POLYSAR

WATER ABSORPTION OF ELASTOMERS

BY

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WATER ABSORPTION OF ELASTOMERS

Considering that water is nearly insoluble in hydrocarbons, one might suppose that the uptake of water by hydrocarbon elastomers would be limited to small quantities, perhaps one or two percent. The reality is quite different; specimens exposed for extended periods, or at high temperatures, may absorb very large amounts of water, often several times the original specimen weight. Such effects have been reported for a variety of polymers by Harrington (1) and Palinchak and Mueller (2), for certain Butyl rubber specimens by Edwards (3), for Neoprene by McCormack et al (4), and for natural rubber by a number of authors to whom further reference will be made. The present work was undertaken in the hope of clarifying the nature of these effects, and in the belief that it should prove possible to secure adequate water resistance with any of the common synthetic elastomers.

In early experiments, directed toward defining a suitable experimental method, strip specimens cut from tensile test sheets of Butyl gum vulcanizates were sealed under boiled distilled water in glass tubes and placed in an oven at 160°C. The increase in length with time was determined by periodic cathetometer sightings through the glass door of the oven. The choice of test conditions was made with two purposes, firstly to accelerate the absorption, which may be very gradual at ordinary temperatures, and secondly to minimize oxidative effects. Network stability under these conditions was known to be satisfactory from previous experience (3).

Figure 1 shows a typical absorption curve obtained in these early tests. In the course of 1000 hours, the specimen increased to more than twice its original volume. Gravimetric determinations following the test showed that actual water contents were higher than would be predicted from the linear measurements; the evidence indicated anisotropic swelling, as the specimens gradually lost the ability to support their own buoyancy. For the case shown in Figure 1, the gravimetric water content was 133 weight percent.

The swollen specimens were soft but not degraded. There was no visible suggestion of moisture, even on freshly cut surfaces. As a matter of curiosity, the freezing and melting behaviour of the water was determined by imbedding a thermocouple in the swollen rubber, suspending the specimen inside a test tube, and centering the tube in a Dewar flask over liquid nitrogen. When freezing had been completed, the nitrogen was replaced with hot water to obtain the warming curve. Figure 2 shows two successive cycles applied to the specimen of Figure 1. In the second cycle the tube was insulated so as to slow the rates of cooling and warming. In both cycles the water froze at an average temperature of -37.5°, and melted slightly below 0°C.

The overall behaviour shown in Figure 2 will bear only one explanation, namely that the water is disposed as perfectly discrete droplets. The true melting point is evidently a little below 0°C., consequently the observed freezing points must represent super-cooling. If a continuous water phase were present, then freezing once initiated would quickly traverse the specimen, and the temperature would rise. This was never observed.

The super-cooling of water droplets has been studied extensively in connection with the seeding of clouds. Experiments pertinent to the present case are described by Mason (5). The median freezing points of unpurified water droplets suspended between pairs of orgainic liquids are reported, and shown to depend upon droplet size as in Figure 3. The nature of the organic medium was not found critical. The effect may be termed statistical super-cooling, the likelihood of nucleation in a given drop being dependent on its volume. Assuming applicability to the present rubber specimens, the relationship points to droplet sizes of the order of 1 - 10μ. Examination of microtome sections at 200 magnifications revealed a cellular structure compatible with this estimate, and gave 3μ as the average cell diameter.

From the total volume of water and the cell size, the number of cell nuclei per unit volume is readily calculated, and proves in this instance to be of the order of 10^{11} per c.c. It is interesting that the number of zinc oxide particles, calculated from a surface area of 3 sq. meters per g., as quoted (6) for the particular grade used, and assuming spherical particles, is also of the order of 10^{11} per c.c. This evidence suggested that water soluble residues based on zinc provided the sites for accumulation of water in this particular system. Supporting evidence was obtained by mixing the curatives with a low molecular weight polyisobutylene, heating in the manner of a cure, dispersing in toluene and extracting by agitation with excess hot water. The curatives as listed in Figure 1 produced 2.2g. of hot-water-soluble, hydrocarbon-insoluble residues containing 11.8 weight percent zinc. While it should not be inferred that soluble zinc residues are a universal, or even common, cause of water absorption, the behaviour of the present vulcanizates is best explained by their presence.

The principal value of these early experiments lay in the clear and unequivocal demonstration of the closed cellular structure of the water-swollen specimens. The existence of such a structure seems implicit in the statements of Lowry and Kohman (7) and others (8) (9), however the implications do not appear to have been pursued in theoretical treatments of absorption.

FIGURE 1

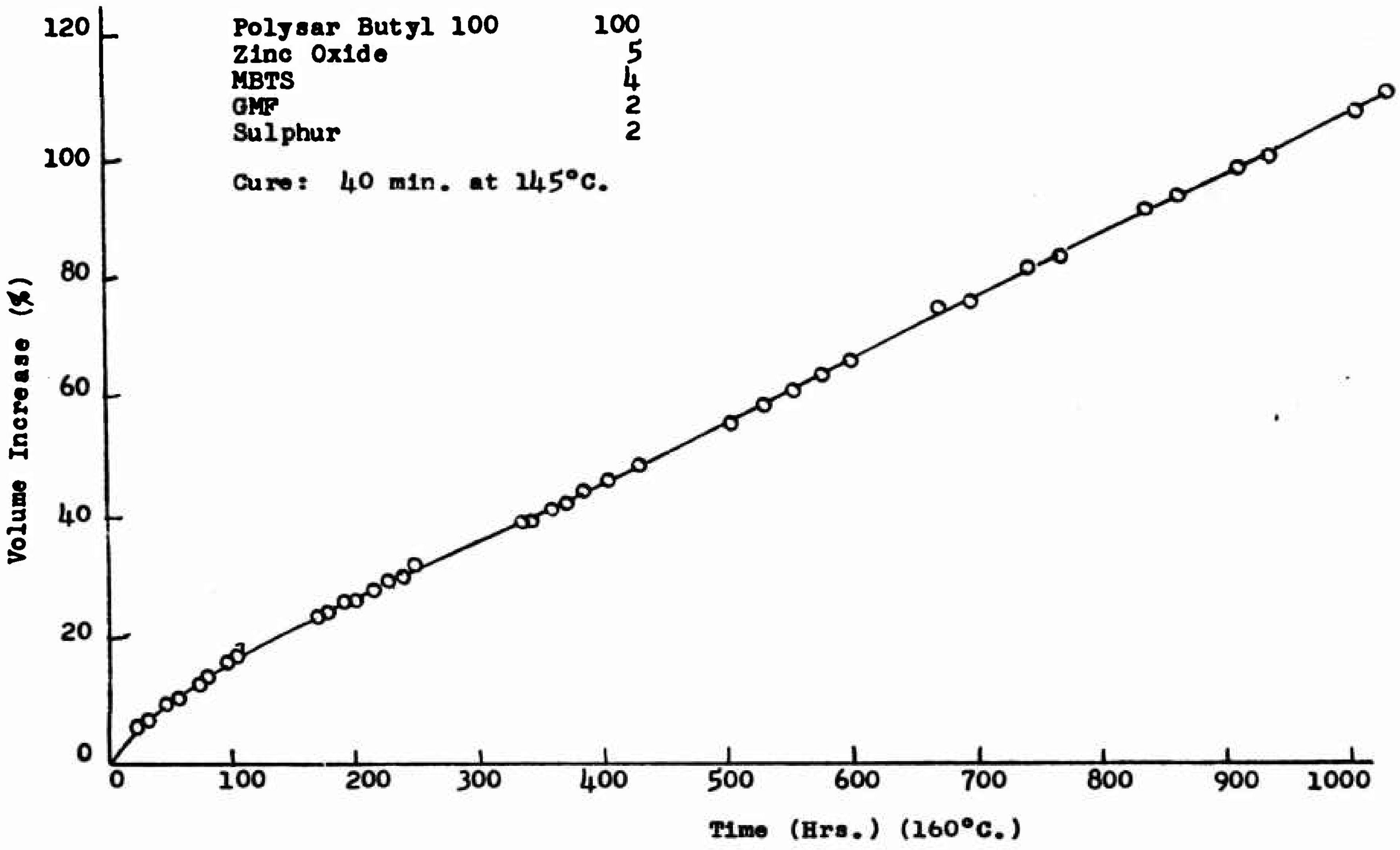

Polysar Butyl 100 100
Zinc Oxide 5
MBTS 4
GMF 2
Sulphur 2
Cure: 40 min. at 145°C.
Volume Increase (%)
0
20
40
60
80
100
120
Time (Hrs.) (160°C.)
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 2
FREEZING-MELTING BEHAVIOUR

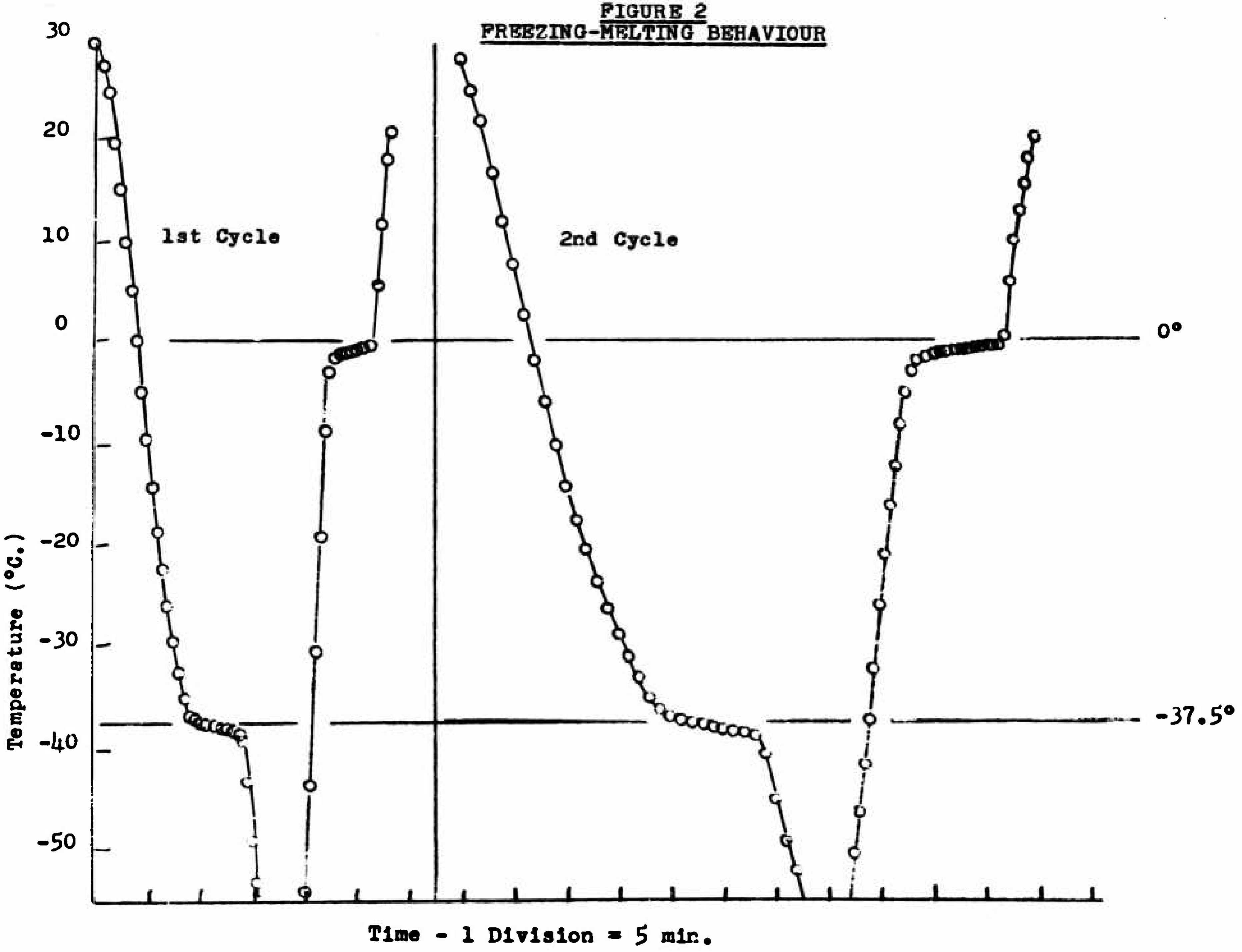
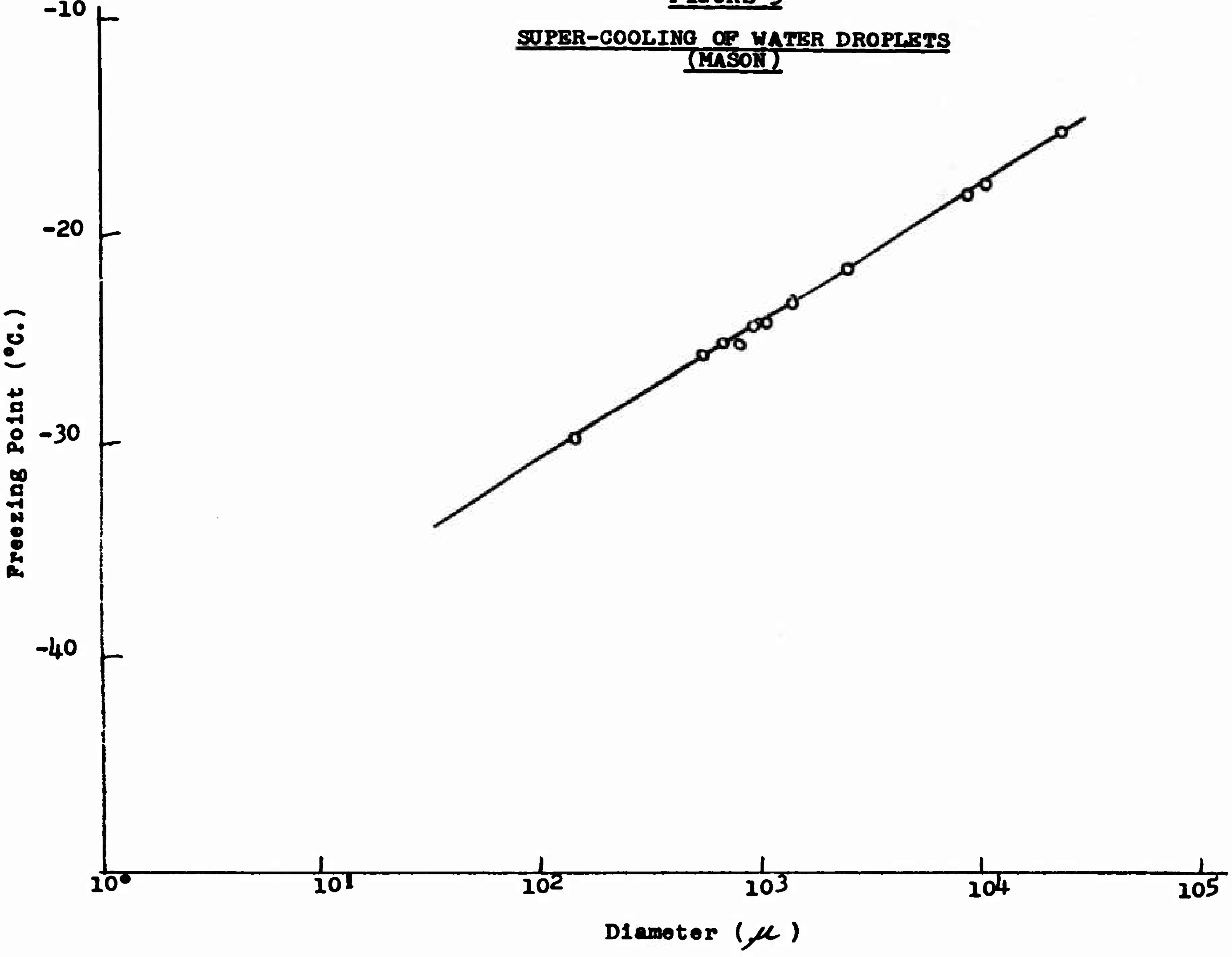


