

this compound is 147 cal./g. of the mix, the thermograph being calibrated from the known heat of reaction of dehydration of copper sulfate:



$$\Delta H_{298} = 54.3 \text{ Kcal./mole}$$

The DTA method thus promises to throw new light on the hard rubber reaction. Detailed results will be published later on.

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The Infrared Spectrum of Cyclized Natural Rubber and Its Retention of Solvents

Recently published infrared spectra¹ of cyclized rubber differ from those previously published,²⁻⁴ and it has been suggested that the strong band at $\sim 800 \text{ cm.}^{-1}$, which increases in intensity with increase in cyclization, is diagnostic for cyclization in rubber. Although it was recognized that this band was in the same region as the C—Cl stretching frequency, such an assignment was dismissed, since no direct chlorination of the polymer was involved in the cyclization process.

Working with rubbers cyclized in benzene by stannic chloride, we have shown that the band at $\sim 800 \text{ cm.}^{-1}$ does not arise from cyclized rubber but is in fact a C—Cl band of the solvent used to prepare the films from which the spectra were obtained.

A film cast from a dilute solution of carbon tetrachloride in benzene gave a spectrum with a doublet at 788 and 768 cm.^{-1} ; a dilute solution of carbon tetrachloride in carbon disulfide showed a doublet at 789 and 767 cm.^{-1} . The ratio of the intensities of the doublet in each case was the same.

Films cast from nonchlorinated solvents show weak bands characteristic of the solvent, these bands are absent when the spectrum is obtained by the potassium bromide disk method,

TABLE I
Solvent Retention of Films Less than 0.2 mm. Thick of a Cyclized Rubber Cast from Various Solvents at Atmospheric Pressure and Room Temperature and Pumped for 3 hr. at 25°C. and 100°C. at 0.5 mm. Hg

Solvent	Molecules solvent retained per 100 moles of C_5H_8 units in polymer	
	25°C.	100°C.
CCl_4^a	13.42	8.55
CHCl_3	9.77	1.64
CH_2Cl_2		0.1
CH_3CHCl_2	7.76	2.89
$\text{CH}_2\text{ClCH}_2\text{Cl}$	9.75	5.54
$\text{CHCl}_2\text{CHCl}_2$	13.1	
$\text{CHCl}=\text{CHCl}$	4.31	4.1
$\text{CCl}_2=\text{CCl}_2$	3.8	6.17
CBr_4		2.05
CHBr_3	11.7	8.3
CH_2Br_2	10.5	7.3
C_6H_6	2.3	
CS_2	1.84	

* After 24 hr. at room temperature and atmospheric pressure, solvent retention for CCl_4 , 19.75; after 3 days at 20°C., and 10^{-4} mm. Hg, 17.75; after 5 hr. at 155°C. and 10^{-4} mm. Hg, 4.56.

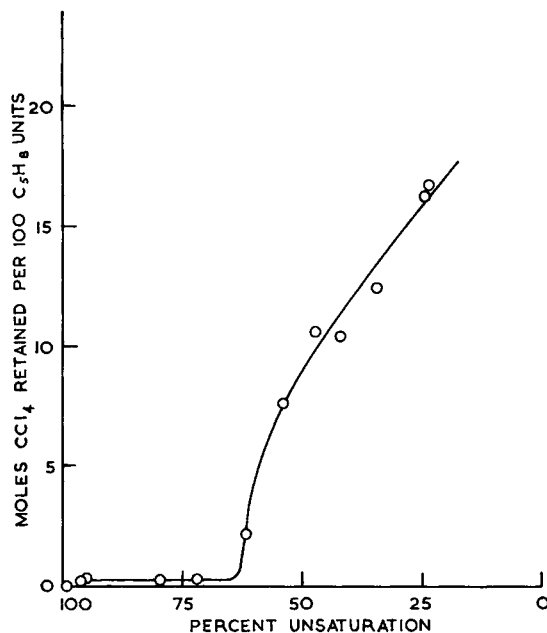


Fig. 1. Dependence of solvent retention by films of cyclized rubber on their unsaturation.

and in both cases no band is observed at $\sim 800 \text{ cm.}^{-1}$. A film cast from carbon disulfide has a band at 1515 cm.^{-1} , i.e., in the same position as a band characteristic of carbon disulfide.

Table I shows that the retention of solvent by cyclized rubber films is not confined to carbon tetrachloride, and furthermore that it is not due to attachment of solvent frag-

ments to the polymer, since extraction with acetone or methanol completely removes the occluded solvent.

