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*I hereby recommend that the thesis prepared under my supervision by* Henno Keskküla

*entitled* A Study of Chloroprene - Methacrylic Acid Copolymers

*be accepted as fulfilling this part of the requirements for the degree of* Doctor of Philosophy

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# A STUDY OF
# CHLOROPRENE-METHACRYLIC ACID COPOLYMERS

A dissertation submitted to the

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by

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# I. INTRODUCTION

Chloroprene-methacrylic acid copolymers as prospective coating materials for the high speed aircraft, were first prepared and investigated by the writer in 1951. (23) The increasing speeds of military aircraft and the resulting failure of conventional coating materials and of metal surfaces when exposed to precipitation at high speeds have produced an urgent need for such coatings. Previous work at this and other laboratories established that satisfactory protection would be provided by coatings which are capable of absorbing the shock of impinging particles without erosion, and which at the same time possess satisfactory adhesion to metal. In a preliminary evaluation (23) a two coat system of chloroprene-methacrylic acid copolymers was observed to exhibit promising characteristics required by an erosion resistant coating.

The nature of chloroprene-methacrylic acid (C-MA) copolymers changes as the acid content is varied. The copolymers which contain less than 20 percent acid are tough, rubber-like materials, while those with more than 20 percent acid become leather-like and possess low elasticity. In this two-coat finish system, the primer is rich in methacrylic acid to provide the necessary adhesion to aluminum. A copolymer containing 27 percent acid has exhibited adhesion values to aluminum of 1,880 pounds per square inch, as determined with the University of Cincinnati ultracentrifuge (29). In early phases of this coating development, it was realized that a resilient, elastic coating exhibits far superior erosion resistance to a hard, brittle resinous material. As a consequence, C-MA copolymer low in acid, was chosen for topcoat application, to protect the primer through its ability to absorb the energy of water impact and prevent erosion. C-MA copolymers of about 60 percent conversion and containing 15 percent acid have exhibited the most satisfactory rain erosion resistance, as determined by the Cornell Rain Erosion Tester (23). The preliminary test results have warranted a more comprehensive investigation of the chloroprene-methacrylic acid system.

The C-MA copolymers are prepared in an emulsion system, using potassium persulfate as an initiator, and sulfur as a modifier. The product obtained as a latex is coagulated, washed, dried and finally plasticized by milling with tetramethyl thiuram disulfide. This plasticized copolymer is brought into solution by using ketone solvents; cyclohexanone and methyl isobutyl ketone have proven to be most satisfactory.

At the outset it was assumed that a material possessing a high tensile strength, high elongation at break and a low permanent set, would exhibit favorable erosion resistance. No such simple correlation with rain erosion phenomenon has been realized. There are, however, many important properties of elastomers like impact strength, fatigue, damping or internal friction which bear little relation to ultimate strength and extensibility (28). These considerations lead to the necessity of a study of the mechanical behavior of C-MA copolymers from a more fundamental stand-point than an empirical attempt at correlation with the tensile strength and elongation at break.

This dissertation concerns itself with a detailed study of chloroprene—methacrylic acid copolymers. To gain some insight into the nature of copolymers the relative reactivity ratios were determined for both bulk and emulsion systems. The mechanical behavior of various polymer compositions and curing systems was depicted by creep functions, obtained by applying a constant stress and recording the time dependence of the deformation. These creep functions were studied in detail and utilized in the determination of the state of cure and aging. Also physical properties like tensile strength, ultimate elongation and permanent set have been investigated in connection with the studies on creep behavior.

## II. HISTORICAL

### A. Neoprene and Copolymers of Chloroprene

In 1931 Niewland and his co-workers (34) announced the production of vinylacetylene from acetylene. Simultaneously Carothers and his associates (10) announced the successful conversion of vinylacetylene to 2-chlorobutadiene and polymerization of the latter compound to a rubberlike material. Since these disclosures, polychloroprene has developed into a highly important commercial product. All the commercial polychloroprenes are similar to natural rubber in many properties but are superior in resistance to the deteriorating effects of sunlight, atmospheric oxygen and ozone, aging, heat, flame, oil, solvents, and are also less permeable to gases. Because of these special properties, polychloroprene has found wide usage despite its higher cost.

Copolymerization can be further utilized to modify and improve the favorable properties of polychloroprene. Since the fundamental work of Carothers, a number of investigators have explored chloroprene copolymerization. In 1937, Chemische Forschungsgesellschaft (11) announced the polymerization of chloroprene in the presence of partly saponified polyvinyl acetate. Subsequently Roedel (37) showed that chloroprene can be copolymerized in a sulfur modified, emulsion system with various vinyl monomers such as methacrylic acid esters, methacrylic anhydride and methacrylonitrile. In this patent by Roedel, the possibility of copolymerizing chloroprene with methacrylic acid was included. However, no examples or data were given and furthermore the possibility of having less than 25 percent methacrylic acid derivative in the copolymer was considered of little interest due to the similarity to the unmodified parent substance. Mighton (32) obtained improved rubberlike products by copolymerizing alpha unsaturated, alpha-beta dicarboxylic esters with chloroprene. Upon proper compounding and curing, the copolymer exhibited good stress-strain properties, and good solvent and oil resistance. Superior copolymers of chloroprene, butadiene and vinyl compounds have been disclosed by Clifford and Wolfe (12). Wagner (42) copolymerized acrylonitrile with chloroprene in good yields, to obtain a material with improved solvent resistance in cured states. Other investigations of chloroprene copolymerization include these of Alfrey (3), Elmore (16) and Wall (47).

## B. Copolymerization

The fundamental work of Mayo, Lewis and Walling(30, 31) has afforded considerable understanding of the copolymerization phenomenon. The preliminary important contribution, however, was made in 1941 by Wall (45), who pointed out that the chemical composition would depend only on the relative reactivities of the two monomers toward the two radicals. Subsequently, Mayo and Lewis were able to give a fuller meaning to relative reactivitives by deriving and confirming the copolymer composition equation:

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1\ )}{(M_2\ )} \frac{r_1M_1 + M_2}{r_2M_2 + M_1}$$

where $M_1$ and $M_2$ represent the molar concentrations of the two monomers, $r_1$ and $r_2$ are the corresponding relative reactivities and $d(M_1) / d(M_2)$ is the ratio of molar concentrations of the two monomers in the resulting copolymer.