FIGURE 3

SUPER-COOLING OF WATER DROPLETS (MASON)



Comparison of Polymers

A broader study was now begun. The main experimental features — high temperature (160°C.) and exclusion of oxygen — were retained, but the determinations were made gravimetrically. Compounds were mixed as 5g. batches on a micro mill. Specimens were two-inch lengths cut from cylindrical moulded rods six inches in length and 0.1 inch in diameter. These were exposed under water in a Cenco-Menzel autoclave. Steam was allowed to vent for 20 minutes before closing the escape valve, this expedient having been shown (3) to be an effective means of excluding air. The specimens were contained in individual open-ended glass sleeves, positioned vertically in numbered cavities in an aluminum tray. Small holes through the bottom of the cavities allowed free access of water, while a stainless steel screen above the tubes prevented the specimens from floating. This method permitted simultaneous testing of a large number of specimens within a limited space.

As a measure of the state of cure, specimens identical to those exposed were strained to 50 percent elongation in an Instron machine at 25°C., and allowed to relax until the decay of stress was less than one percent per minute. This value was taken as an estimate of the equilibrium 50 percent modulus. Consideration of the Mullins effect mitigated against the use of repeated strains or of strains higher than that for which the value was desired; in the water absorption case, only the first extension would be involved. To minimize post-curing effects, the specimens were given a prolonged initial cure.

A comparison of polymers as gum peroxide vulcanizates is shown in Table I and Figure 4. Referring to Figure 4, it is seen that the vulcanizates all exhibit equilibrium absorption. The approach to equilibrium is preceded by diffuse maxima in natural rubber and SBR, an effect often encountered in these tests. A degree of mechanical breakdown of the cellular structure may occur in these cases, however we shall be concerned with gross effects and will not attempt to rationalize the details of absorption-time behaviour.

Substantial absorption occurs with SBR and natural rubber. Nitrile rubber is unique in showing a rapid but moderate absorption at an early stage, followed by gradual decline. The solution polymers, cis-polybutadiene and ethylene-propylene rubber, both absorb relatively trivial quantities of water, about one percent. This shows that they are essentially pure hydrocarbons as normally recovered, and also that peroxide vulcanization residues do not contribute significantly to absorption.

TABLE I

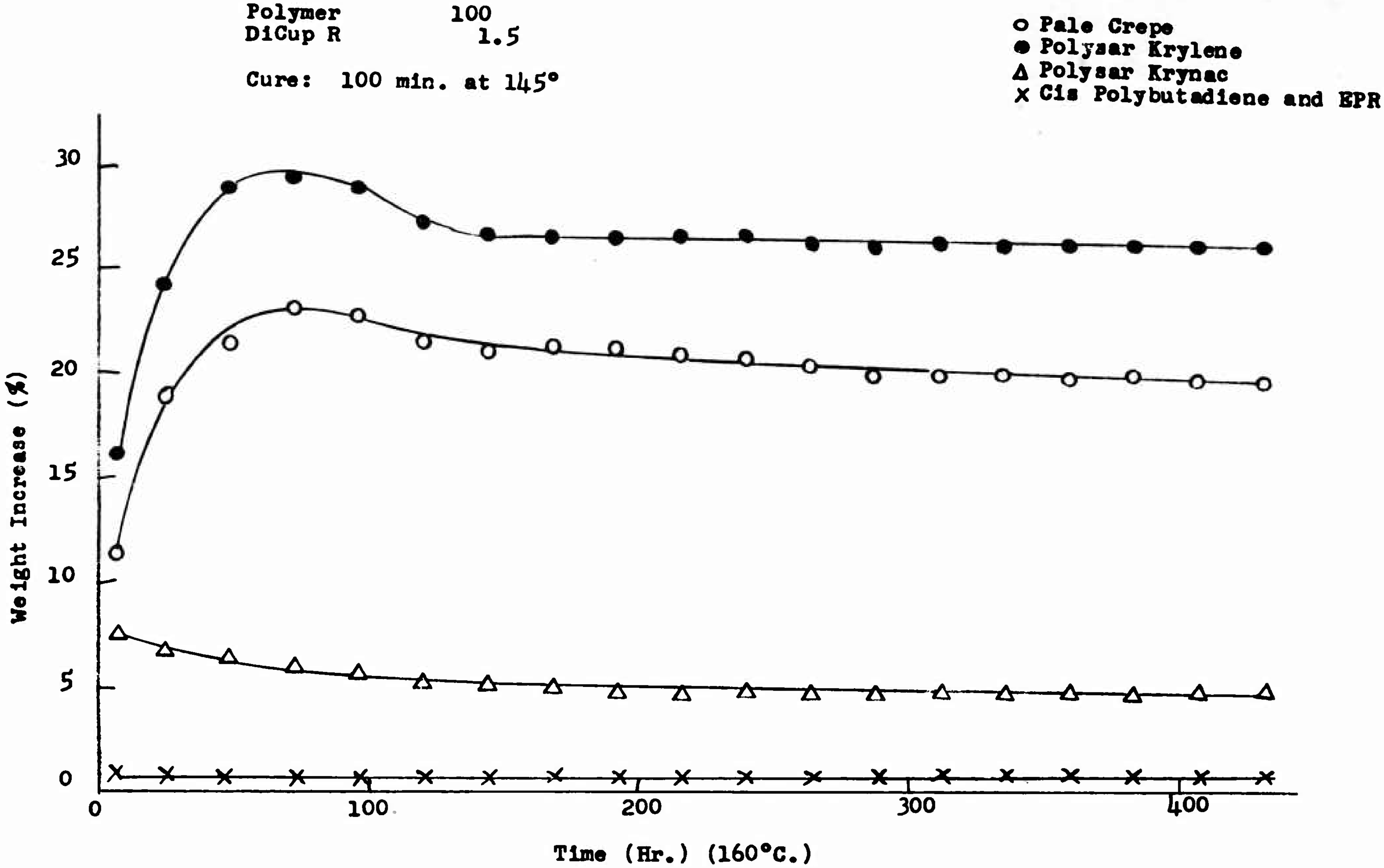
COMPARISON OF POLYMERS

Polymer	DiCup R (phr)	M50 (psi)	Equ. Wt. Increase (%) (160°C.)
Pale Crepe	1.0	43	30
Pale Crepe	1.5	72	19
Polysar Krylene	1.0	119	33
Polysar Krylene	1.5	128	26
Polysar Krynac 800	1.0	79	6.5
Polysar Krynac 800	1.5	119	4.9
Cis-Polybutadiene	1.0	139	1.0
Cis-Polybutadiene	1.5	188	0.8
EPR	4.0	82	1.1

Cure: 100 min. at 145°C.

FIGURE 4

COMPARISON OF POLYMERS



Polymer 100
DiCup R 1.5

Cure: 100 min. at 145°

Emulsion Polymerization Residues

The results of the foregoing tests led to the choice of cis-polybutadiene as a base polymer for the study of model systems. The relatively ideal elastic behaviour of this polymer, as well as its amenability to diverse curing systems, contributed to this selection.

A first series of experiments sought to isolate the effects of various classes of emulsion polymerization residues: salts, soap, fatty acid, glue. Compounds were prepared and tested as indicated in Table II. The salts were powdered to a particle size of 4 μ by violent agitation with glass beads. The sodium stearate (Mallinckrodt Cosmetic Grade) was available as a fine powder.

General comparative effects are shown by selected absorption curves in Figure 5. Equilibrium absorption occurs throughout. As might be expected, sodium chloride, weight for weight, is much the most efficient source of absorption. Soap and glue, in the small quantities normally present in emulsion polymers, make relatively minor contributions to absorption, while the fatty acid, being soluble in the polymer, is leached out.

It follows that recovery procedures used in the production of electrical grades of SBR, and which are designed for exclusion of salts and emulsifiers, should result in minimal hot water absorption. This was confirmed for the case of Polysar Kryflex 200, as shown in Figure 6. A slight loss in weight occurs.

TABLE II

CIS-POLYBUTADIENE: EFFECT OF ADDITIVES

Additive	Loading (phr)	DiCup R (phr)	M50 (psi)	Equ. Wt. Increase (%) (160° C.)
None	–	0.4	53	3.3
	–	0.6	69	2.4
	–	1.0	87	1.4
NaCl	0.2	0.4	58	27
	0.2	0.6	70	20
	0.2	1.0	94	14
	0.5	0.4	53	46
	0.5	0.6	72	47
	0.5	1.0	80	31
	1.0	0.4	53	137
	1.0	0.6	74	74
	1.0	1.0	88	47
	2.0	0.4	50	264
	2.0	0.6	71	135
	2.0	1.0	91	78
Na_2SO_4	0.5	0.4	52	39
	0.5	0.6	67	24
	0.5	1.0	81	16
Na Stearate	0.5	0.6	115	3.2
	1.0	0.6	123	4.3
	2.0	0.6	127	6.2
	4.0	0.6	121	12
Stearic Acid	0.5	0.6	69	1.9
	1.0	0.6	61	1.8
	2.0	0.6	69	0.9
	4.0	0.6	71	-1.0
Glue	1.0	0.6	70	2.5

Cure: 100 min. at 145° C.

FIGURE 5

EMULSION POLYMERIZATION RESIDUES

Cis Polybutadiene	100
DiCup R	0.6
Additive	as shown

Cure: 100 min. at 145°.

