360 average molecular weight and 47.2 dynes/cm surface energy ($30^{\circ}$) is cured with diethylaminopropylamine of surface energy 27.0 dynes/cm, the surface tension of the mixture increases from 33.3 to 46.5 dynes/cm over a seven hour period. No correlation was found between the initial properties of the epoxy adhesives and their steel-to-steel lap shear strengths.

Patterson[8] has increased the accuracy of surface energies obtained by the pendant drop method, freeing the method from the measurement of arbitrary drop dimensions. From a photo-graph, the x, z coordinates (see Figure 1) of the drop profile at eight to fifteen points on the profile are used as input to a Fortran program which calculates the surface energy by an iterative method. Using this program and careful optical alignment techniques, Patterson reports accurate surface energies precise to $\pm$ 0.2%.

EXPERIMENTAL

Following Patterson's procedures we have assembled the apparatus shown in Figure 2 and Photographs 1-3. Vibration, a major impediment to obtaining sharp drop images, was eliminated
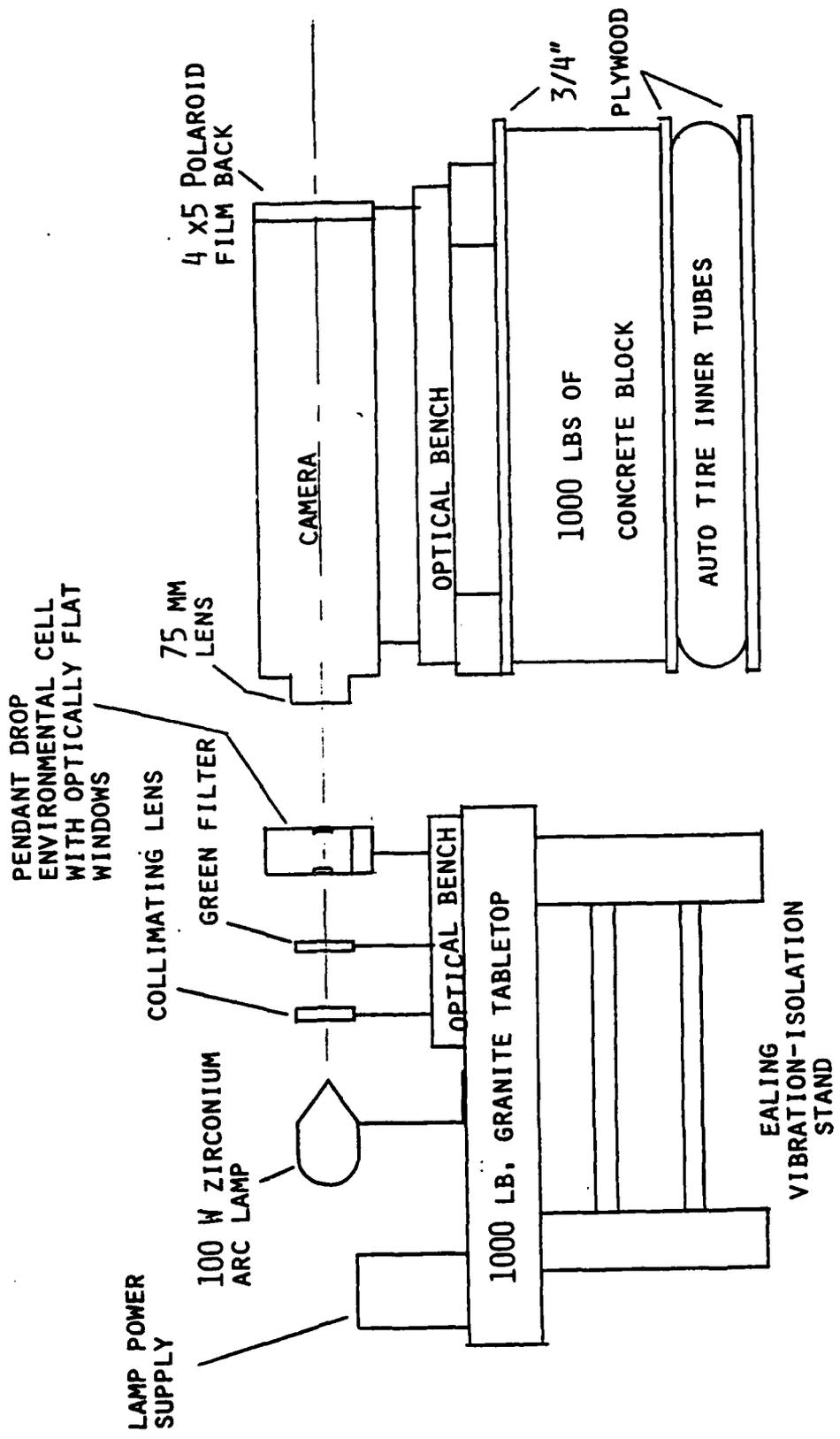
FIGURE 2. SCHEMATIC OF EXPERIMENTAL APPARATUS FOR PENDANT DROP PHOTOGRAPHY.