Aside from steric effects, the most important factors to be considered in this presentation are the polarity of radical and monomer and the relative resonance stabilization of the radicals. An attempt to find a set of characteristic numbers in terms of these two effects has been made by Alfrey and Price (35, 36). It is suggested that the various influences are separable and can be represented by "Q" value, which indicates the mean reactivity of a monomer, and by e, which is the measure of the effective charge on the end of the radical. In this scheme, the copolymerication ratios can be given by the following equations:

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp \left(-e_1 (e_1-e_2)\right)$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp \left(-e_2 (e_2 - e_1)\right)$$

When applying the Q and e equations to the data on dienes, no satisfactory results have been obtained. In deriving the Q-e equations, the equality of effective charges for monomer and radical was assumed. In dienes, particularly when the inductive effect of a substituent decreases the electron availability, a modification has to be introduced (47).

$$r_1 = \frac{Q_1}{Q_2} \text{ exp. } (-e_1^* (e_1 - e_2))$$

where $e^*$ represents the e value for the radical. For chloroprene, Simha (39) reported the following values: $Q = 2.2$, $e = 0.9$ and $e = -0.6$.

Copolymerization in emulsion systems has been treated by Wall (46), who has postulated that the relative reactivities of a copolymer system are changed by the distribution coefficient between oil and aqueous phases. If one of the monomers is quite water soluble, the portion of the monomer which is present in aqueous solution is not available for reaction, and hence this monomer will exhibit apparently lower copolymerization reactivity in emulsion. These conclusions have been borne out by the work of Fordyce and Chapin (17) on styrene-acrylonitrile system and of Fordyce and Ham (18) on styrene-itaconic acid copolymerization.

## C. Viscoelastic Properties of Polymers

Rubber-like substances are unique in their ability to undergo large, almost reversible deformations under the application of relatively small stresses. Under the action of a stress the total time and temperature dependent elastic deformation comprises three effects, and may be expressed generally as (15, 7):

$$D(t\ T) = D_{oel} + D_{hel} + D_{visc.}$$

where $D_{oel}$ is the ordinary elastic deformation, exhibited also by inorganic crystals and metals, due to reversible changes in the mean distance between structural elements. The high elastic deformation $D_{hel}$, depends on the degree of rearrangement of molecular chains. It is determined by the statistical equilibrium between the orienting action of the external field and the disturbing action of the heat motion of the chains. The last, irreversible term, $D_{visc}$, refers to viscous flow.

A creep function is obtained by recording the complex time dependent deformation under the application of a constant stress at constant temperature. If, instead of applying a constant stress at zero time a constant deformation is applied, then it is found that a gradual decrease of load or relaxation takes place. Dynamic properties of a polymer are determined by subjecting it to forced or free vibration of a given frequency. Creep, stress relaxation and dynamic studies have shown by Kuhn (25), Gross (20) and by Tobolsky and Dunell (14) to be closely interrelated.

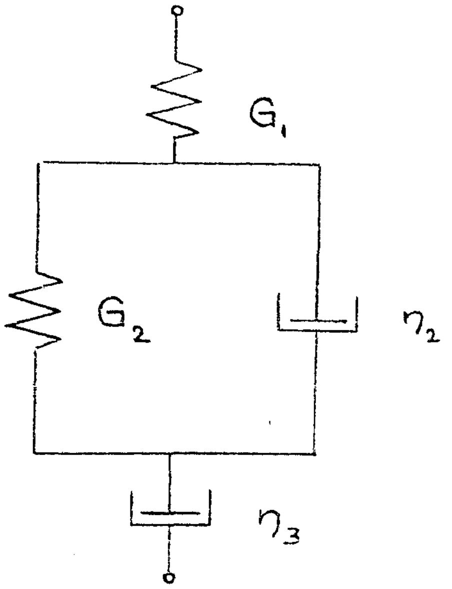
The classical experiment on creep was carried out by Weber (43) at Gottingen in 1835. Whilst investigating the mechanical properties of raw silk filaments, Weber found that under application of a longitudinal load the filament showed immediate elastic extension which gradually increased with time. Weber also observed the creep recovery following the removal of the load. Both these effects were denoted by the term "elastische Nachwirkung".

F. Kohlrausch can be considered as one of the first investigators to study primary creep experimentally. Kohlrausch's tests on rubber threads (24) represent the first systematic study of the creep properties of high polymers. He studied the residual twist due to deformation through constant angle, the longitudinal creep under constant load followed by measurement of the recovery after removal of load and also the "memory" effects after complex loading history.

Two years before Kohlrausch published his work, Boltzmann (8) treated the primary creep and creep recovery in a theoretical fashion. In this paper Boltzmann introduced the superposition principle, stating that the deformation at any instant of a body manifesting creep is due not only to the load acting at that instant but to the entire previous loading history.

In order to account for the mechanical properties of high polymers in terms of interatomic forces, one has to set up some kind of structural model which would explain in simple terms the structure and mechanism of deformation . Both Boltzmann and Maxwell gave this problem their attention and advanced purely qualitative theories based on concepts of atomic structure (26). Later Maxwell's ideas were given a mathematical formulation by Wiechert. The first mechanical model, however, was not proposed until 1902 by Poynting and Thomson to illustrate the relaxation properties of glass. Since that time a great number of such models have been proposed (27).

The very simplest mechanical behavior, which can be expected from an amarphous polymer, is that represented by the model of Figure I. (Model A) (2).



Model A: Instantaneous elasticity, retarded elasticity and flow.

Model A: Instantaneous elasticity, retarded elasticity and flow.

$G_1$ represents the instantaneous elastic response. The second mechanism ($G_2$, $\eta_2$) is the retarded elastic response caused by the uncurling of molecular chains, while the third term, $\eta_3$, represents the flow mechanism by a viscosity term.

The deformation-time curve at constant stress for Model A is of the general form:

$$\gamma = S\left[\frac{1}{G_1} + \frac{1}{G_2}\left(1 - e^{-t/\tau}\right) + \frac{1}{\eta_3} t\right]$$

where: $\gamma$ is the strain, S is the stress, $G_1$ and $G_2$ represent the instantaneous and retarded moduli respectively, $\tau$ is the retardation time, $\eta_3$ is the viscosity term, and t the time.

Model A can be considered only as a first approximation in relating the mechanical behavior of high polymers. The idea of a spectrum of retardation times has to be introduced for the configurational elasticity, as one would expect that each different size of molecular segment would exhibit a different retardation time for the changes of its shape. The corresponding model would have a continuous set of retarded elements in series. Then the deformation-time curve at the constant stress, S, is given by the integral expression:

$$\gamma = S\left[ \frac{1}{G_1} + \int_0^\infty J(\tau)\left(1 - e^{-t/\tau}\right) d\tau + \frac{1}{\eta_3} t \right]$$

where

$$J(\tau) = \frac{1}{G(\tau)}$$

If a material possessing a wide distribution of retardation times is investigated by experiments whose time scales are all the same order, some of the retarded elastic mechanisms will appear as ideal elastic responses and some will appear as flow. Only those having retardation times in the same order of magnitude as the experimental time scale will exhibit their true elastic character. Consequently, part of the continuous set of retarded elements will be represented by a single retarded element of intermediate $\tau$. By introduction of more retarded elements, an empirical model (Model E) can be constructed, which will approximate the behavior of the continuous model more closely than is possible with the four parameter model, for a given time scale (2).