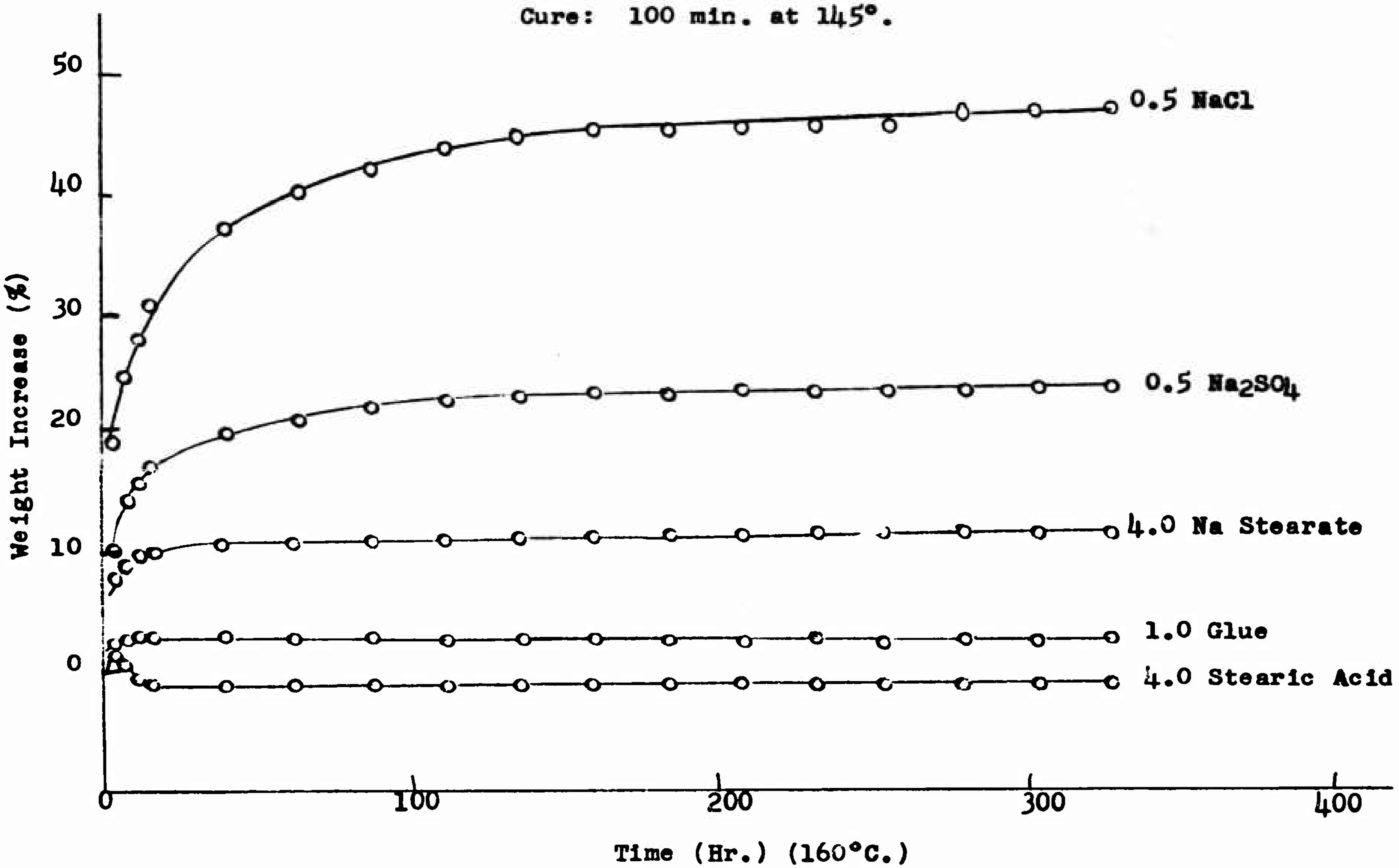
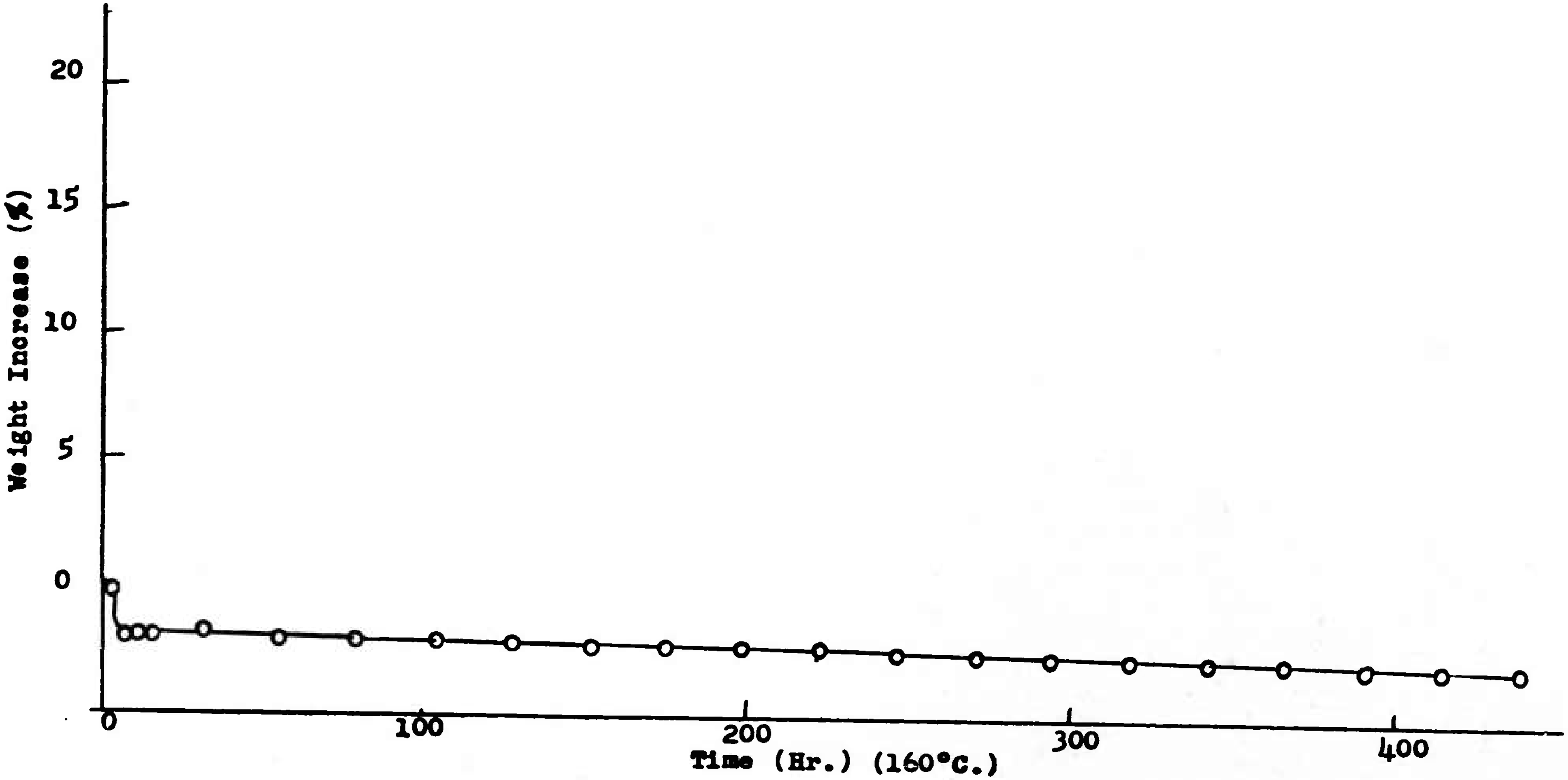


FIGURE 6

ELECTRICAL GRADE SBR

Polysar Kryflex 200	100
DiCup R	1.5

Cure: 100 min. at 145°C.
M50 135



Theory of Equilibrium Absorption

The model specimens containing salt (Table II) were designed to give broad coverage of the two variables, degree of contamination and state of cure. It is instructive to attempt a rationalization of the observed equilibria from first principles. The outlines of the mechanism of water absorption have been stated previously (7) (8) (9). Water enters the polymer, in which it is slightly soluble, and accumulates in pools around particles of water-soluble hydrocarbon-insoluble impurities. The driving force is the difference in vapour pressure between the internal solution and the external water. This gradient tends to diminish as absorption proceeds, owing both to the dilution of the internal solution and to the application of pressure by the distended rubber. Equilibrium is established if and when the rubber pressure becomes equal to the osmotic pressure of the internal solution.

The estimation of equilibrium absorption requires a knowledge of the dependences of osmotic pressure, and rubber pressure, on the water content.

Expressed in terms pertinent to water absorption, the osmotic pressure is:

$$P_o = \frac{1000gnIRT}{MW} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where I is the weight of impurity per 100 gm. specimen, M its molecular weight, n is the number of fragments into which a solute molecule dissociates, and W is the weight percent water. The osmotic coefficient g approaches one for dilute solutions and will be neglected for the present purposes.

For the estimation of the rubber pressure, a model is required. Considering each particle of salt to be separately imbedded in the rubber, we may ascribe to each a spherical envelope of rubber with dimensions appropriate to the volume ratio of rubber to salt in the compound. The model then becomes a very thick-walled balloon, and the problem is to estimate the pressure-volume relationship upon inflation.

For a balloon with original radii Ri (internal) and Ro (external), inflated radii ri and ro respectively, and an internal pressure P, equating the internal pressure to the rubber pressure gives

$$P\pi r_i^2 = \int_{r_i}^{r_o} t 2\pi r dr$$

where t is the biaxial tension (force per unit strained cross-sectional area).

Rubber elasticity theory (10) gives the biaxial tension as

$$t = G(\lambda^2 - \frac{1}{\lambda^4})$$

where G is a modulus (proportional to network density and temperature) and λ is the biaxial extension ratio.

On substitution and integration, the expression obtained is:

$$P = \frac{2aG}{r_i^2}\left[2\left(\frac{1}{r_i} - \frac{1}{b}\right) + \frac{a}{12}\left(\frac{1}{r_i^4} - \frac{1}{b^4}\right) + \frac{4a^2}{63}\left(\frac{1}{r_i^7} - \frac{1}{b^7}\right)\right.$$

$$\left. + \frac{35a^3}{810}\left(\frac{1}{r_i^{10}} - \frac{1}{b^{10}}\right) ---- \right] \quad \ldots\ldots\ldots\ldots\ldots (2)$$

where $a = r_i^3 - R_i^3$ and $b = (R_o^3 + a)^{1/3}$

The estimate of G is obtained from the relaxed modulus measurement (10) by

$$\frac{f}{A} = G(\alpha - \frac{1}{\alpha^2})$$

where f is the measured force, A the original cross-sectional area and α the extension ratio.

The theoretical balloon is based on a stress-strain relationship known to apply only at small extensions. It takes no account of the upward sweep in the stress-strain curves of real vulcanizates at high strains. One therefore anticipates an upward deviation in the real pressure-volume relationship as compared to (2). To determine the extent of this for one case, an actual balloon was prepared from natural rubber. The finished balloon had an outside diameter of 2 inches, an inside diameter of 0.5 inch, and a G (by subsequent measurement of a cut section) of 25.5 p.s.i. Inflation was achieved by thrusting a sharpened 0.0625 inch O. D. steel tube into the central cavity and introducing nitrogen under controlled pressure. The volume was determined by water displacement. Inflation proceeded satisfactorily and without leakage up to 130 percent, when the balloon broke.

The real and theoretical pressure-volume curves are compared in Figure 7. The agreement at low inflations is fairly good; the theory successfully predicts a rapid early increase in pressure to a maximum, followed by gradual decline, and the values for maximum pressure agree within a few percent. At higher inflations the real balloon, although representing a soft vulcanizate, shows a substantial upward deviation in pressure. A positive slope might be expected for higher states of vulcanization.

A better approximation of the real case could undoubtedly be made by graphical integration of real biaxial stress-strain curves. Unfortunately these cannot be obtained at high extensions for synthetic rubber gum vulcanizates of low extensibility. We choose therefore to make the simplest approximation, namely that the theory gives a good estimate of the maximum pressure, and that pressure thereafter is insensitive to volume. In this event the rubber pressure curve for moderate to large extensions is given by

$$P = F\max G$$

where Fmax is the factor appropriate to the particular Ro/Ri ratio.

Figure 8 shows a plot of F vs. V (the percentage volume inflation) for various values of Ro/Ri, as obtained from (2). Fmax for other ratios may be obtained by interpolation of the listed maxima.