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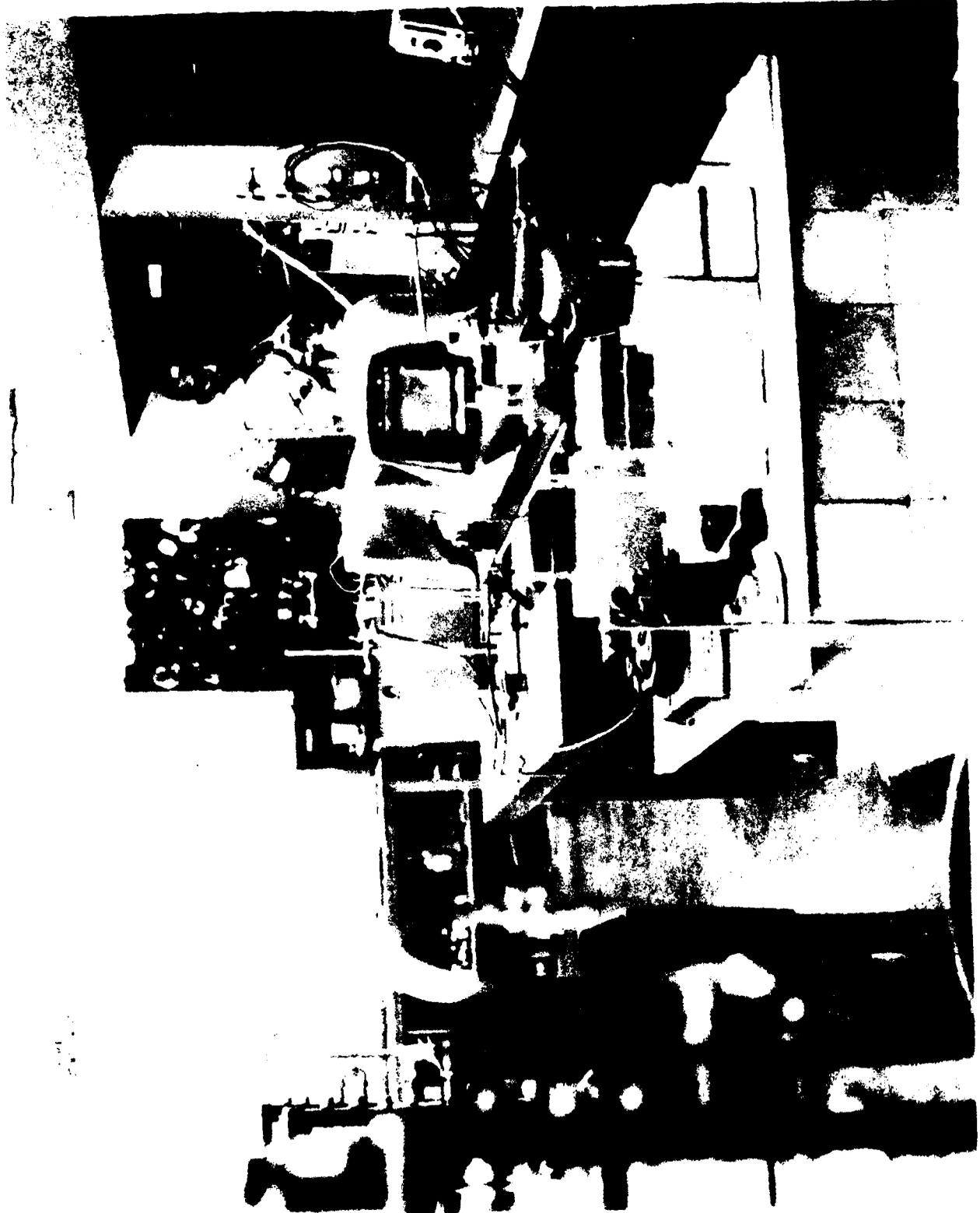
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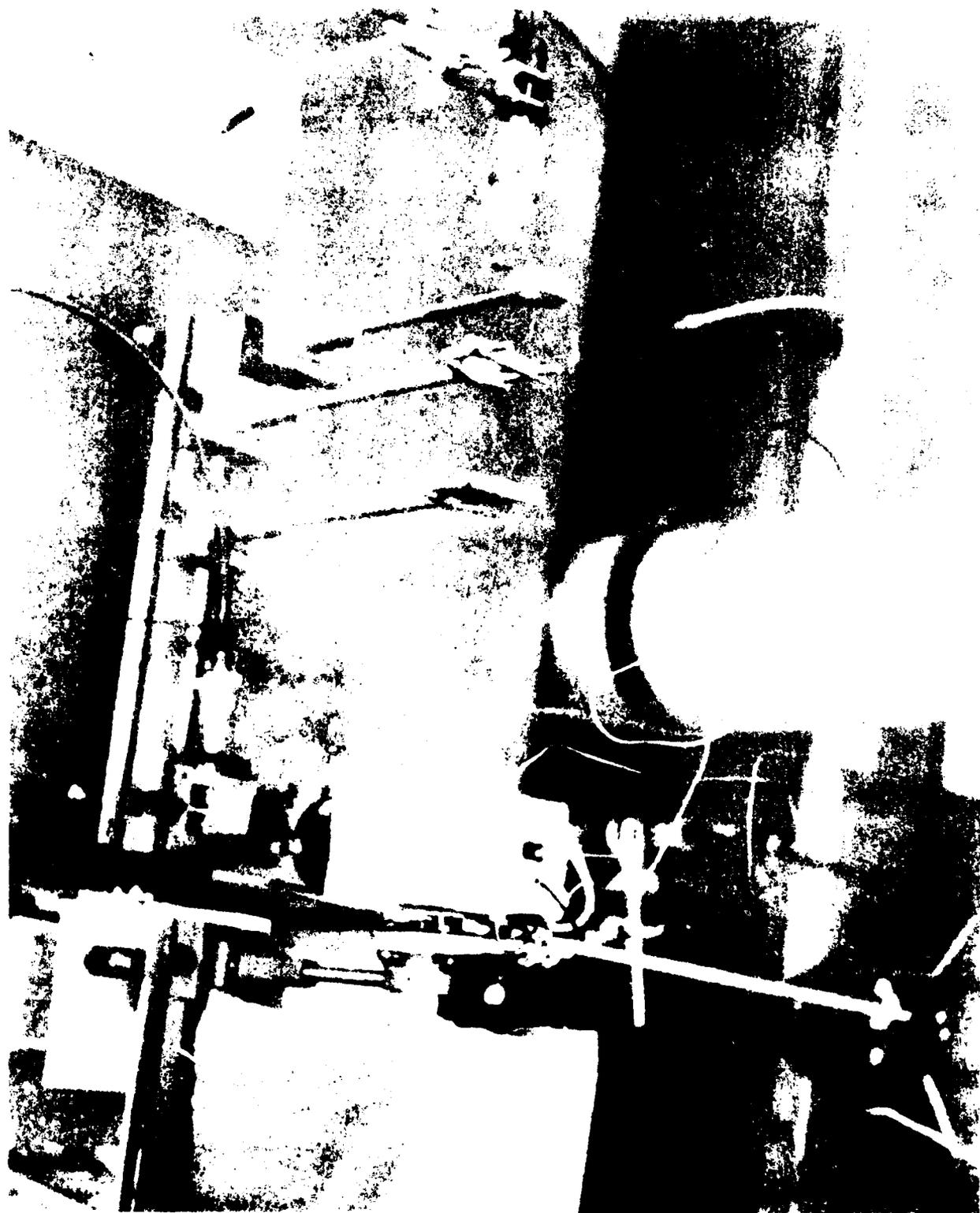
PHOTO 2. OPTICAL BENCH AND
PENDANT DROP CELL.

PHOTO 3. MANN COMPARATOR
AND APPLE II COMPUTER

by placing all equipment on two vibration-isolation systems. A Bruel-Kjaer vibration meter measured a vibrational acceleration of less than 0.1 meter/sec$^2$ from 10 Hz to 10 kHz on the vibration-isolation systems compared with a vibrational acceleration of 0.3 meter/sec$^2$ on an unisolated benchtop in the same room. Alignment procedures[8] insured that the light source, pendant drop, camera lens and camera film plane were all linear. Subsequent adjustment of the camera lens and film plane placed them precisely perpendicular to the optical path. A plumb line, placed in the rear of the camera near the film plane, provided a vertical reference line which appears on each photo negative. In addition to the pendant drop image and plumb line, each negative also displayed the image of a precision steel ball ( 0.1250 $\pm$ 0.00005 inch diameter) as a calibration standard. Focusing was done by movement of the pendant drop, which could be displaced precisely in any one of three mutually perpendicular directions. To facilitate vertical alignment, the syringe needle, from which the drop was suspended, could be precisely moved through a 5$^{\circ}$ arc perpendicular to the light path. With the 75 mm camera lens and the drop in focus, the combination of object and image distances afforded a magnification of about twelve diameters. A mechanical shutter, mounted independently of either vibration-isolation system, yielded exposures of sharp contrast with shutter speeds of 1/4 to 1/2 second. The pendant drop was formed within a closed container (see Photo 2 and Figure 9) to eliminate vibration due to air currents and to provide a controlled drop environment. The temperature of the

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container was precisely ($\pm$ 0.1$^{\circ}$C ) controlled by six 50 watt
cartridge heaters powered by a proportional controller and
utilizing a platinium resistance thermometer. The container
could be readily evacuated and/or filled with an inert gas.