A theoretical interpretation of creep and related phenomena, in terms of molecular processes requires a satisfactory mathematical representation of the experimental data. Two general methods have been suggested to characterize deformation processes.

The analytical approach which utilizes the empirical model (Model E), consisting of only one retarded element has not been found satisfactory in order to cope with a spectrum of retardation times. Consequently, a number of retarded elements will be necessary to completely describe the creep behavior of a polymer. Simha (38) has shown that a distribution function G ($\tau$) for the retardation times can be derived, and subsequently further approximations of the distribution function (2) have been proposed.

The integral approach, discussed by Buchdahl and Nielsen (9), utilizes the relation, first suggested by Nutting. The integral approach does not attempt the separation of total deformation into different processes.

## III. RESULTS AND DISCUSSION.

### A. Copolymerization of Chloroprene and Methacrylic Acid.

1. Preparation of the C-MA Copolymers. - Copolymers of chloroprene and methacrylic acid have been prepared and studied, containing 5 to 25 percent methacrylic acid. The following typical emulsion recipe was employed:

| | |
|---|---|
| Monomers | 100 gms |
| Redistilled water | 200 gms |
| Triton X-301 (emulsifier) | 9.3 gms. |
| Sulfur (modifier) | 0.3 gms. |
| Potassium persulfate (initiator) | 0.304 gms. |

Polymerization was carried out both at 30° C and 50° C. As expected, the rate of polymerization was found to depend on the temperature. Utilizing 40 percent methacrylic acid in the charge, at 30° C, 55 percent conversion was achieved in 5 hours, while at 50° c for a similar charge 80 percent conversion was realized in 90 minutes. Most polymerizations have, however, been carried out at 30° C, as the preliminary results (23) indicated that polymers of superior physical properties are attained by utilizing the lower polymerization temperature, presumably by obtaining a more linear polymer. For polychloroprene the effect of polymerization temperature has been investigated by Walker and Mochel (44), who reported markedly improved polymer characteristics for decreased polymerization temperatures.

The rate of polymerization was also found to depend on the monomer charge ratio. At 30° C, ten and thirty percent methacrylic acid charge produced 74 and 64 percent conversion copolymers respectively, employing identical reaction times.

The resulting copolymer latices were shortstopped and coagulated in the usual manner (see experimental section). After drying to constant weight in vacuo, the copolymers were plasticized with 2-1/2 % tetramethyl thiuram disulfide to improve solubility. The best solvents for the copolymer were cyclohexanone, methyl isobutyl ketone and dioxane. Plasticizing was followed by addition of antioxidants and fillers on a rubber mill. Subsequent solution on a ball mill resulted in lacquers which on addition of curing agents were ready for application.

2. Proof of Copolymer Existence. - Chloroprene has found to outstrip methacrylic acid in its rate of entering the polymerization reaction. Despite the difference in reactivity between chloroprene and methacrylic acid in emulsion, it has been established that true copolymerization is achieved.

Polychloroprene and polymethacrylic acid have found to be incompatible. Polychloroprene is a typical rubber and easily milled, while polymethacrylic acid is hard, brittle resinous material, completely unworkable on a rubber mill. Attempts to mill even small portions of polymethacrylic acid into polychloroprene have been quite unsuccessful. The C-MA copolymers have found to be workable on a rubber mill, even at relatively high methacrylic acid contents (ca.30 percent) in the copolymer.

Further evidence of the existence of a true copolymer is presented by the extraction data of gum samples of the C-MA copolymer, containing 12.7 percent acid. The Soxhlet extraction with methanol, in which polymethacrylic acid is soluble, for 48 hours, yielded the extracted copolymer containing 12.2 percent acid as determined by chlorine analysis. Extraction with petroleum ether yielded also a product containing 12.2 percent acid. This extraction data would imply that a true chloroprene-methacrylic acid copolymer exists, exhibiting a reasonably homogeneous composition, since there was no indication of fractional extraction of the copolymer in the two characteristically different solvents, methanol and petroleum ether.

3. Effect of Composition and Conversion.- The effect of composition and conversion on the mechanical properties has been investigated for the copolymers prepared at 30° C. In the range of compositions and conversions investigated, the optimum properties are achieved with copolymers containing 12 to 16 percent acid and of conversions between 50 and 60 percent. It can be observed from the data in Table I that for compositions above 16 percent acid, tensile strength and elongation at break exhibit a downward trend. A converse trend exists in the permanent set data.

## Table I

The C-MA Copolymer Properties*: Effect of Composition.

| Conversion % | Acid % | Tensile psi. | Elongation at break % | ASTM set % |
|---|---|---|---|---|
| 61 | 11.6 | 4730 | 740 | 17 |
| 52 | 12.4 | 6030 | 730 | 13 |
| 60 | 12.5 | 5320 | 840 | 14 |
| 61 | 14.3 | 5530 | 710 | 14 |
| 61 | 15.5 | 6360 | 670 | 13 |
| 64 | 15.5 | 6020 | 650 | 18 |
| 66 | 15.9 | 5730 | 670 | 21 |
| 65 | 16.1 | 5020 | 640 | 18 |
| 68 | 16.2 | 5650 | 620 | 34 |
| 57 | 16.8 | 5210 | 575 | 44 |
| 68 | 20.9 | 4980 | - | - |

*/ 1 part MgO was added just prior to use as a slurry. Films air-dried one day, baked 2 hours at 120° C.

The effect of conversion becomes apparent from the data of Table II. Gum specimens of the C-MA copolymer, containing 15 percent acid exhibit tensiles of 1350 and 2680 for 29 and 55 percent conversion respectively; similar change in tensile is apparent for copolymers of 21 percent acid. On the other hand, data in Table I seem to indicate that conversion above 65 percent will result in poorer elastic properties, presumably because of increased branching and cross-linking during polymerization.

### Table II

The C-MA Copolymer Properties*; Effect of Conversion.

| Conversion % | Acid % | Tensile psi | Elongation at break % | ASTM set % |
|---|---|---|---|---|
| 33 | 6.4 | 980 | 1600 | 72 |
| 29 | 15 | 1350 | 1140 | 75 |
| 55 | 15 | 2680 | 840 | 66 |
| 33 | 21 | 3330 | 770 | 60 |
| 48 | 21 | 3820 | 690 | 45 |

*/ Copolymers air-dried for 20 days. No curing agent added. Four parts tuads milled in to attain complete solubility.