Returning now to the case of the salt-loaded polybutadiene vulcanizates: at equilibrium the osmotic pressure should equal the rubber pressure, whence

$$\frac{1000nIRT}{MW} = F\max G_{160°}$$

R_o/R_i, from which Fmax is obtained, is given by

$$R_o/R_i = \left[\frac{(100 - I)d_I}{Id_R}\right]^{1/3}$$

where d_I and d_R are the densities of salt and polymer respectively.

Table III shows the estimated equilibria in comparison with the observed values. The agreement is good considering the limitations of the rubber pressure theory and the extreme experimental conditions. Moreover the deviations are generally in the expected directions: estimates tend to be too low at low states of cure and too high at high states of cure.

The graphical representation shown in Figure 9 will serve to clarify the picture. This shows a plot of the osmotic pressure curve for the case where two parts of sodium chloride are present. The horizontal lines represent the assumed rubber pressure curves; the points where these intersect the osmotic pressure curve represent the estimated equilibria. Observed equilibria corresponding to the three states of vulcanization, are shown as dotted lines. Consideration of this graph leads one to conclude that very refined theory, both as to rubber pressure and osmotic pressure, would be necessary for material improvement of the estimates.

FIGURE 7

INFLATION OF THICK-WALLED BALLOON

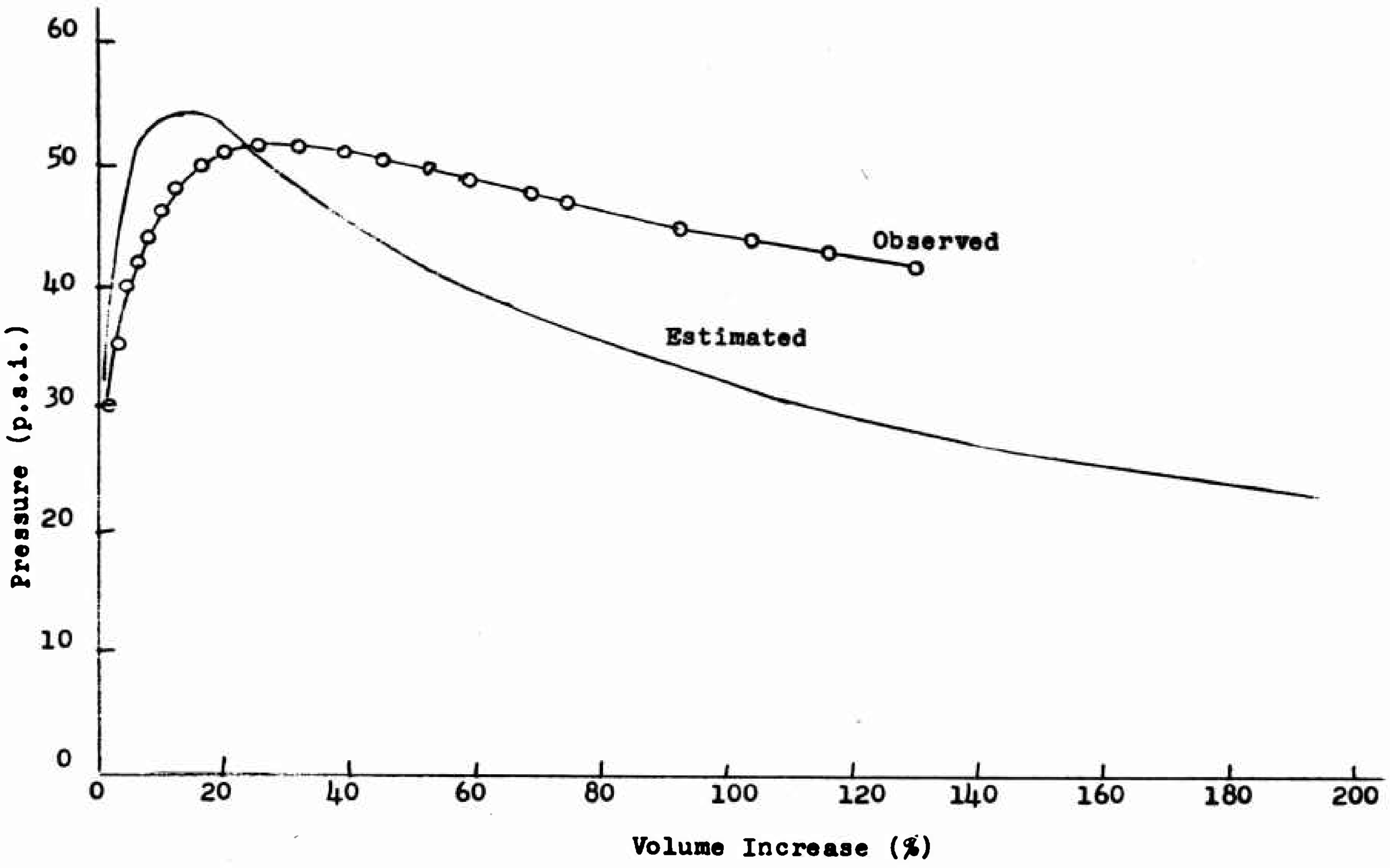
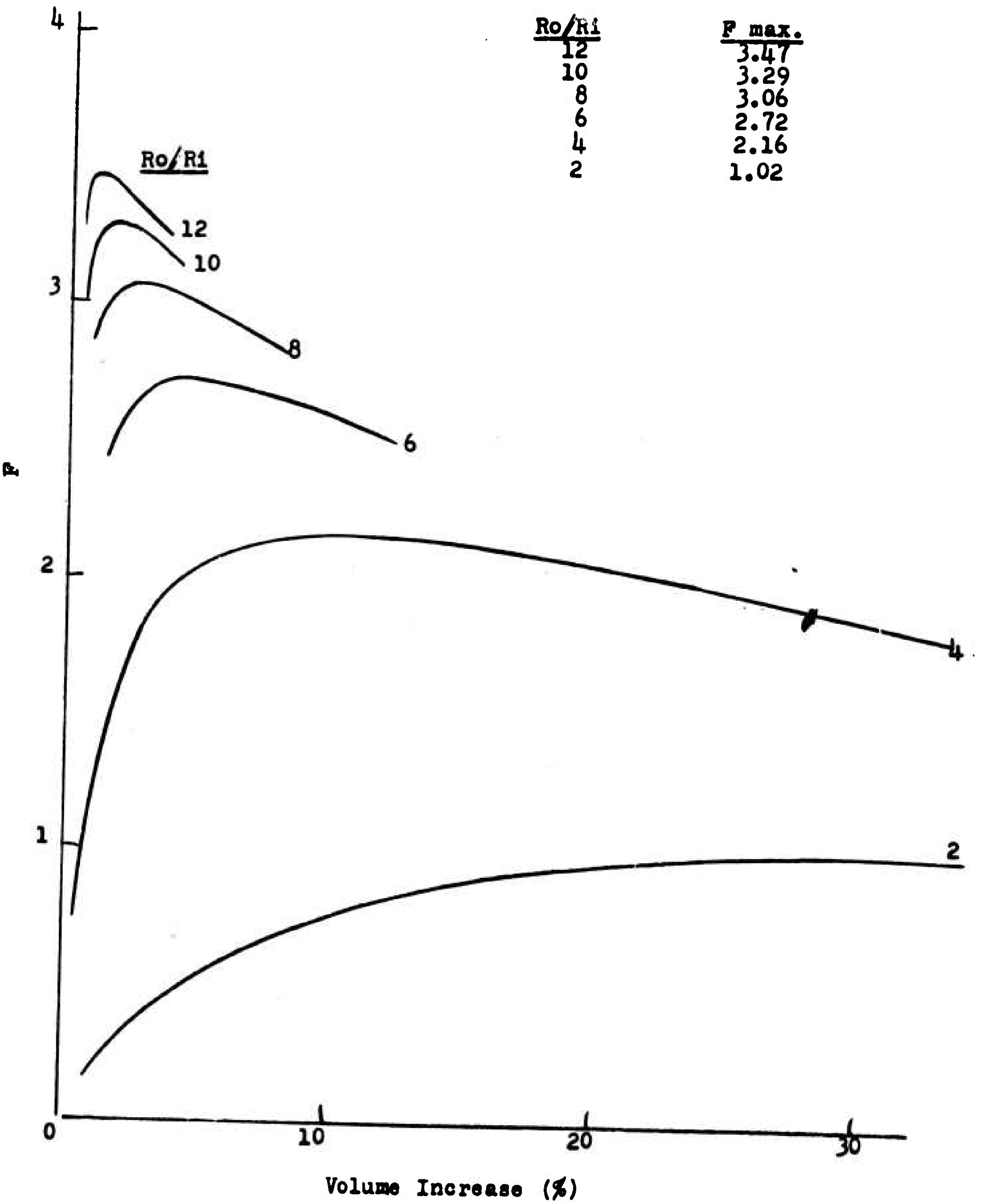


FIGURE 8

F VS. V



Ro/Ri	F max.
12	3.47
10	3.29
8	3.06
6	2.72
4	2.16
2	1.02

FIGURE 9

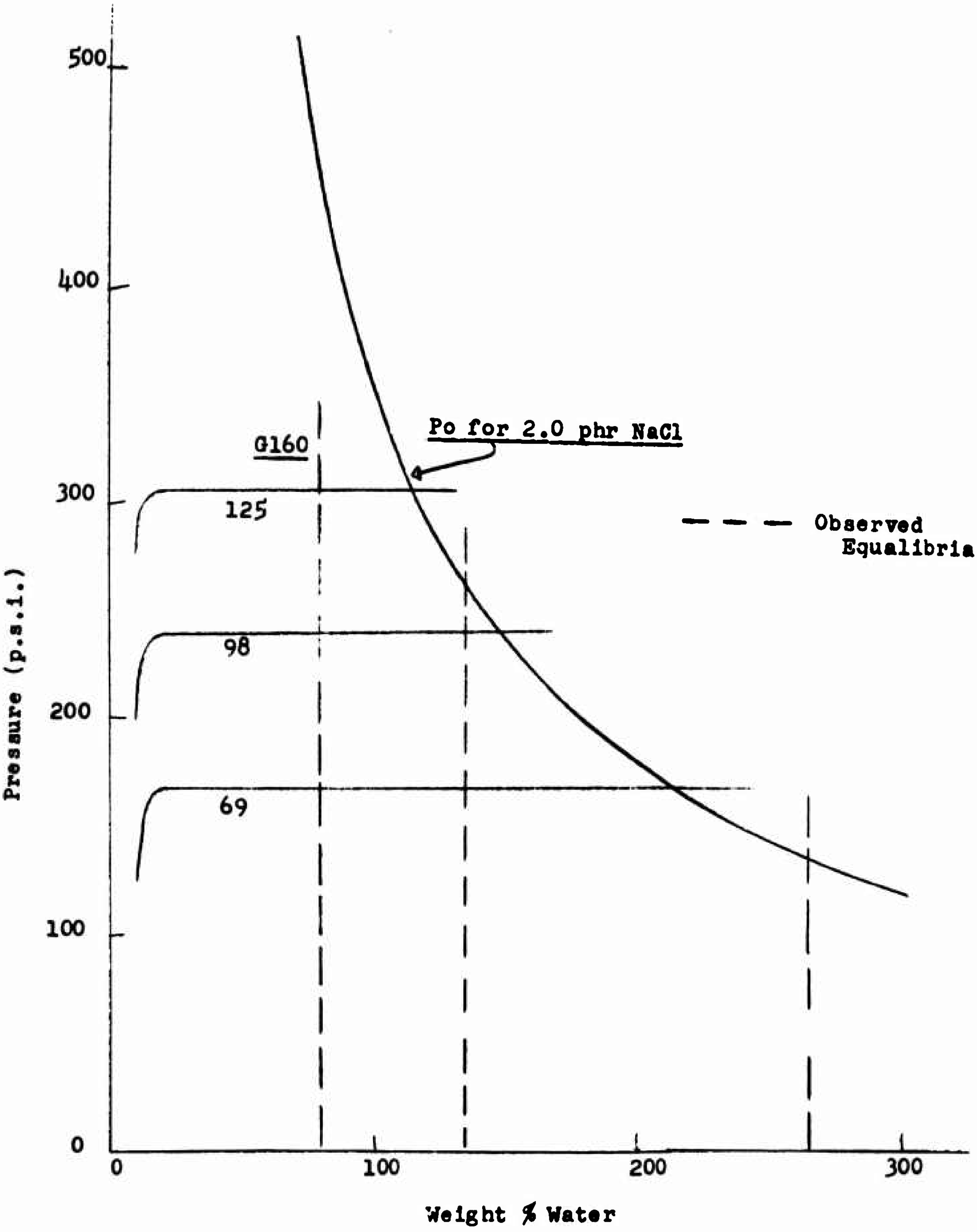

500
400
300
200
100
0
Pressure (p.s.i.)
0
100
200
300
Weight % Water
G160
125
98
69
Po for 2.0 phr NaCl
Observed Equalibria

TABLE III

NaCl	Ro/Ri	Fmax	G160	W(Wt. %)	
				Estimated	Observed
0.2	10.58	3.34	80	13	27
0.2	10.58	3.34	96	11	20
0.2	10.58	3.34	129	8	14
0.5	7.78	3.03	73	40	46
0.5	7.78	3.03	99	30	47
0.5	7.78	3.03	110	27	31
1.0	6.17	2.75	73	89	137
1.0	6.17	2.75	102	64	74
1.0	6.17	2.75	121	54	47
2.0	4.88	2.44	69	212	264
2.0	4.88	2.44	98	143	135
2.0	4.88	2.44	125	117	78

Classes of Water Absorption Behaviour

In general the water absorption of simple systems can be classified into three types: (A) low equilibrium absorption; (B) moderate or high equilibrium absorption; and (C) non-equilibrium absorption. Figure 10 is a schematic representation of possibilities with respect to osmotic and rubber pressure curves designed to illustrate how these classes of behaviour can arise. The dotted lines A, B and C represent rubber pressure curves for three states of cure. The solid lines represent: (I) a soluble substance present in low molar concentration; (II) a soluble substance present in large concentration; and (III) a substance of slight solubility present in the same molar concentration as (II). In this latter case the osmotic pressure remains constant at a moderate level until solution is complete (at point d).