The densities of epoxy resins were determined at various
temperatures using a pycnometer and a dilatometer. Densities
of low viscosity liquids were determined by a bouyancy method.

Low viscosity liquids were generally purified by fractional
distillation, then stored in a dry box. These liquids were
further characterized by boiling point, refractive index and
density determinations. Water, of $1 \times 10^{-7}$ mhos conductivity,
was obtained from a Continental Deionized Water System. We
received epoxy resin samples from Miller-Stephenson Chemical
Company and determined their surface energies under a nitrogen
atmosphere after degassing the resins at 50-75$^{\circ}$ at pressures of
1-3 torr for 20-30 minutes.

A Mann linear comparator equipped with a Bausch & Lomb
Accu-Rite digital readout was used to measure pendant drop
dimensions from photographic negatives. Data reduction was
done on a VAX 780 or Apple II computer.

RESULTS & DISCUSSION

Several tests were made of the accuracy of the photographic
pendant drop technique. The average diameter of a precision
steel ball, calculated from a photo negative displaying the
ball and a millimeter scale, was accurate to $\pm$ 0.1%, while
the magnification factor ( MAG = measured ball diameter from

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the negative divided by 0.1250 inches, the actual ball diameter)
over six negatives remained precise to 0.08% (MAG = 12.124
± 0.009). Butler and Bloom[9] recommend that a magnification
factor precise to 0.02% be maintained in order to achieve surface
energies as accurate as those afforded by measuring pendant
drop dimensions directly (no photograph). Table 1 summarizes
the results of surface tension measurements on several liquids
calculated by Andreas' two parameter method, while Appendix 2
contains physical properties of the purified liquids. Table
II contrasts surface energies of water calculated by the two-
parameter method and the iterative computer program of Patterson.
In addition to a calculated $\gamma$, Patterson's program calculates
SDEV, a parameter which measures the "goodness of fit" of the
experimentally determined coordinates of the drop profile to
the theoretically determined profile coordinates. From our
data, large differences in $\gamma$ calculated by the two methods
generally parallel large SDEV values. We believe that having
a sharp profile edge around the entire drop perimeter and finding
the coordinates of it is more critical for the determination
of $\gamma$ by the computer program than by the two-parameter method.
The surface energies which follow were all calculated by the
two-parameter method.

Surface energy measurements of Epon 828(see Figure 3)
prior to degassing are presented in Figure 4. Prior to the
calculation of surface energies, the density of Epon 828 at
several temperatures was determined. These values are tabulated
in Table III. For mixtures of Epon 828 with Epon 1007F, mixture

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TABLE I. EXPERIMENTAL SURFACE ENERGIES AT $20^{\circ}$ COMPARED WITH LITERATURE VALUES.

| FLUID | $\gamma$ THIS STUDY | | PRECISION- STANDARD DEV. AS % OF AVG. | $\gamma$ LITERATURE[8] |
|---|---|---|---|---|
| | $mNm^{-1}$ | $p \cdot ft^{-1} \times 10^{-3a}$ | | $mNm^{-1}$ |
| WATER | $72.58 \pm 0.82$ | $(4.973 \pm 0.0056)$ | 1.1 | 72.88 |
| CYCLOHEXANE | $24.52 \pm 0.37$ | $(1.680 \pm 0.0025)$ | 1.2 | 24.98 |
| BENZENE($30^{\circ}$) | $27.25 \pm 0.18$ | $(1.867 \pm 0.0012)$ | 0.6 | 27.47 |
| HEXANE | $18.22 \pm 0.15$ | $(1.248 \pm 0.0010)$ | 0.8 | 18.41 |

a - English units for $\gamma$, $1 \ mNm^{-1} = 6.852 \times 10^{-5} \ p \cdot ft^{-1}$ .

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TABLE II. CALCULATED SURFACE ENERGIES FOR WATER AT 25° C.

| EXPOSURE | $\gamma$-TWO PARAMETER | | $\gamma$-COMPUTER | SDEV ( $\times 10^{-4}$) |
|---|---|---|---|---|
| EW1-32-13 | 70.93 mNm$^{-1}$ | (4.860 $\times$ 10$^{-3}$p·ft$^{-1}$) | 69.03 mNm$^{-1}$ | 1.32 |
| EW1-32-11 | 70.00 | (4.796 $\times$ 10$^{-3}$) | 63.41 | 1.20 |
| FW2-12-82 | 73.26 | (5.019 $\times$ 10$^{-3}$) | 77.83 | 0.89 |
| EW1-32-14 | 71.31 | (4.886 $\times$ 10$^{-3}$) | 70.76 | 0.57 |
| Patterson's results[8] | 72.93 | (4.997 $\times$ 10$^{-3}$) | 72.68 | 0.14-0.65 |

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TABLE III. DENSITIES OF RESINS & RESIN MIXTURES AT VARIOUS TEMPERATURES.

DENSITY(kg/ m$^3$)

| SAMPLE | 20° | 30° | 40° | 75° | 90° | 150° | TEMPERATURE |
|---|---|---|---|---|---|---|---|
| EPON 828 | 1168 (72.90) | 1159 (72.35) | 1152 (71.91) | 1126 (70.29) | 1117 (69.72)[a] | | |
| MPDA | 1135 (70.88) | 1129 (70.45) | | 1099 (68.61) | 1087 (67.85) | | |
| EPON 1007F | 1160 (72.4) | | | | | 1080 (estimated) (67.4) | |
| 1% EPON 1007F IN EPON 828 | 1168 (72.90) | 1159 (72.35) | 1152 (71.91) | 1126 (70.29) | 1117 (69.72) | | |
| 5% EPON 1007F IN EPON 828 | 1168 (72.90) | 1159 (72.35) | 1152 (71.91) | 1126 (70.29) | 1117 (69.72) | | |
| 14.6 g MPDA &[b] 100 g EPON 828 | 1160 (72.9) | 1150 (71.8) | | 1120 (69.9) | 1110 (69.3) | | |

a- Densities in units of lb·ft$^{-3}$

b- These values calculated from equation 2.