4. Modification and Milling.- Sulfur has been used as a modifying agent throughout this investigation to render the polymer soluble in appropriate solvents for lacquer application. The mechanism of sulfur modification for polychloroprene has been investigated by Mochel and Peterson (33), who concluded that sulfur enters the polymer as a comonomer because some thirty sulfur atoms are combined in each polymer molecule, some 2 to 6 sulfur atoms in a row, randomly distributed through the chain. On subsequent treatment with tetramethyl thiuram disulfide, the sulfur-sulfur bonds are broken and the improved solubility of the polymer achieved by reducing the average molecular weight below the critical value of gelation.

Presumably a similar mechanism of modification prevails for the C-MA copolymer. In the preliminary investigation the use of 1.5 to 3 percent sulfur produced no apparent change in solubility or in the polymer properties (23). Subsequently, the effect of variations in the method of introducing the sulfur modifier into the polymerization system was studied with 1/4 and 1/2 part sulfur. In one method, the sulfur was first dissolved in carbon disulfide, then dispersed in the aqueous phase and the carbon disulfide removed by boiling, followed by the addition of monomers and the initiator. When this method was used instead of the common method of dissolving the sulfur in the chloroprene monomer, the polymerization rate was approximately doubled. No significant difference in the tensile properties of the resultant polymers was observed (Table III). The difference between 1/4 and 1/2 part sulfur as reflected in polymer properties also was very slight.

Table III

The C-MA Copolymer Properties*; Effect of Sulfur Modification.

| Parts sulfur | Method of Addition of Sulfur** | Conversion % | Acid % | Tensile psi. | Elongation at break % | ASTM set % |
|---|---|---|---|---|---|---|
| 1/4 | Chloroprene solution | 71 | 7.8 | 1670 | 910 | 10 |
| 1/2 | " | 71 | 7.8 | 1360 | 800 | 7 |
| 1/4 | $CS_2$ | 55 | 4.6 | 1200 | 990 | 10 |
| 1/2 | " | 79 | 7.8 | 1380 | 910 | 15 |
| 1/2 | Ball milled | 68 | 8.3 | 1240 | 980 | 8 |

*/ No curing agent used.

**/ Methods of sulfur addition:
Chloroprene solution: Dissolved in the chloroprene phase before it was dispersed in the water phase.

Ball milled: Dispersed in the water phase by ball milling with water plus Triton X-301 before potassium persulfate and monomers were added.

$CS_2$: Added to water phase as solution in $CS_2$; before adding potassium persulfate and monomers, $CS_2$ is flashed off.

The effect of variations in milling of the copolymer has been investigated. It is evidently not subject to variations in treatment within reasonable limits. Plasticizing for 5 minutes with moderately tight rolls effects the desired improvement in solubility without significant change in film properties from those of the polymers not subjected to milling ( Table IV). However, milling for 20 minutes caused a significant decrease in tensile strength and an increase in permanent set. Milling for even a short time with excessively tight rolls caused curing on the mill as evidenced by grainy solutions, low tensile and elongation.

Table IV.

The C-MA Copolymer Properties*; Effect of Milling.

| Conversion % | Acid % | Polymer** treatment | Nature of film | Tensile, psi. | Elongation at break,% | ASTM set,% |
|---|---|---|---|---|---|---|
| 71 | 7.8 | a | smooth | 1670 | 880 | 8 |
| 71 | 7.8 | b | fairly s. | 1000 | 570 | 5 |
| 71 | 7.8 | c | smooth | 1670 | 910 | 10 |
| 55 | 4.6 | a | smooth | 1620 | 920 | 8 |
| 55 | 4.6 | b | fairly s. | 760 | 670 | 4 |
| 55 | 4.6 | c | smooth | 1200 | 990 | 10 |
| 88 | 10.8 | c | rough | 2300 | 690 | 14 |
| 88 | 10.8 | d | smooth | 1670 | 750 | 26 |

*/ No curing agent used.
**/ Polymer Treatment:
- (a) No additional milling after phenyl beta napthylamine added; Tuads added as slurry.
- (b) 15 minutes additional milling with very tight rolls without plasticizer; Tuads added as a slurry.
- (c) Tuads milled in for 5 minutes with moderately tight rolls.
- (d) Tuads milled in for 20 minutes with moderately tight rolls.

5. Copolymer Stability.- There is evidence that C-MA copolymers are subject to free radical initiated simultaneous degradation and cross-linking processes on storage, common to all rubbers. Accordingly, one part of phenyl beta naphthylamine as an antioxidant is milled into the polymer. When not treated with phenyl beta naphthylamine degradation of the polymer is evidenced by the evolution of hydrogen chloride. Even when the anti-oxidant is incorporated, the polymer will undergo some stiffening on prolonged standing, accompanied with reduction in solubility. This decrease in solubility is readily overcome by milling, without any apparent detrimental effect on polymer properties. Corresponding stiffening of the films cast from the lacquer solutions will be discussed in a later section of this report. The shelf stability of the lacquers has been found to be satisfactory as evidenced by no appreciable change in the lacquer viscosity on prolonged periods of storage (23).

6. Copolymer Cure.- The C-MA copolymers were cured with a number of inorganic and organic compounds. Heat cures were affected with metal oxides like magnesia, zinc oxide and litharge and with magnesium carborate for the primer copolymer (high acid and conversion). A number of organic compounds and also zinc oxide and magnesia were found to produce varying degrees of air cure. Aromatic diamines and polyhydroxy benzenes were found to be the most effective organic compounds. The effect of these curing agents will be discussed in detail in connection with the discussion on viscoelastic properties.

7. Kinetics of Copolymerization .- To gain some insight into the nature of the copolymer, the extent to which chloroprene and methacrylic

acid enter into polymerization has to be considered. Consequently, relative reactivity ratios have been determined for both emulsion and bulk polymerization. The results are as follows: in emulsion at 30°C, $r_C$= 5.9±0.5, $r_{MA}$=0.14±0.05; in bulk at 30°C, $r_C$=1.4±0.5, $r_{MA}$=0.16±0.07. These relative reactivity ratios were calculated from the data of the copolymerization experiments, carried out

from the data of the copolymerization experiments, carried out

with different initial monomer charges. The method of calculation has been developed by Mayo and Lewis (30), using the integrated form of the copolymer composition equation to adjust for the appreciable drift in monomer concentration, if polymerization is carried to relatively high conversion. They corrected for conversion utilizing the following equation:

$$r_2 = \frac{\log \frac{M_2^o}{M_2} - \frac{1}{p} \log \frac{1 - p\frac{M_1}{M_2}}{1 - p\frac{M_1^o}{M_2^o}}}{\log \frac{M_1^o}{M_1} + \log \frac{1 - p\frac{M_1}{M_2}}{1 - p\frac{M_1^o}{M_2^o}}}$$

where p=(1-$r_1$) / (1-$r_2$), $M_1^o$and $M_2^o$ are the initial molar concentrations of the two monomers, and $M_1$ and $M_2$ are the moles of the monomers unpolymerized at the end of the polymerization. The constants $r_1$ and $r_2$ were evaluated graphically. The intersections of the straight lines for different experiments on $r_1$ versus $r_2$ plot, gave unique solution for $r_1$ and $r_2$. The size of the area into which these intersections fell gave indication of the error involved in the values of $r_1$ and $r_2$. The data utilized for these calculations are summarized in Table V.