Class A absorption will occur in any case where the concentration of soluble substances is very small, since intersection of the rubber curve with the osmotic curve (I) must always take place at low absorption. An interesting observation is that Class A absorption will also occur for nearly insoluble impurities, regardless of their concentration, provided that the state of cure is sufficiently high. This is illustrated by the intersections of rubber curves B or C with osmotic curve III.

Class B absorption will occur wherever substantial amounts of soluble impurities are present and the state of cure is sufficiently high. For these cases the equilibria should be approximated by

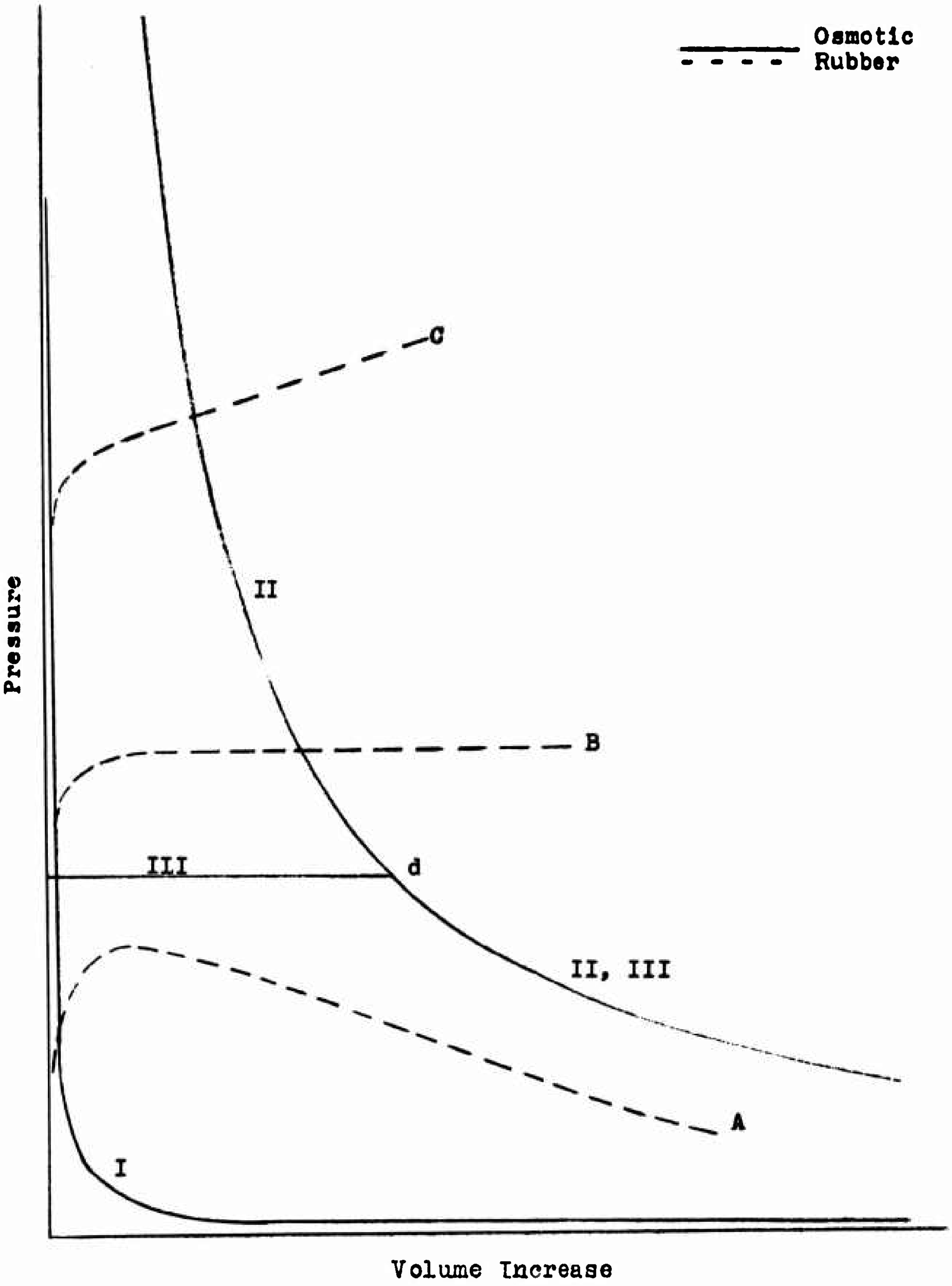
$$W = k \frac{I}{M50}$$

Class C absorption is illustrated by rubber curve A in conjunction with osmotic curves II or III. There is no intersection. It is evident that impure unvulcanized elastomers must always exhibit indefinite absorption, and that indefinite absorption will not be uncommon wherever low states of cure are involved, or where oxidative degradation can occur.

To explore the case of an impurity of limited solubility, a model system with lead chloride as the contaminant was tested as shown in Table IV and Figure 11. The state of cure and the test temperature were varied. The solubility of lead chloride at 75°C. is .087 mol./litre. At 160°C. (by extrapolation of data from the International Critical Tables) the solubility is 0.22 mol./litre. The maximum possible osmotic pressures are 110 and 345 p.s.i. respectively. We should therefore expect, for changes in state of cure and/or temperature, to find transitions from

FIGURE 10

SCHEMATIC REPRESENTATION OF CASES



Class A to Class C absorption. These are shown in Figure 11. At 75° C., the lowest cure exhibits Class C behaviour, the second cure is borderline, and the others are Class A. At 160° C., the first two cures are Class C, the third is borderline, and the others remain as Class A. This experiment serves to illustrate how extreme changes in behaviour can occur through changes in cure or temperature of test.

TABLE IV

Cis Polybutadiene	100
Lead Chloride*	5

Cure: 100 min. at 145° C.

DiCup R	M50	Wt.- % Increase after:	
(phr)	(phr)	500 hr., 75° C.	250 hr., 160°C.
0.1	26	64+	280+
0.2	54	13+	112+
0.4	74	4.0	20+
0.6	92	2.5	8
1.0	102	1.5	4.2

Notes:

* particles 8 x 45μ

\+ indicates continuing absorption.

Nitrile Rubber

The good high temperature water resistance of nitrile rubber has been noted in the literature (1) (2) and has occasioned some surprise. We have seen (Figure 4) that the gum vulcanizate shows unique absorption-time behaviour, a rapid initial uptake of water followed by gradual decline in weight. This behaviour suggested the possibility that nitrile rubber functions inefficiently as a semi-permeable membrane, permitting the extraction of water soluble residues. To pursue this possibility, specimens containing powdered salt were prepared and tested with results as shown in Figure 12. It is seen that water enters the polymer rapidly, to an extent dependent upon the salt content. Following this initial period, the water content decreases progressively. While this result is compatible with the view that nitrile rubber permits the diffusion of ions, it does not prove the case, since the same result could arise through mechanical breakdown of the cellular structure.

Satisfactory independent evidence for a diffusion process was obtained by preparing a vulcanized membrane of thickness 0.003 inch, and using this to separate a saturated copper sulphate solution from a body of distilled water. Blue colouration of the water side was discernible after a few days at 75 °C. In 25 days the membrane, whose diameter was 0.75 inch, allowed the passage of 0.33g. of the anhydrous salt. In the case of an SBR membrane of the same dimensions, the solids on the water side totalled 0.006g.

This evidence is sufficient to explain the performance of nitrile rubber articles in hot water. Evidently we must distinguish between water resistance in the sense of low water permeability and water resistance in the sense of low equilibrium absorption. The two are unrelated. For extended high temperature exposure, one cannot rely on low water permeability as a criterion of performance.