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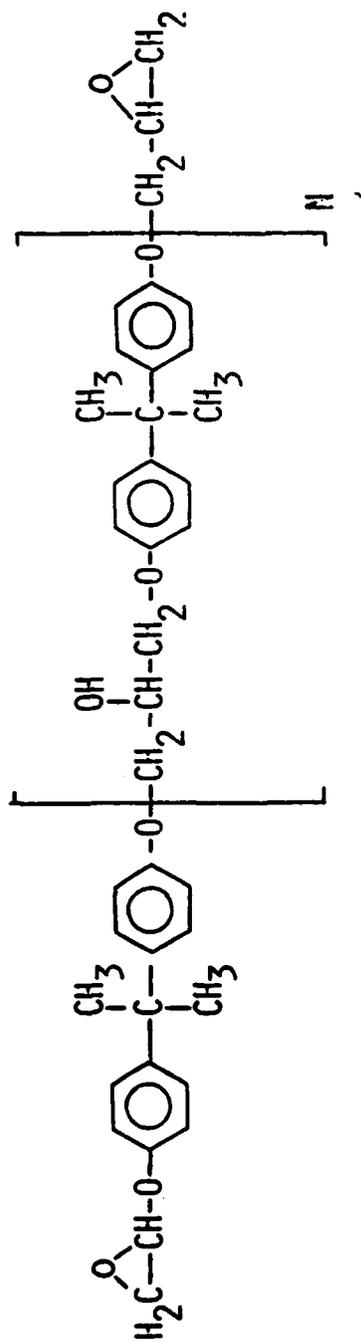
X-22,    N= 0

EPON 828 , N= 0 (75%), N= 1 (25%)

EPON 1001 , N=0 (11%), N= 1 (16%),  N= 2-8 (72%)

EPON 1007F, N= 14.0  (AVERAGE).

FIGURE 3.  STRUCTURES OF EPON BISPHENOL A-EPICHLOROHYDRIN RESINS.

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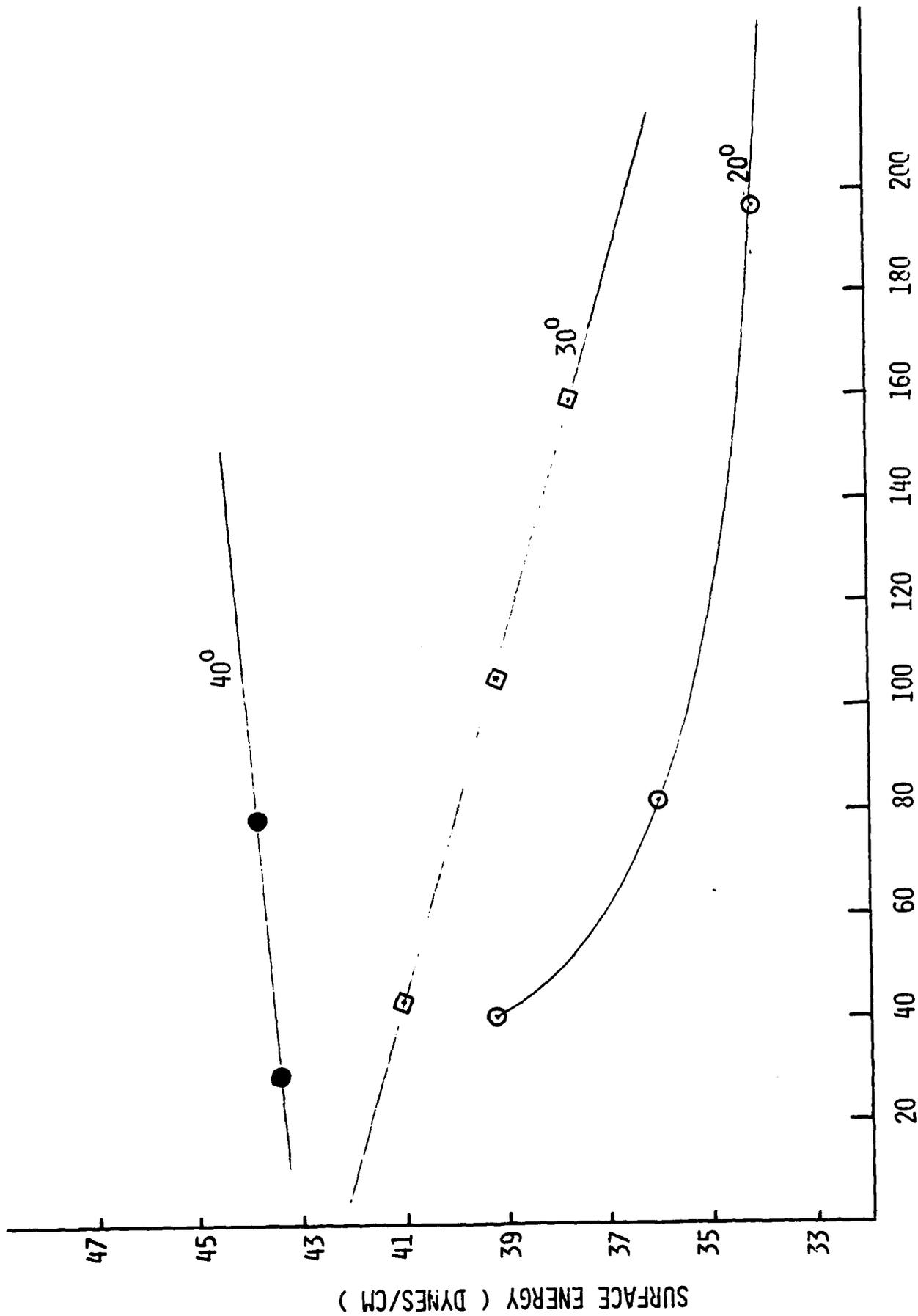
FIGURE 4. SURFACE ENERGY OF UNDEGASSED EPON 328 AT SEVERAL TEMPERATURES.

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densities were assumed to be the same as the density of Epon 828 at that temperature. Equation 2[7] was used to calculate the densities of meta-phenylenediamine/Epon 828 mixtures.

EQUATION 2 $\quad \delta_{mixture} = (\delta_{828}) V_{828} + (\delta_Z) V_Z$

where $\delta_{mixture}$ = density of mixture

$\delta_{828}$ = density of Epon 828

$V_{828}$ and $V_Z$ = volume fractions of Epon 828 and other mixture component, respectively.

From Figure 4, we attribute the gradual decrease in surface tension over time to the presence of a surface active impurity in commercial Epon 828 which slowly diffuses to the interface lowering the surface tension. At $40^{o}C$ surface energies increase, probably due to evaporation of the impurity from the resin surface. When Epon 828 was degassed before pendant drop formation surface tension values remained constant over one to two hour intervals. Attempts to trap the volatile component from commercial Epon 828 and identify it by spectroscopy are so far unsuccessful. According to Paul Jones of Shell Oil in Texas, Epon 828 contains epichlorohydrin(less than 1 ppm), water (0.04-0.05%), and acetone( at the ppm level). The latter two polar compounds have surface tensions greater than that of degassed Epon 828 suggesting that they could not be responsible for the decreasing surface energies we observed.