Table V

Composition of the C-MA Copolymers

| Charge Wt. % methacrylic acid | Polymer Composition Wt.% Methacrylic Acid | Conversion % |
|---|---|---|
| Emulsion Polymerization(1) | | |
| 10 | 3.0 | 74 |
| 20 | 4.8 | 20 |
| 30 | 9.5 | 64 |
| 40 | 15.6 | 57 |
| 50 | 16.8 | 25 |
| 70 | 28.3 | 4.1 |
| 90 | 61.1 | 6.4 |
| Bulk polymerization (2) | | |
| 20 | 17.5 | 24 |
| 40 | 29.1 | 5 |
| 50 | 29.0 | 10 |
| 70 | 48.2 | 5 |
| 90 | 66.4 | 15 |

(1) Emulsion polymerization recipe: 100.5 gms redistilled water, 4.65 gms Triton X-301, 0.182 gms $K_2S_2O_8$, 50 gms monomers.

(2) Bulk polymerization recipe: 0.25 gms benzoyl peroxide, 50 gms monomers.

It is readily observed that there is a considerable difference in the relative reactivity ratios between emulsion and bulk systems. This result is not unexpected as methacrylic acid is quite water soluble: its concentration is effectively reduced in the polymerizing phase. Consequently methacrylic acid will exhibit an apparently lower copolymerization reactivity in emulsion. These results are in accordance with the treatment of Wall (46), who stated that the difference in reactivities between bulk and emulsion polymerization depends on the distribution coefficients between the oil and aqueous phases. The reactivities for emulsion polymerization are consequently a function of the monomer-water charge ratio.

The instantaneous monomer polymer composition relationship for both emulsion and bulk systems are depicted in Figure II. These curves are obtained by utilizing the copolymer compostion equation. Both curves are typical schematic copolymerization curves, where one reactivity ($r_1$) is less than unity and the other ($r_2$) is greater, i.e. monomer $M_2$ is more reactive than monomer $M_1$ with both types of growing free radical. It is also apparent from Figure II that for any monomer combination the copolymer from bulk polymerization has a more uniform composition than the one from the emulsion polymerization by containing less of the more reactive monomer, chloroprene, in its initial composition.

The instantaneous and average polymer composition are plotted as a function of conversion in Figure III and IV. These curves indicate the conversion at which the instantaneous composition starts to deviate appreciably from the average composition. These curves are restricted to a particular monomer charge. Thirty weight percent (30.7 mole percent) methacrylic acid was chosen as a representative initial charge. It can be observed from this representation that in emulsion system polymerization can be carried out to 60-65 percent conversion without appreciable drift in composition. In bulk for conversions up to 70 percent quite a homogeneous copolymer will result.