FIGURE 11

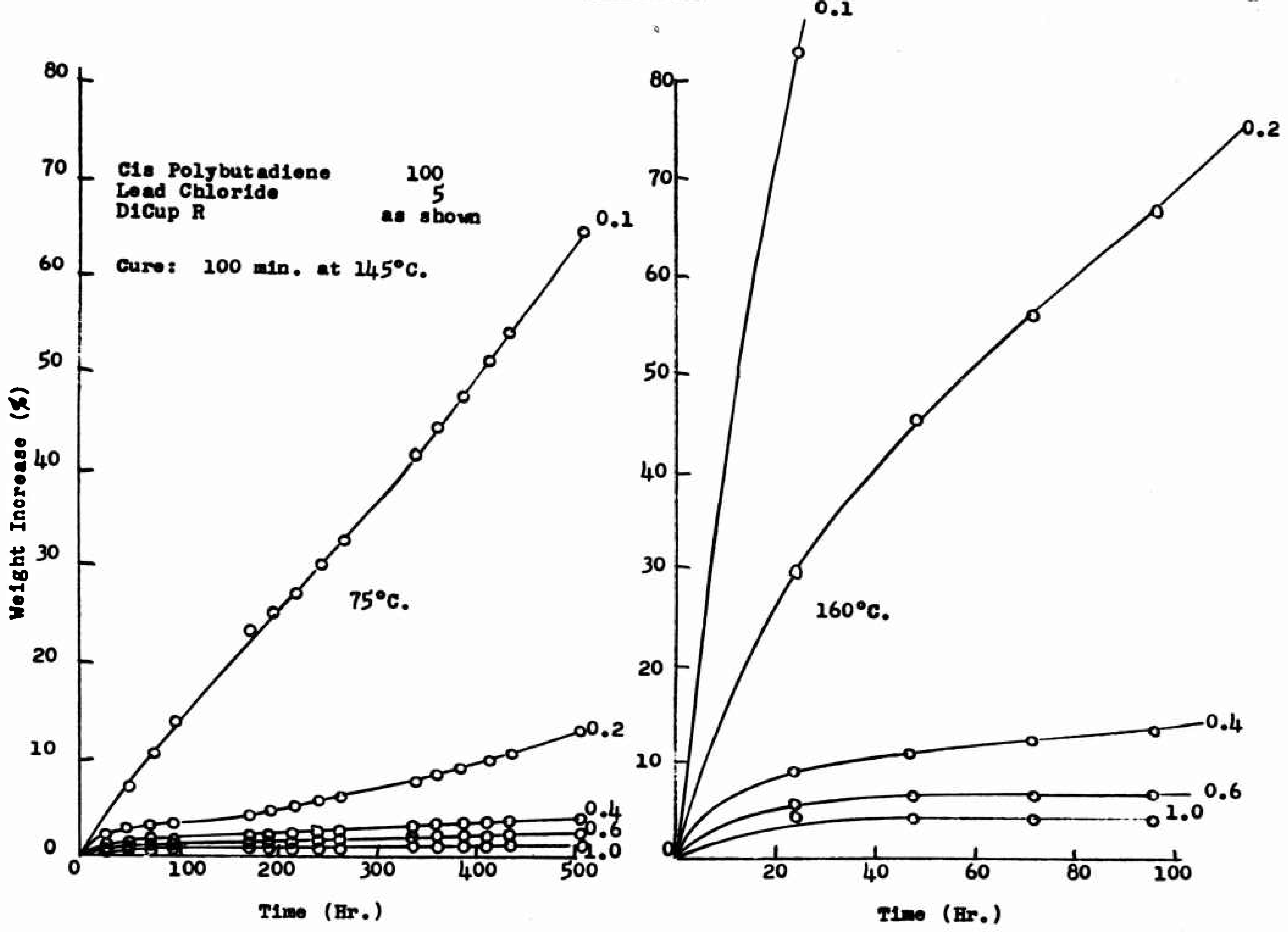
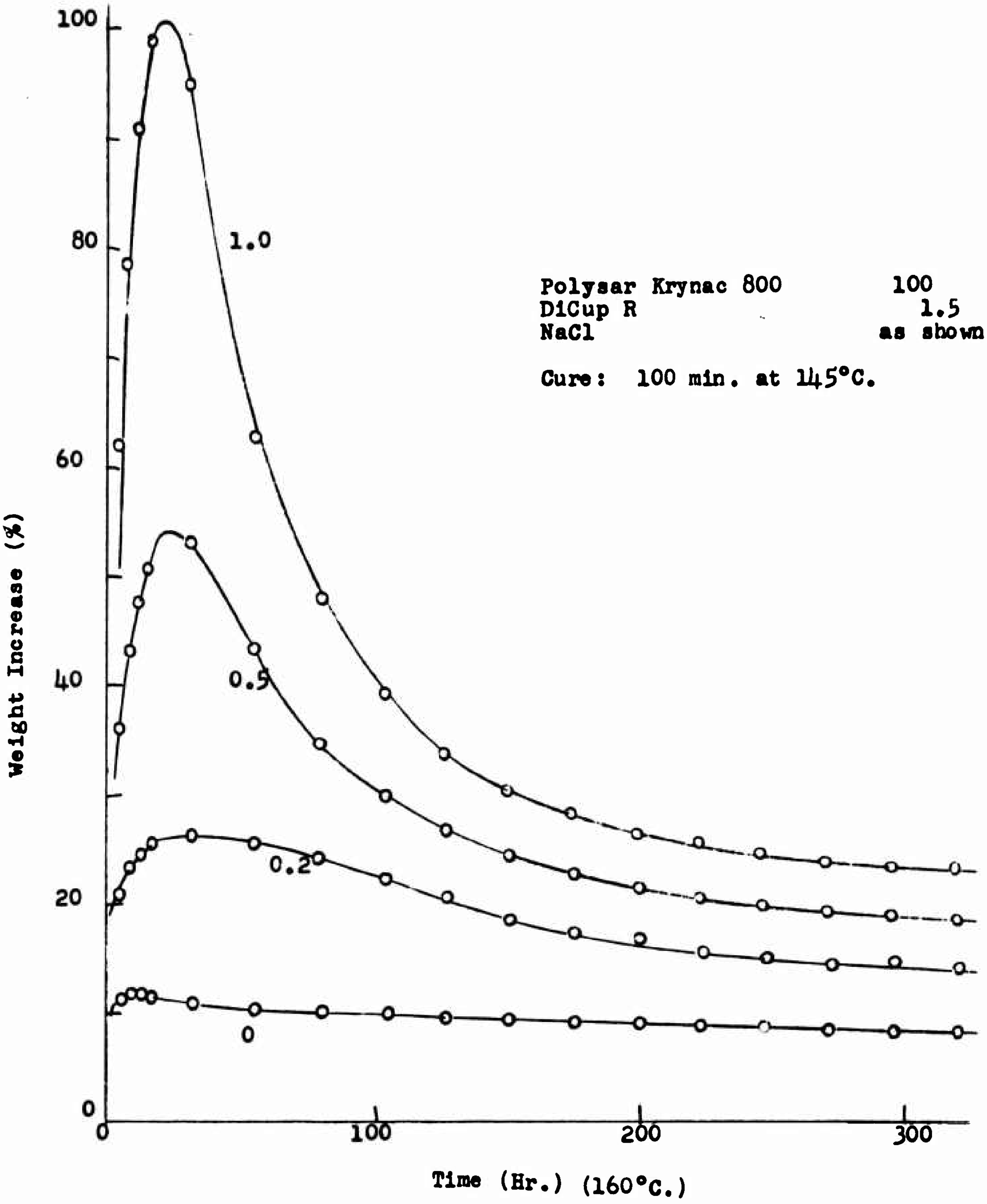

Cis Polybutadiene 100
Lead Chloride 5
DiCup R as shown
Cure: 100 min. at 145°C.
Weight Increase (%)
0
10
20
30
40
50
60
70
80
0
100
200
300
400
500
Time (Hr.)
75°C.
0.1
0.2
0.4
0.6
1.0
160°C.
0.1
0.2
0.4
0.6
1.0
0
10
20
30
40
50
60
70
80
20
40
60
80
100
Time (Hr.)

FIGURE 12

NITRILE RUBBER CONTAINING SALT



Polysar Krynac 800	100
DiCup R	1.5
NaCl	as shown

Cure: 100 min. at 145°C.

Temperature Dependence

To make a meaningful comparison of polymers with respect to temperature dependence of absorption it is necessary to choose conditions that will minimize the effects of inherent residues, the effect of state of cure, and the effect of temperature on the solubility (and therefore the solution vapour pressure) of the contaminant. These considerations led to the compounds shown in Table V. The specimens contained a high loading of sodium chloride, whose solubility is only slightly temperature-dependent. The loading was such as to overwhelm the effects of any inherent residues. A low state of cure was maintained by appropriate choice of curative loadings. The measure of rate was taken as the inverse of the time in hours required for 10 weight percent absorption to occur. Suitable time schedules for the gravimetric determinations were specified following preliminary tests at each temperature. The specimens were exposed to boiled distilled water under nitrogen.

The rate data are shown graphically in Figure 13. The differences in rate are quite remarkable; to consider the extremes, natural rubber or nitrile rubber at 92°C. absorb at about 30,000 times the rate for Butyl at 25° C. The room temperature point for Butyl represents about 60 weeks. This test is in progress, the absorption after 15 weeks being 4 percent. The very low permeability of Butyl to water (the rate at room temperature is some 20 times slower than the nearest polymer tested) is undoubtedly a major contributing factor to its serviceability in electrical insulations.

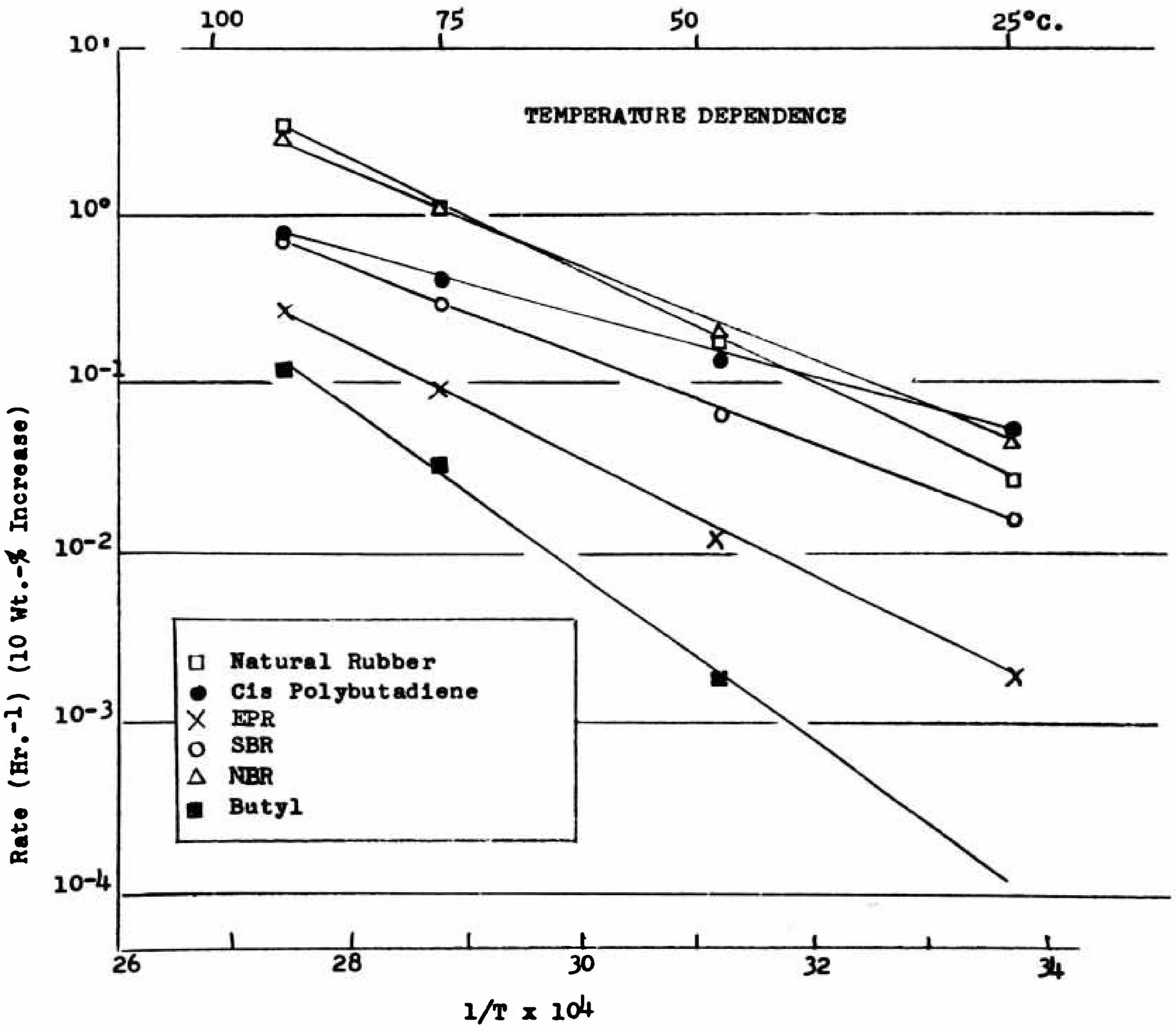
Before leaving the subject of temperature dependence it is worth while to record that difficulty was experienced in obtaining useful data from exposure of specimens to boiling water. The rates were always lower than values extrapolated from lower temperatures, and repeated tests gave erratic results. The continuous nucleation of bubbles on the surface of the specimen may bear on this result.

TABLE V

TEMPERATURE DEPENDENCE

	A	B	C	D	E	F
Pale Crepe	100	–	–	–	–	–
Polysar Butyl 100	–	100	–	–	–	–
EPR	–	–	100	–	–	–
Cis Polybutadiene	–	–	–	100	–	–
Polysar Krynac 800	–	–	–	–	100	–
Polysar Krylene	–	–	–	–	–	100
NaCl	2	2	2	2	2	2
DiCup R	0.5	–	1.5	0.2	0.5	0.5
GMF	–	2	–	–	–	–
Red Lead	–	5	–	–	–	–
M50 (p.s.i.)	24	28	38	40	33	50
Rate of Absorption						
(hr^{-1}) at 25° C.	.029	–	.0018	.054	.048	.017
48	.18	.0018	.016	.15	.19	.066
75	1.1	.035	.095	.41	1.1	.31
92	3.3	.11	.28	.80	3.0	.74
E (Kcal)	15.4	22.8	16.3	8.1	13.2	12.0

FIGURE 13


100
75
50
25°C.
TEMPERATURE DEPENDENCE
10¹
10⁰
10-1
10-2
10-3
10-4
Rate (Hr.-1) (10 Wt.-% Increase)
□ Natural Rubber
● Cis Polybutadiene
✕ EPR
○ SBR
△ NBR
■ Butyl
26
28
30
32
34
1/T x 10⁴

Compounding Considerations

(a) Fillers

An assessment of the water absorption of 33 common fillers and reinforcing agents was made by exposing 0.2g. specimens, contained in individual glass vials equipped, for weighing, with polythene caps, to an atmosphere of 100 percent humidity at 25° C. For this purpose the specimens were placed inside a closed dessiccator over distilled water and removed periodically for weight determinations. They were conditioned initially for 24 hours at 25°C., 50 percent relative humidity. The conditions of this test are analogous to the conditions for water absorption by rubber, except that in this case there is no rubber to impede the diffusion or raise the pressure on the absorbed water.

The fillers tested are listed in Table VI, which also shows the increases in weight after 30 days. The absorption curves are shown in Figure 14.

In general the silicas, silicates and some of the clays take up large quantities of water, the reinforcing carbon blacks are intermediate, and the oxides, non-reinforcing blacks, carbonates, talcs and calcined clay absorb little water. Magnesia, which forms indefinite hydroxide hydrates, is a unique case. Where continuing absorption occurs, the presence of electrolyte impurities may be suspected. (A vial of salt which was included for comparison showed a nearly linear increase to a 30-day value of 702 percent). In view of the various possible mechanisms by which water may collect on or in the fillers, it would be misleading to consider the effects in terms of the nominal composition of the materials. As Dannenberg and Opie (11) have shown for the case of carbon black, the absorption is controlled to a large extent by the presence of water soluble residues, although surface area and surface chemistry also play substantial roles. The filler specimens tested in this work were those that happened to be available. They may or may not be fully representative of their classes, depending on the nature and degree of processing variations involved in their manufacture.