Figure 1 shows that the unsaturation (measured by reaction with perbenzoic acid) of cyclized rubber must be lower than 65% of that of the original rubber for solvent retention to occur, and thereafter the amount of solvent retained increases as the unsaturation falls.

The nature of the association between the solvent and cyclized rubber cannot from information at present available be specified, but the formation of a clathrate type of compound is unlikely, since markedly different sizes of solvent molecules are retained to similar extents.

A similar degree of solvent retention is exhibited by cyclized gutta-percha.

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Distortion of Polyethylene Extrudates

When molten polymers are extruded through dies, distortions in the extrudate appear at high shear rates. Visual observation of the flow through capillary dies with square-edged inlets¹⁻⁴ indicated (1) that the melt formed a natural approach cone with an included angle of 30-40°; (2) that the melt trapped in the "stagnant" zone directly above the shoulder of the die and outside the approach cone circulated within this zone; (3) that extrudate irregularities originated at the die inlet. Some disagreement exists on this point, based in part on the short length of the dies used.^{5,6}

The melt flow experiments reported in this note were carried out with a commercial polyethylene designated DFD-0114 (Union Carbide Plastics Co.) having a density of 0.922 g./cm.³ at 25°C. A screw extruder fed melt into a channel of 1-in. diameter³ leading to a capillary die 11.44 cm. in length, with a 0.175-cm. radius and an included inlet angle of 60°. A removable cylindrical insert terminating in a 60° conical tip fitted snugly into the conical inlet. It had a capillary of 0.177-cm. radius and 2.42-cm. length, which was a direct extension of the first capillary. The upper surface of the insert was flat, i.e., it changed the entry to the capillary from an included angle of 60° to one of 180°.

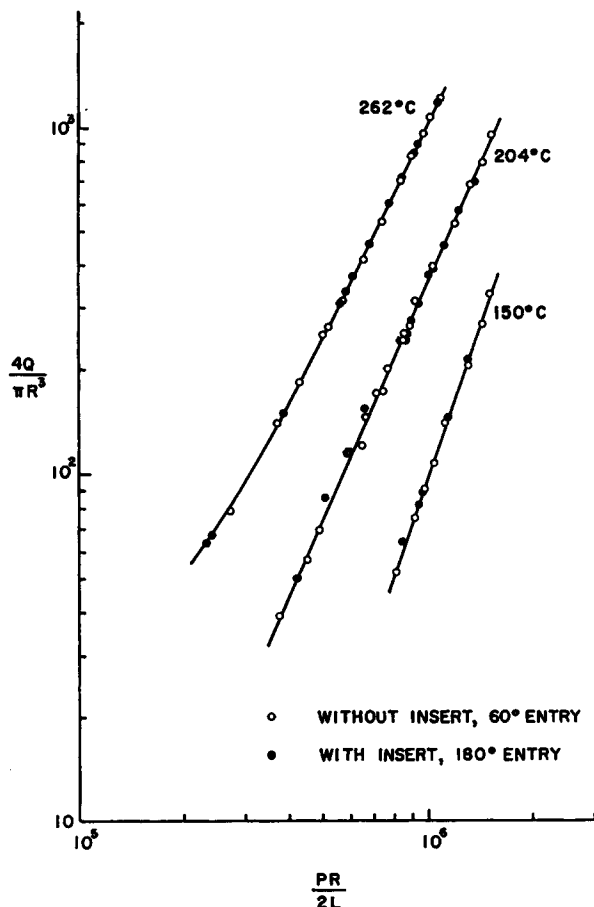


Fig. 1. Flow curves obtained with and without square-edged insert coincide despite extrudate irregularities introduced by insert.

With the square-edged insert, the extruded rod became wavy above a critical shear rate D_c .³ Between 50 and 600 sec.⁻¹, D_c is related to temperature by

$$D_c = 1.79 \times 10^8 \exp \left\{ -12,783/1.987T \right\}$$

Without the insert, no extrudate irregularity was observed at any of the three temperatures throughout the range of shear rates tested. The highest shear rates attained without the insert were from four to six times larger than the critical shear rates with the insert. Streamlining the inlet retards the appearance of extrudate distortions by at least that factor. This agrees with previous results²⁻⁴ but disagrees with Metzner's data.⁷

The origin of the irregularities in the extrudate is at the capillary inlet, since the only change introduced in the die geometry by the insert, which brought on these irregularities, was an increase in entry angle. Upstream propagation of the irregularities from the die exit⁶ is unlikely, considering that the length-radius ratio is 79.

The isothermal flow curves determined with and without the insert coincide, despite the fact that distorted extrudates were obtained with the insert over most of the flow curve at