FIGURE II

CHLOROPRENE-METHACRYLIC ACID COPOLYMER

INSTANTANEOUS COMPOSITION CURVES

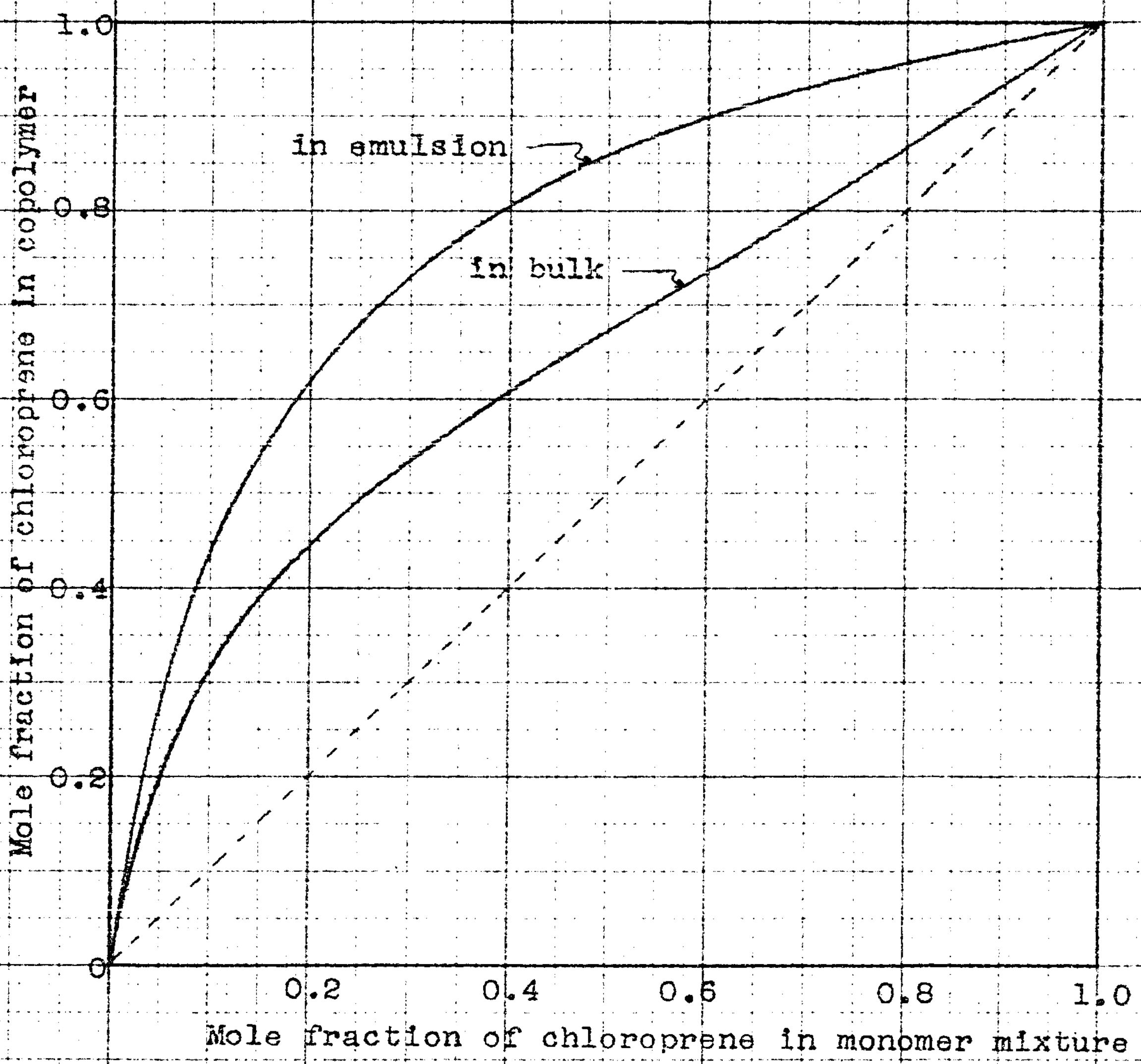
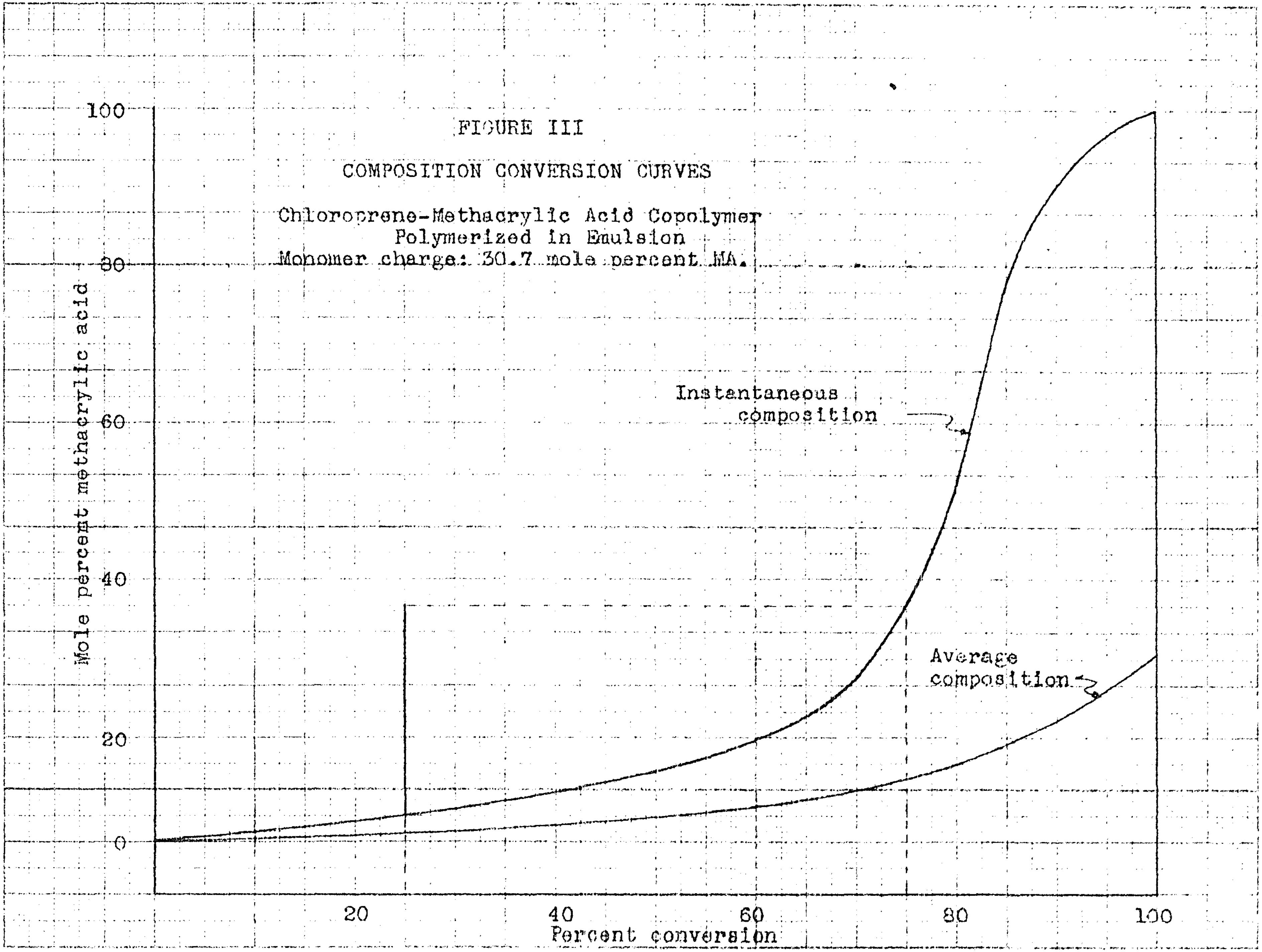


FIGURE III

COMPOSITION CONVERSION CURVES

Chloroprene-Methacrylic Acid Copolymer
Polymerized in Emulsion
Monomer charge: 30.7 mole percent MA.