For practical purposes, the choice of fillers from the low-absorption group is straight-forward and reliable. But it is most interesting that the use of hydrophyllic fillers is not necessarily disadvantageous. Indeed McCormack (4) and Palinchak and Mueller (2) show the use of hydrated calcium silicate and silicas to be of great practical value in some systems. Having experienced the case of nitrile rubber, where leaching of electrolytes can occur, it appeared likely that the silica and calcium silicate fillers, combining as they do the properties of reticulate structure formation in rubber mixes and an affinity for water, might serve as channels for the migration of ions. In this event leaching would take place, and the equilibrium absorption would correspond to that of the pure materials, free of electrolyte impurities.

The compounds shown in Table VII were prepared for the purpose of testing this possibility. The group comprises various loadings of hydrated calcium silicate and hydrated silica, with and without the presence of added sodium chloride. Compounds containing acetylene black were included to represent the case of a high structure non-hydrophyllic material.

In all cases equilibrium absorption was found. The equilibrium values are shown graphically in Figures 15 and 16. The left hand graph in Figure 15 applies to hydrated silica without added salt. The data are treated in the manner appropriate to Class B absorption by plotting equilibrium absorption against I/M 50, where I in this case is the weight of filler per 100g. of compound. The behaviour is "normal" up to 20 p.h.r. At 40 p.h.r. the value falls well below the line. In the right-hand graph the absorption values are plotted against filler loading for the cases where added salt was present or absent from the mixture. The compounds containing added salt show higher equilibrium absorption up to 20 p.h.r., but at 40 p.h.r. the distinction has disappeared. Hydrated calcium silicate, treated in the same manner in Figure 16, shows much the same behaviour.

These results support the view that fillers of this type serve to promote the extraction of electrolytes, when the filler loading is such that extensive chains of particles may form. A degree of electrolyte contamination of the fillers is indicated by the similarity of the trends whether or not sodium chloride is purposely introduced.

While further study of these systems could profitably be made, the present results are sufficient to justify two practical suggestions: firstly, substantial loadings should be used; a low loading may be worse in terms of equilibrium absorption than none at all. Secondly, one should avoid compounding procedures designed to induce particulate dispersion. The mechanism of low absorption must be presumed on present knowledge to depend on the existence of particle chains.

TABLE VI

WATER ABSORPTION BY FILLERS

Filler No.	Composition	Supplier	Weight Increase (%) in 30 days at 25° C., 100% Humidity
1	Fumed Silica	A	57 +
2	Bentonite Clay	B	29 +
3	Barytes	C	0.5
4	Al. Silicate Clay	D	9
5	Fumed Silica	E	67 +
6	ppt. $CaCO_3$	F	5.0
7	ppt. $CaCO_3$, 2 % tall oil	G	3.0
8	Diatomaceous Earth	H	1.5
9	Hyd. Al. Silicate (Hard Clay)	I	19
10	ppt. Hyd. Silica	G	92 +
11	Lithopone	J	3.5
12	Magnesium Oxide	K	102 +
13	Hyd. Al. Silicate (Soft Clay)	I	8
14	Hyd. Mg. Silicate	L	4
15	Ground Limestone	M	0.8
16	ppt. coated $CaCO_3$	N	8
17	ppt. Hyd. Ca. Silicate	G	82 +
18	Hard Clay	O	16
19	Talc	P	1.8
20	Titanium Dioxide	Q	3.0
21	Calcined Hard Clay	D	3.5
22	Hyd. Na. Si. Aluminate	O	63 +
23	Zinc Oxide	R	1.5
24	EPC Black		15
25	MPC Black	E	13 +
26	SAF Black	E	21 +
27	ISAF Black	E	14 +
28	HAF Black		14 +
29	FEF Black	S	3.5
30	SRF Black	T	19
31	FT Black	I	0.7
32	MT Black	I	0.6
33	Acetylene Black	U	2.5

Note: The + notation indicates continuing weight increase at 30 days

FIGURE 14

WATER ABSORPTION BY FILLERS

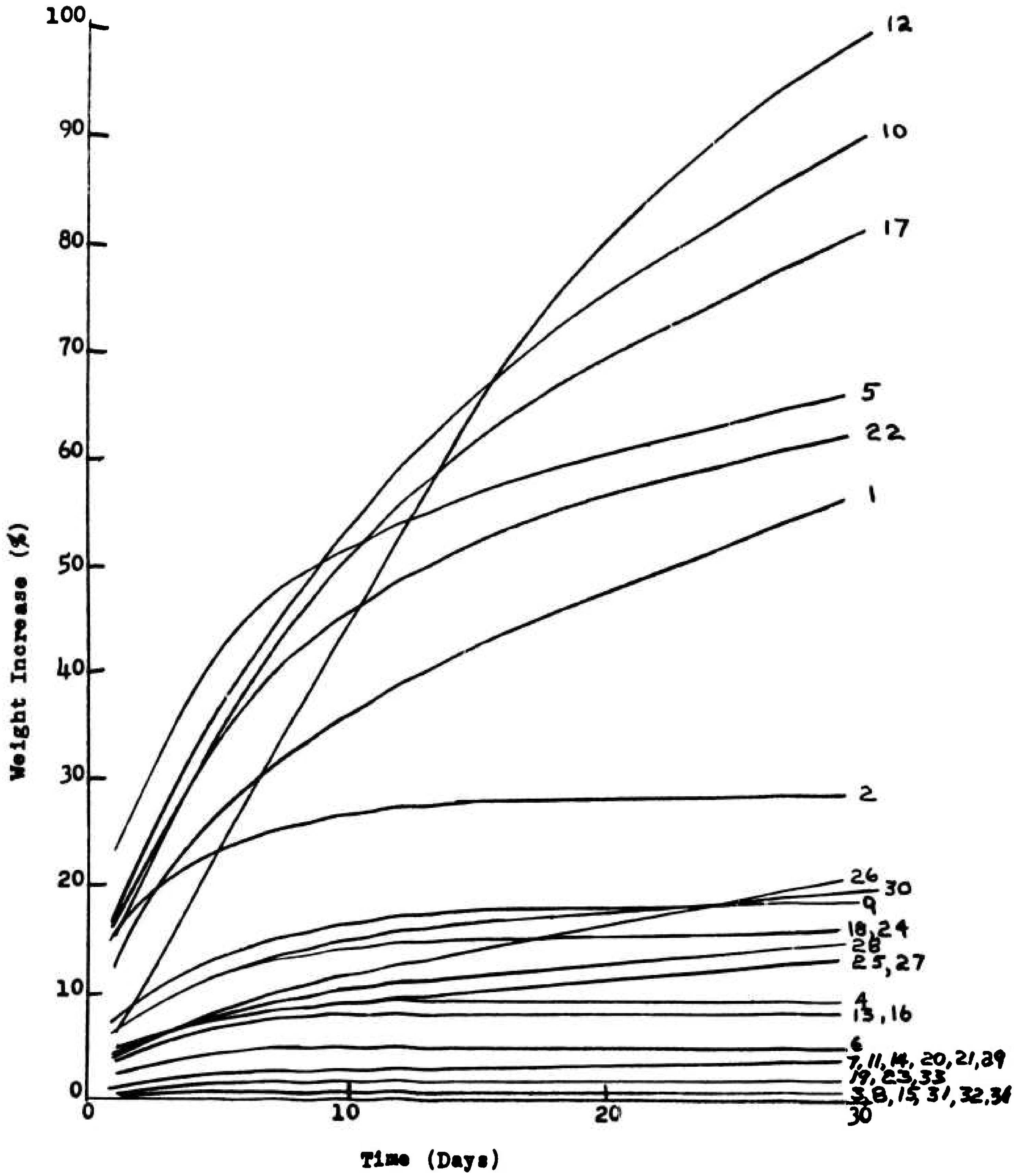


TABLE VII

HIGH STRUCTURE FILLERS

Cis Polybutadiene	100
DiCup R	0.6
Filler	Variable

Cure: 100 min. at 145° C.

Filler	Loading (phr)	NaCl (phr)	M50 (psi)	Equilibrium Weight Increase (%) (250 hrs. at 160° C.)
None	–	1	70	45
Hyd. Ca. Silicate	5	1	123	27
	10	1	153	31
	20	1	171	44
	40	1	271	17
Hyd. Silica	5	1	80	64
	10	1	92	68
	20	1	111	53
	40	1	164	5.7
Acetylene Black	5	1	76	53
	10	1	77	51
	20	1	92	48
	40	1	110	41
None	–	0	77	1.5
Hyd. Ca. Silicate	5	0	121	7.2
	10	0	153	10
	20	0	172	18
	40	0	330	15
Hyd. Silica	5	0	83	5.6
	10	0	88	8.7
	20	0	100	15
	40	0	189	6.3
Acetylene Black	5	0	82	1.7
	10	0	87	1.7
	20	0	88	1.7
	40	0	99	1.3