To follow the rate of approach to hydrodynamic equilibrium

we tested the conformity of the drop profile, at various times, to the known differential equation which describes pendant drop profiles( Roe's procedure ). Table IV contains our results. Constant 1/H values within 10 minutes of pendant drop formation confirm that hydrodynamic equilibrium has been reached.

Figure 5 displays Epon 828 surface energies from 20-140°C and yield a calculated temperature coefficient of $-0.111$ mNm$^{-1}$°C$^{-1}$. The apparent "break" in the line at 40° we believe to be an experimental artifact. The 20,30 and 40° surface energies were determined in a water-thermostatted Helma glass cell, while the remaining surface energies were determined in the electrically heated aluminium block cell. Our temperature coefficient of $-0.111$ compares favorably with a value of $-0.1$ mNm$^{-1}$°C$^{-1}$ reported by Dearlove[7] for a comparable bisphenol A-epichlorohydrin epoxy resin.

Mixing longer chain epoxy resins with Epon 828 yields amine-cured adhesives with better flexibility. Accordingly we have prepared 1% and 5% solutions of Epon 1007F in Epon 828 by heating the mixtures in dry air at 130° for 1.5 and 63 hours respectively. Surface tension values at various times and temperatures are presented in Figures 6 and 7. We believe the initial slight rise in surface tension in going from Epon 828 to the 1% Epon 1007F in Epon 828 ( from 47.47 to 48.63 at 20° and from 41.28 to 42.29 at 90°) reflects a surface composition which is the same as the bulk resin mixture, 99% Epon 828 and 1% Epon 1007F. A slightly higher surface tension for this surface composition implies that Epon 1007F has a higher surface tension than Epon 828. At 150°C this is indeed the case(see Table V ).

TABLE IV. 1/H VALUES OBTAINED FROM SEVERAL PENDANT DROP
DIAMETERS (SEE FIGURE 1).

| EXPOSURE NO. | $S_8$ | $S_9$ | $S_{10}$ | $S_{11}$ |
|---|---|---|---|---|
| FW-1-504 | 0.9007 | 0.8107 | 0.6939 | 0.5598 |
| 1/H | 0.8211 | 0.8207 | 0.8224 | 0.8216 |

(Exposure 504 taken 124 minutes after drop formation).

TABLE V. SURFACE ENERGIES OF EPOXY RESINS OF DIFFERING
AVERAGE MOLECULAR WEIGHT.

| RESIN | AVG. M.W. | $\gamma$ AT 150$^{\circ}$ | |
|---|---|---|---|
| X-22 | 340 | 29.0 mNm$^{-1}$ | (1.98 x 10$^{-3}$ p·ft$^{-1}$) |
| EPON 828 | 380 | 35.1 | (2.40 x 10$^{-3}$) |
| EPON 1007F | 4316 | 38.2 | (2.62 x 10$^{-3}$) |

(See Figure 3 for resin structures).

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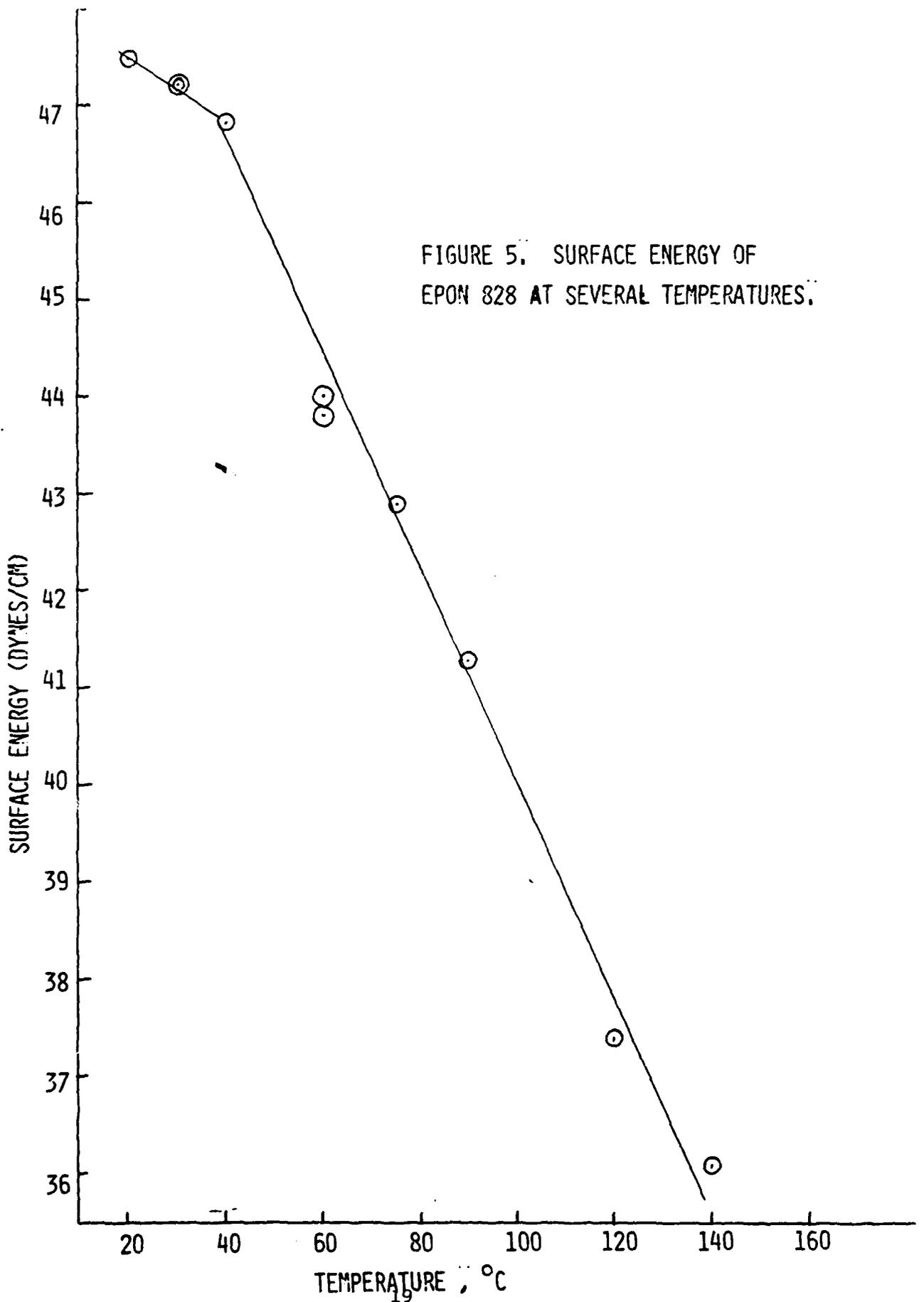
FIGURE 5. SURFACE ENERGY OF EPON 828 AT SEVERAL TEMPERATURES.