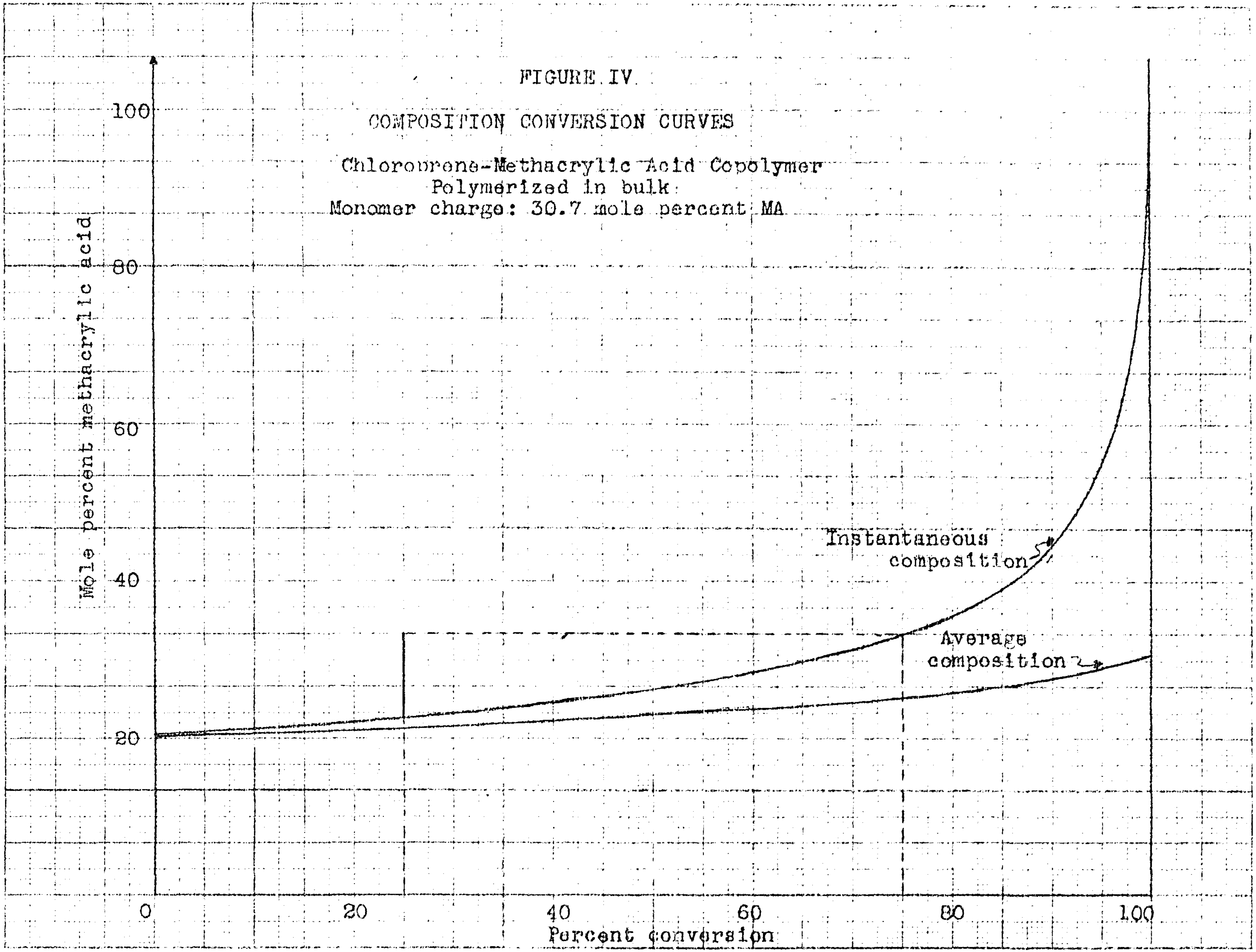


FIGURE IV

COMPOSITION CONVERSION CURVES

Chloroprene-Methacrylic Acid Copolymer
Polymerized in bulk
Monomer charge: 30.7 mole percent MA

The average copolymer composition versus conversion was calculated from the determined relative reactivity ratios, utilizing the equation given by Walling and Briggs: (48):

$$\frac{M_2}{M^\circ_2} = \frac{(M_1)^\Omega}{(M^\circ_1)^\Omega} \qquad \text{where:} \qquad \Omega = \frac{r_2 \frac{M^\circ_2}{M^\circ_1} + 1}{r_1 + \frac{M^\circ_2}{M^\circ_1}}$$

The curves for instantaneous composition versus conversion were obtained from the average composition calculations by plotting the moles of methacrylic acid ($M_1$) as a function of the total moles of monomer ($M_1$+$M_2$) in the copolymer. The slope of this curve will represent the instantaneous composition of the copolymer at the conversion corresponding to the abscissa of the point. These curves of the composition of the polymer forming instantaneously, plotted against the conversion are thus integral distribution curves of the copolymer composition.

Skeist (40) has analyzed the drift of copolymer composition as a function of conversion. According to Skeist the heavy vertical lines in Figure III and IV, indicating the portions of the curves which lie between 25 percent and 75 percent conversion, are called "interquartile ranges" and they give a numerical measure of the dispersion of composition in the high conversion polymer. The dispersion is satisfactory in both cases, especially for the copolymer obtained by bulk polymerization, exhibiting an "interquartile range" of 23 to 33 compared with 10 to 37 for emulsion system.

It is interesting to note that the instantaneous composition curves for bulk and emulsion systems approach 100 percent conversion in markedly different manners. The "bulk curve" has an infinite slope at finish, while the "emulsion curve" has a small finite slope. The characteristic differences are brought out more strikingly when the slopes of the integral distribution curves are plotted against the instantaneous copolymer composition. Figures V and VI are the resultant differential distribution curves showing the fraction of the final copolymer which possesses a composition in each range, i.e. the area under the curve between any two instantaneous compositions represents the fraction of the total charge that has been converted to copolymer of the given composition range. These differential distribution curves are supplied with an auxiliary conversion axis, indicating the corresponding conversions involved.

The differential distribution curve for the bulk system exhibits only a single peak, whereas the curve for the emulsion copolymer is U-shaped indicating cleavage of the copolymer composition into two different groups. It can be noted, however, that no appreciable cleavage will occur below 85 percent conversion.

## B. Mechanical Properties of the Chloroprene-Methacrylic Acid Copolymers.

1. Introduction.- In typical amorphous rubber the thread-like molecules are sufficiently long to become thoroughly entangled and do not interact strongly enough to become crystallized. The side chains in the molecule are relatively apolar. These side chains produce steric