FIGURE 15

HYD. SILICA

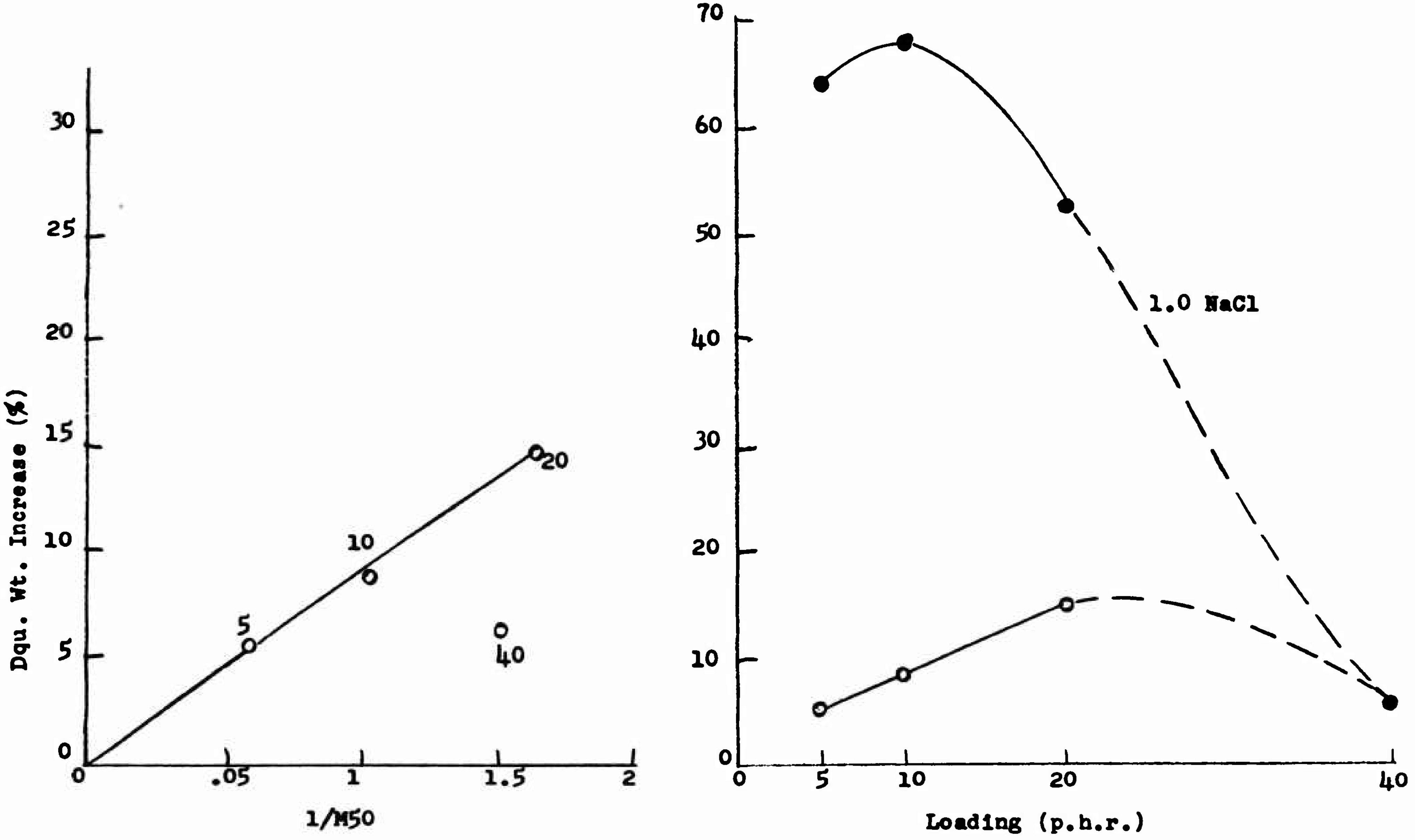
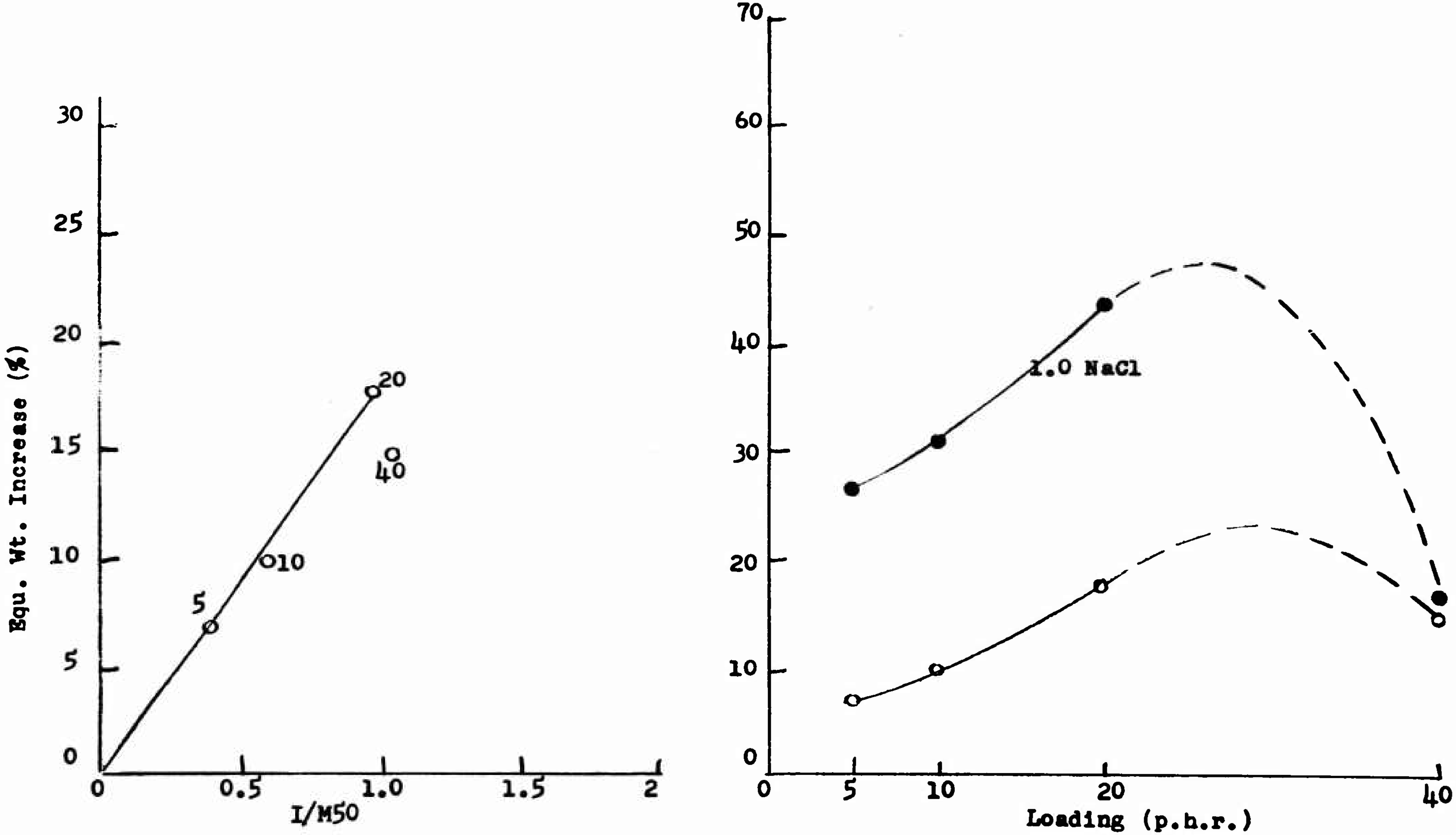


FIGURE 16

HYD. Ca SILICATE



(b) Curing Systems

Since the early experience had suggested that large effects might arise depending on curative residues, a comparison was made of several curing systems typical of various aspects of rubber technology. Two series of compounds, one based on cis-polybutadiene, and one on Polysar Butyl 200, were tested, and in each case two test temperatures, 75°C. and 160°C., were employed. To obviate any possible contribution by inherent residues, the Butyl rubber was purified by solution in toluene, repeated washing with distilled water, and precipitation in methanol.

The recipes and data are given in Tables VIII and IX. The cis-polybutadiene specimens (Table VIII) showed little absorption at either temperature. In many cases a decrease in weight was found. There is evidence (comparing E, K and L) that extraction of stearic acid accounted for some of the loss.

In the case of Butyl rubber (Table IX) the states of cure were generally about one-half those obtained with cis-polybutadiene. At 75°C., absorption was very gradual and, with the single exception of compound I, very slight up to 500 hours. But at 160°C. nearly all of the specimens showed evidence of indefinite absorption. Equilibrium absorption was found in only one case (P) where an unactivated resin cure was employed. The combined results suggest that most systems produce sparingly soluble or high molecular weight residues, but that these are not sufficient to cause high absorption at moderate temperatures or at high states of cure. In most instances it appears that the choice of curatives may best be made to suit other considerations.

Water Resistant Compounds

An initial objective of this study was to determine whether there exists, in principle, any barrier to the preparation of low water absorption vulcanizates from any of the elastomeric classes considered. Referring specifically to hot water absorption (that is, neglecting oxidation, which has not been considered in this work) the experience is sufficient to show that no fundamental impediment exists. Given the requisite polymer purity and the careful selection of compounding ingredients, it should generally be possible to keep absorption within moderate limits. State of cure and reinforcement have been shown to be important, sometimes even decisive, factors. Where water absorption is a critical consideration, the elastic modulus should be as high as possible, commensurate with other physical requirements. Maximum purity in all the ingredients is essential; the use of recipes with as few ingredients as possible will minimize chance contamination and simplify the diagnosis of such difficulties as may arise.

Table X shows compounds based on the various elastomeric types considered in this study. These recipes have no reference to specific applications and have not been evaluated in any respect other than water absorption. Their sole purpose is to show that low water absorption can be secured in all cases, even at very high temperatures, by application of the foregoing principles. The only case requiring comment is that of Butyl rubber. It has been shown that Butyl is by far the most water resistant of the polymers in terms of water permeability, and that low absorption can be secured at moderate temperatures without difficulty. At the higher temperature (160°C.), even though Butyl is the preferred polymer for curing bags and bladders, where such conditions are encountered, it is not easy to prevent gradual indefinite swelling. Activated resin cures have been shown in earlier work (3) to take up substantial quantities of water, owing probably to the formation of zinc salts in several systems, or to the presence of stannous chloride when this type of activation is used. Since the state of cure in Butyl vulcanizates is usually low compared to other classes of rubber, attention to purity and to high reinforcement is particularly important for this case.

Acknowledgement

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TABLE VIII

CURING SYSTEMS

Base Polymer: Cis Polybutadiene

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	–
Stearic Acid	1	1	1	1	1	1	1	1	1	1	3	–	–	–	–
Benzothiazyl Disulphide	2	–	–	–	–	1	1.5	–	–	1	–	–	–	4	–
Mercaptobenzothiazole	–	–	1	–	1.5	–	–	–	–	1	1.5	1.5	–	–	–
Diphenyl Guanidine	0.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tetramethylthiuram Disulphide	–	0.5	–	–	1.5	–	–	2.5	1	–	1.5	1.5	–	–	–
N-Cyclohexyl-2-Benzothiazole Sulphenamide	–	1	–	–	–	–	–	1	–	–	–	–	–	–	–
Zinc Dimethyldithiocarbamate	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–
Dipentamethylene Thiuram Tetrasulphide	–	–	–	4	–	–	–	–	–	–	–	–	–	–	–
Tellurium Diethyldithiocarbamate	–	–	–	–	–	1.5	–	–	–	–	–	–	–	–	–
Tetramethylthiuram monosulphide	–	–	–	–	–	–	0.5	–	–	1	–	–	–	–	–
Sulphur	1.5	1.5	1.5	–	1.5	1.5	1.5	0.5	–	2	1.5	1.5	1	2	–
4,4 Dithiomorpholine	–	–	–	–	–	–	–	–	3	–	–	–	–	–	–
p-Quinone Dioxime	–	–	–	–	–	–	–	–	–	–	–	–	2	2	–
Red Lead	–	–	–	–	–	–	–	–	–	–	–	–	10	–	–
DiCumyl Peroxide	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.6
Cure: 100 min. at 145°C.															
M50 (p.s.i.)	95	96	102	118	118	115	96	105	98	116	94	94	97	95	98
Equilibrium Wt. Increase (%):															
250 hr. at 75° C.	0.8	0.3	-0.1	-1.4	-1.4	-0.4	-0.2	-1.2	2.3	-2.1	-1.2	-0.7	2.0	1.8	0.5
250 hr. at 160°C.	-0.1	-1.0	-1.5	-2.5	-2.7	-1.9	-1.4	-3.1	-0.8	-2.2	-4.1	-1.6	-1.1	-0.4	-0.6

TABLE IX

CURING SYSTEMS

Base Polymer: Butyl 200

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5	5	5	5	5	5	5	–	5	–	–
Stearic Acid	1	1	1	1	1	1	1	1	1	1	3	–	–	–	–	–
Benzothiazyl Disulphide	2	–	–	–	–	1	1.5	–	–	1	–	–	–	–	–	–
Mercaptobenzothiazole	–	–	1	–	1.5	–	–	–	–	1	1.5	1.5	–	4	–	–
Diphenyl Guanidine	.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tetramethylthiuram Disulphide	–	.5	–	–	1.5	–	–	2.5	1	–	1.5	1.5	–	–	–	–
N-cyclohexyl-2-benzothiazole sulphenamide	–	1	–	–	–	–	–	1	–	–	–	–	–	–	–	–
Zinc Dimethyldithiocarbamate	–	–	1	–	–	–	–	–	–	–	–	–	–	–	–	–
Dipentamethylene thiuram tetrasulphide	–	–	–	4	–	–	–	–	–	–	–	–	–	–	–	–
Tellurium diethyldithiocarbamate	–	–	–	–	–	1.5	–	–	–	–	–	–	–	–	–	–
Tetramethylthiuram monosulphide	–	–	–	–	–	–	.5	–	–	1	–	–	–	–	–	–
Sulphur	1.5	1.5	1.5	–	1.5	1.5	1.5	.5	–	2	1.5	1.5	1	2	–	–
4,4′ Dithiomorpholine	–	–	–	–	–	–	–	–	3	–	–	–	–	–	–	–
p-Quinone Dioxime	–	–	–	–	–	–	–	–	–	–	–	–	2	2	2	–
Red Lead	–	–	–	–	–	–	–	–	–	–	–	–	10	–	10	–
Dimethylol phenol resin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	10
Cure: 100 min. at 145°C. except P: 100 min. at 171°C.																
M50 (p.s.i.)	44	51	52	51	55	63	56	51	50	60	62	57	45	42	20	26
Wt. Increase (%) after:																
500 hr. at 75°C.	1.2	1.5	1.2	1.5	1.1	0.6	0.9	1.5	6.2	1.0	1.1	1.7	2.5	2.5	2.2	1.0
250 hr. at 160°C.	12+	15+	15+	20+	12+	10+	10+	15+	29+	11+	9+	15+	12+	19+	18+	5

TABLE X

	A	B	C	D	E
Polysar Kryflex 200	100	–	–	–	–
Polysar Krynac 800	–	100	–	–	–
Cis Polybutadiene	–	–	100	–	–
Polysar Butyl 600	–	–	–	100	–
EPR	–	–	–	–	100
Zinc Oxide	5	5	5	–	–
Stearic Acid	1	1	1	–	–
Hyd. Mg. Silicate	50	–	–	–	–
Calcined Clay	50	–	–	–	–
pptd. $CaCO_3$ + 2% Tall Oil	–	–	50	–	–
FEF Black	–	–	50	65	50
MT Black	–	75	–	–	–
DiCup R	–	–	–	–	4
Dimethylol Phenol Resin	–	–	–	10	–
Benzothiazyl Disulphide	1.25	1.5	1	–	–
Tetramethyl Thiuram Monosulphide	–	0.5	–	–	–
Sulphur	2.5	1.5	2	–	–

Cure: 100 min. at 145° C. except D: 100 min. at 171° C.

	A	B	C	D	E
M_{50} (p.s.i.)	169	150	147	150	168
Wt. Increase % at 250 hr., 160° C.	3.5	12.5	5.8	5.7	4.5