SURFACE ENERGY (DYNES/CM)
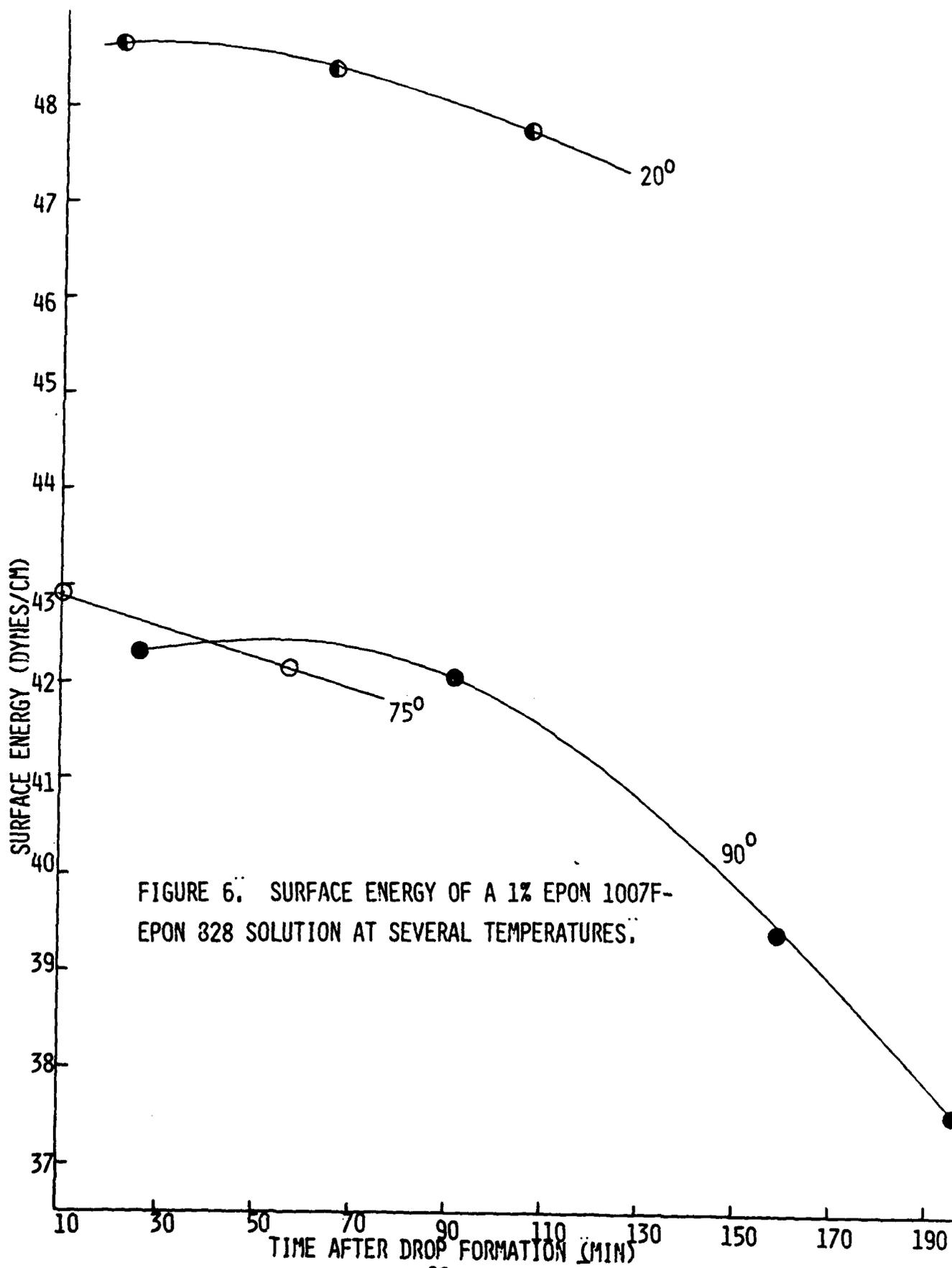
TEMPERATURE, °C

FIGURE 6. SURFACE ENERGY OF A 1% EPON 1007F-
EPON 828 SOLUTION AT SEVERAL TEMPERATURES.

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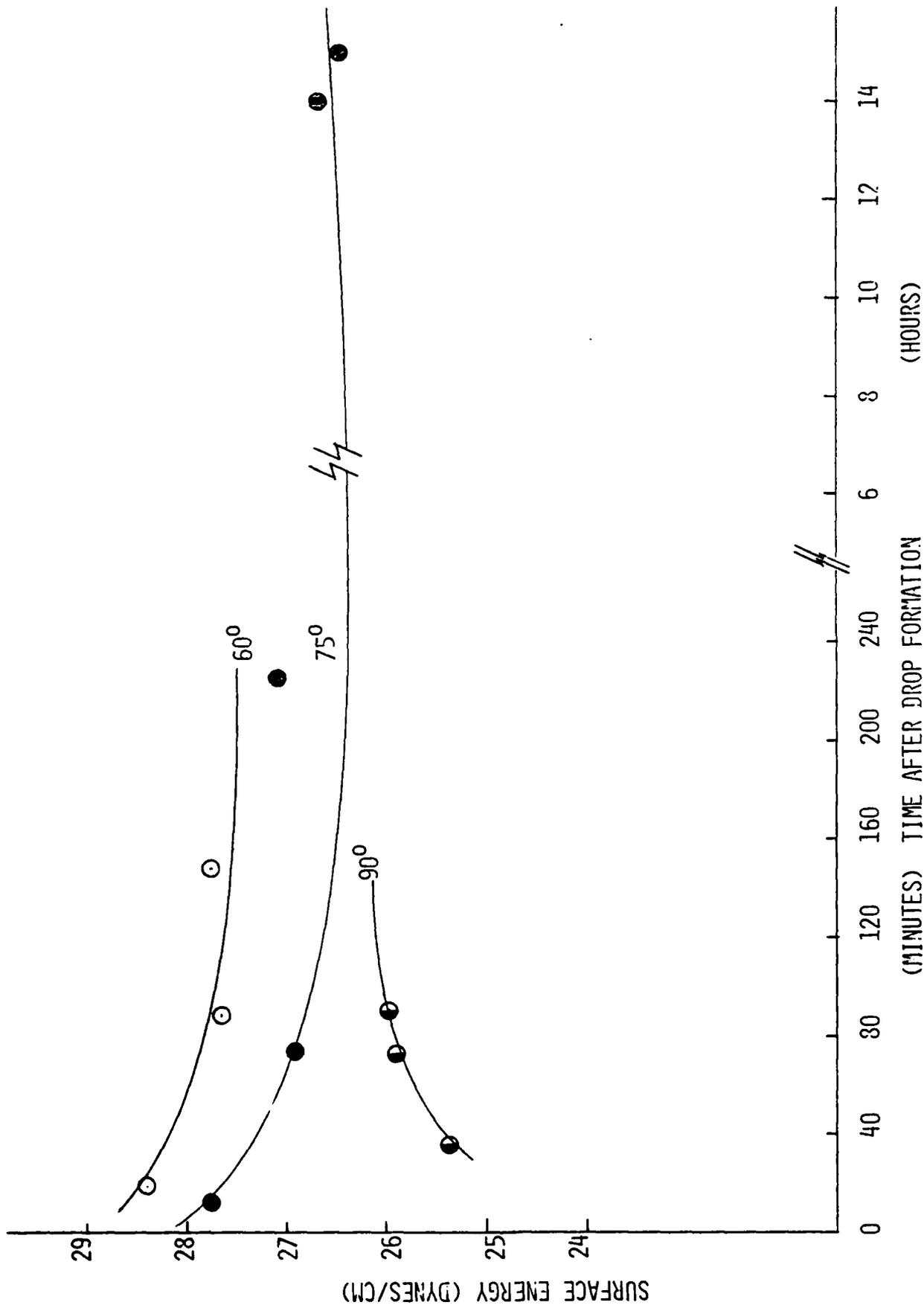
FIGURE 7. SURFACE ENERGY OF 5% EPON 1007F IN EPON 323 AT SEVERAL TEMPERATURES.

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The decrease of mixture surface energy with time is baffling, however it may be due to the presence of a surface active impurity in the mixture. There is some indication[9] that the Epon resins designated "F" are prepared by catalytically reacting Epon 828 with bisphenol A. Epon 1007F therefore could contain a surface active catalyst which diffuses to the mixture surface lowering the surface energy. After a long period of heating, the 5% mixture displays rather constant surface energies with time suggesting a surface "equilibrium" has been reached. This equilibrium surface, with a $\gamma$ of 26-28 $mNm^{-1}$ should be entirely composed of the catalyst impurity which, due to the relatively low $\gamma$, must be considerably less polar than the epoxy resins.

The surface energy of meta-phenylenediamine (MPDA), an aromatic amine curing agent, was measured. Although the solid amine oxidizes upon heating above the melting point ($64^{\circ}$), at elevated temperatures we found surface energies constant over intervals of 100 minutes. Table VI lists MPDA results.

The MPDA-Epon 828 mixture was prepared by mixing stoichometric amounts of the melted tetrafunctional amine (heated under $N_2$) and the difunctional Epon 828 (14.6g of MPDA per 100g of Epon 828) at $60^{\circ}$. Surface energies of the mixture are listed in Table VII. At $30^{\circ}$ the resin-amine pendant drop was clearly fluid, although viscous, after three hours. Between four and five hours the drop became rigid. At $75^{\circ}$ the first pendant drop photo was taken one hour after mixing the epoxy resin and the amine, and the mixture cured to a hard solid 30 minutes later. Within the first ten minutes of drop formation the drop profile conformed to the theoretical drop profile as indicated by constant 1/H values at $S_8$, $S_{11}$, and $S_{12}$, however as the viscosity increased the shape of the hanging mass of fluid became increasingly unsymmetrical generally resulting in a completely cured irregularly-shaped mass of polymer adhering to the needle tip. In summary, the surface energy

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TABLE VI. SURFACE ENERGY OF MPDA AT SEVERAL TEMPERATURES.

| EXPOSURE NO. | TEMP.(°C) | TIME AFTER DROP FORMATION | $\gamma$ mNm$^{-1}$ (p·ft$^{-1}$ x 10$^{-3}$) | DENSITY kg·m$^{-3}$ (lb·ft$^{-3}$) |
|---|---|---|---|---|
| 622 | 75 | 36 minutes | 49.26 (3.375) | 1099.2 (68.61) |
| 623 | 75 | 136 | 49.64 (3.401) | |
| 624 | 90 | 20 | 47.77 (3.273) | 1087 (67.85) |
| 625 | 90 | 49 | 47.56 (3.258) | |

MPDA PURIFIED BY FRACTIONAL DISTILLATION, MP.- 63-64°C.

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TABLE VII.  SURFACE ENERGIES OF A STOICHOMETRIC EPON 828-MPDA
MIXTURE.

| MIXTURE | TIME AFTER DROP FORMATION | $\gamma^{30°}$ (mNm$^{-1}$) | TOTAL CURING TIME @ 30° |
|---|---|---|---|
| MPDA-EPON 828 | 34 minutes | 46.2 (3.16 x 10$^{-3}$) | 100 minutes |
| | 84 | 46.2 (3.16 x 10$^{-3}$) | 150 |
| | 144 | 45.9 (3.14 x 10$^{-3}$) | 244 |
| MPDA-EPON 828 & AMINE OXIDATION PRODUCTS | 33 | 47.1 (3.22 x 10$^{-3}$) | 123 |
| | 61 | 47.1 | 151 |
| | 102 | 47.1 | 192 |
| | 150 | 46.8 (3.21 x 10$^{-3}$) | 240 |
| | 203(75°) | 39.5 | 293 |
| MPDA-EPON 828 | | $\gamma^{75°}$ | CURE TIME @ 75° |
| | 5 | 42.3[a] (2.89 x 10$^{-3}$) | 110 |
| | 19 | 42.8 (2.93 x 10$^{-3}$) | 58 |
| | 7 | 42.6 (2.92 x 10$^{-3}$) | 62 |

[a] - these values obtained with different pendant drops.

| FOR COMPARISON; | | $\gamma^{30°}$ | $\gamma^{75°}$ |
|---|---|---|---|
| | EPON 828 | 47.26 | 42.89 |
| | MPDA | - | 49.45 |

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TABLE VIII.   SURFACE ENERGIES OF MPDA-EPON 828 MIXTURES
             AT 75°C.

| PARTS MPDA PER 100 PARTS EPON 828 | $\gamma^{75°}$ $(\text{mNm}^{-1})$ |
|---|---|
| 5 | $42.3 \pm 0.2$ $(2.89 \times 10^{-3} \text{ p.ft}^{-1})$ |
| 14.6 | $42.6 \pm 0.3$ $(2.92 \times 10^{-3})$ |
| 20 | $44.2 \pm 0.5$ $(3.03 \times 10^{-3})$ |

TABLE IX.   SURFACE ENTROPIES OF RESINS AND RESIN MIXTURES.

| SUBSTANCE | $-\delta\gamma/\delta T$ |
|---|---|
| EPON 828 | 0.111   $\text{mNm}^{-1}/°C$ |
| MPDA | 0.119 |
| 14.6 PARTS PER HUNDRED MPDA-EPON 828 | 0.077 |
| EPON 1001F[a](AVG. M.W. OF 1000) | 0.063 |

[a] $\gamma = 41.62 \pm 0.39$ at $90°$ and $40.99 \pm 0.13$ at $100°$.

of Epon 828-MPDA mixtures at 30 and 75°C is slightly lower

than γ for Epon 828 alone and these mixture surface energies

do not change with time.  Secondly, it is not possible to follow

surface energy changes during the latter stages of resin-amine

curing because symmetrical pendant drops can not be maintained.

To evaluate the effect of molecular weight on the surface

energy of a series of bisphenol A-epichlorohydrin resins we

have formed pendant drops of X-22, a pure sample of the

diglycidyl ether of bisphenol A (melting point 46°) and Epon

1007F.  The results are summarized in Table V.  As with other

organic homologous series, the surface energy increases with

increasing molecular weight.

CONCLUSIONS

We have used the pendant drop method to accurately measure

the surface energy of liquid epoxy resins and resin mixtures.

Typically, over a temperature range of 20-100°C, γ values are

reproducible to ± 0.2 mNm$^{-1}$.  Even viscous liquid surface energies

were measured by working at higher temperatures(160°) under an

inert atmosphere and following the attainment of hydrodynamic

equilibrium in the pendant drop.  With resin-amine mixtures

our accurate measurement of surface energies was limited

somewhat by the accuracy of measurement of resin mixture densities.

Surface energy measurements are one method of inspecting

surface compositions.  The Epon resins we examined all contained

impurities produced in the manufacturing process.  We have

found that such impurities do significantly change epoxy resin

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surface composition, however they can be removed generally by high temperature-reduced pressure degassing. Once impurities are removed, changes at the surface of epoxy resins and resin-resin mixtures are negligible as indicated by constant $\gamma$ values over time.

Curing mixtures of Epon 828 and MPDA display little change in surface energy with changing bulk composition(see Table VIII.). Nor does the surface energy change as curing proceeds to form high molecular weight polymers( Table VII). That curing is indeed occurring is reflected in the decrease in surface entropy(Table IX) as we proceed from resin and amine starting materials to highly polymerized products. The $\delta\gamma/\delta T$ value of $-0.077$ mNm$^{-1}$/$^{o}$C for a stoichometric Epon 828-MPDA mixture cured for 100 minutes is comparable to values for other polymeric liquids($-0.05-0.075$ mNm$^{-1}$/ $^{o}$C).

Additional work with the Epon resin systems which would further clarify resin surface properties include: complete molecular and ionic characterization of the Epon resins; more extensive investigation of resin molecular weight and its influence on surface properties; measurement of Epon resin interfacial tensions with model metals and/or model hydrocarbons.
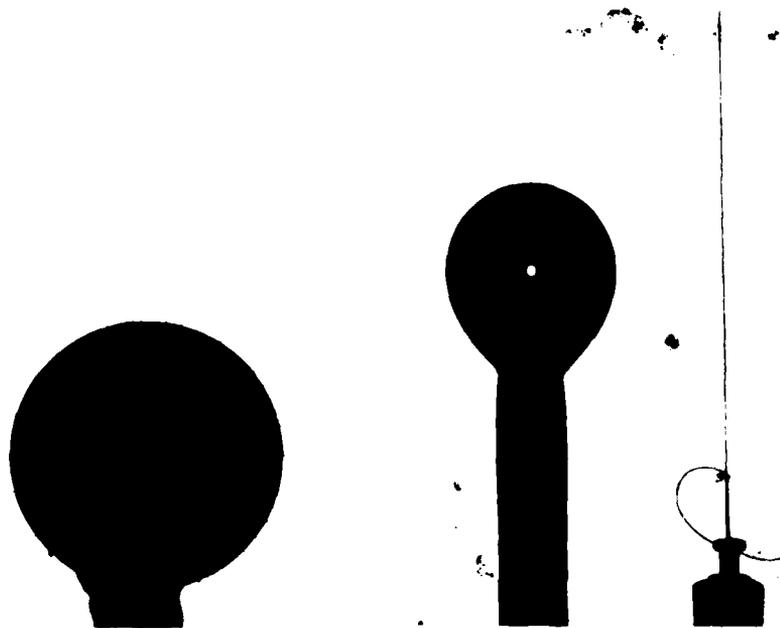
FIGURE 8.   TYPICAL PENDANT DROP PHOTO NEGATIVE SHOWING
CALIBRATION BALL AND VERTICAL REFERENCE LINE.

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FIGURE 9. Schematic of High Temperature Aluminum Block Cell.
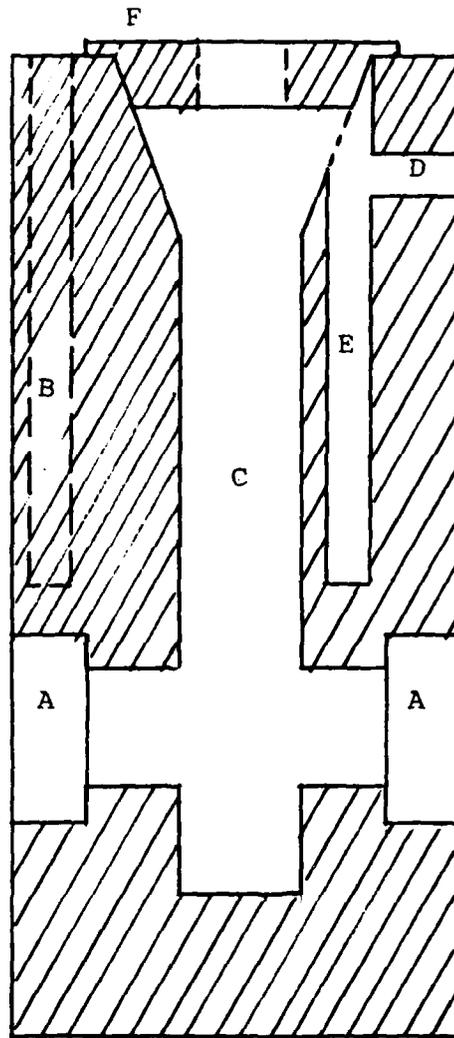
A— optically flat windows

B— Cavities for cartridge heaters

C— Cavity for syringe and needle

D— Gas inlet

E— Thermocouple well

F— Cell cover with opening

APPENDIX 1.

The profile of a pendant drop is given by

$$\frac{1}{(\delta/b)} + \frac{\sin\phi}{(x/b)} = 2 + \lambda\left(\frac{z}{b}\right)$$

where x, z, and $\phi$ are shown in Figure 1, $\delta$ is the radius of curvature at (x,z) and b equals $\delta$ at (0,0). The size of the drop is determined by b, and its shape is determined by $\lambda$, where

$$\lambda = \frac{\Delta\rho g b^2}{\gamma}$$

and $\Delta\rho$ is the density difference between the two phases.

APPENDIX 2. Physical Properties of Purified Liquids

| Liquid | Boiling Pt.($^O$C) | Index of Refraction($20^O$) | Density($20^O$) |
|---|---|---|---|
| cyclohexane | 81 (80.7) | 1.4264 (1.4266)[a] | 0.7769(0.7785g/ml) |
| ethylene glycol | 88/7torr | 1.4324 (1.4318) | 1.1139(1.1088) |
| water | – | 1.3330 (1.3329) | 0.9981(0.9982) |
| benzene | (80.1) | (1.5011) | (0.8786) |
| hexane | (68.9) | (1.3750) | (0.6603) |

[a] – Literature values( Handbook of Chemistry & Physic⌐. 54th Ed.) listed in parentheses.

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9. Conversation with Justin Bolger

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