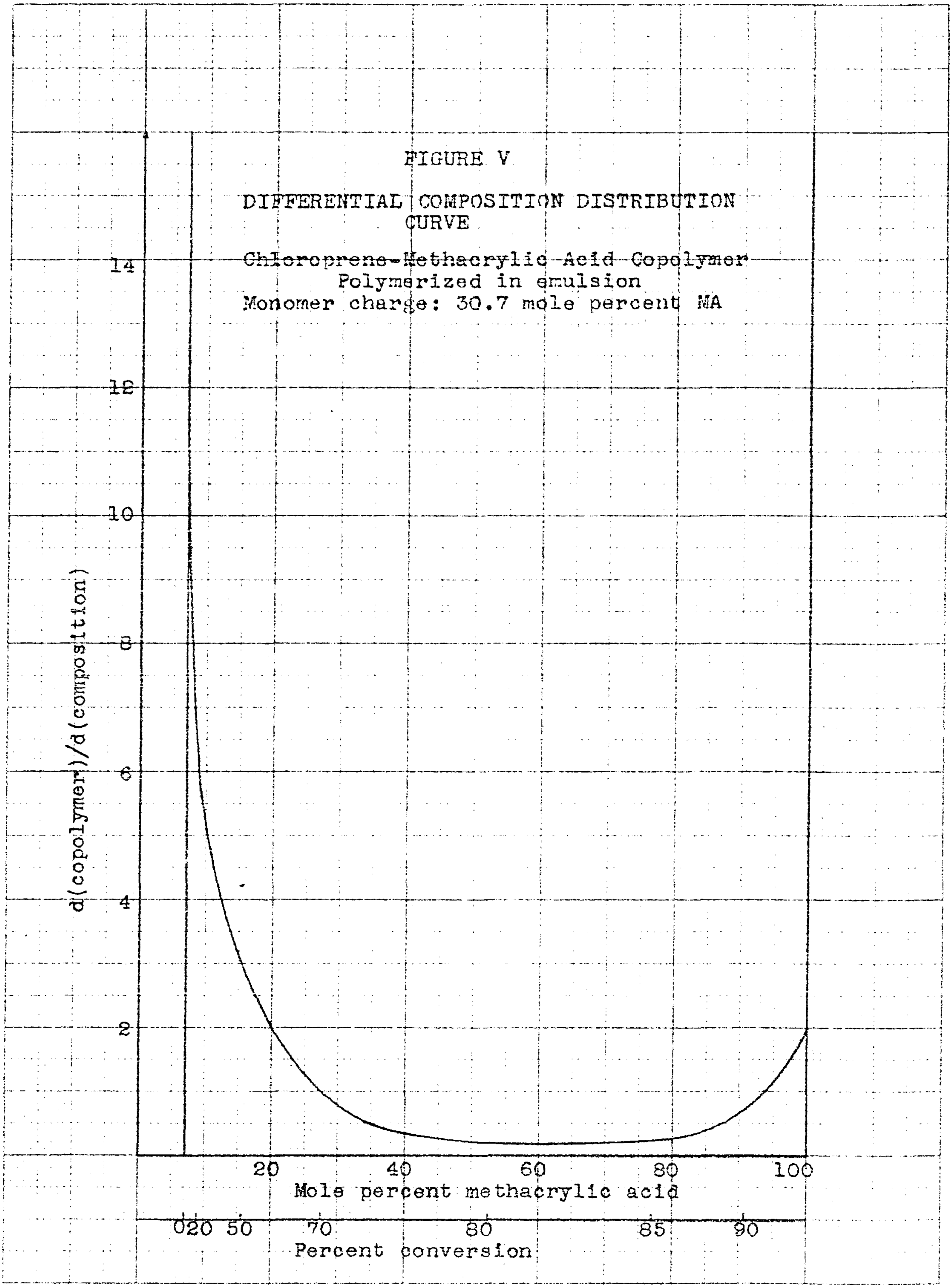


FIGURE V

DIFFERENTIAL COMPOSITION DISTRIBUTION CURVE

Chloroprene-Methacrylic Acid Copolymer
Polymerized in emulsion
Monomer charge: 30.7 mole percent MA

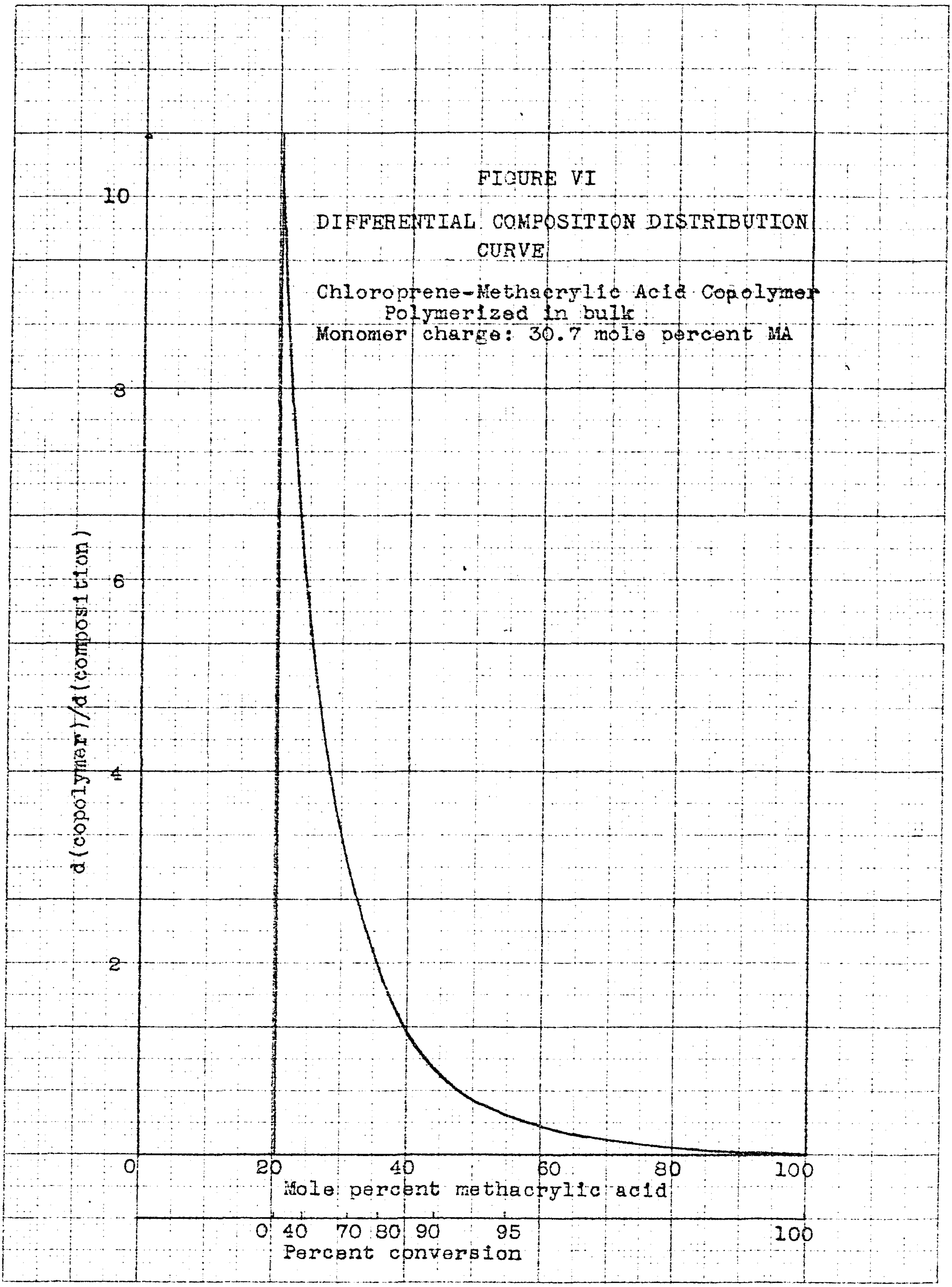


FIGURE VI

DIFFERENTIAL COMPOSITION DISTRIBUTION CURVE

Chloroprene-Methacrylic Acid Copolymer
Polymerized in bulk
Monomer charge: 30.7 mole percent MA

hindrance to free rotation, but also prevent easy crystallization by making close packing more difficult. In a rubber special kinks are introduced by double bonds which reduce the tendency to pack together and crystallize.

The chloroprene-methacrylic acid copolymers seem to possess some of the factors, which retard the rubber-like elasticity. The polar side groups are provided by the carboxyl groups, which induce interchain attractions and reduce the elasticity. However, the carboxyl groups present will at the same time repress the crystallization commonly observed in polychloroprene (19).

If an elastomer is subject to external stresses some motion of chain segments results. In amorphous polymers, the presence of stress causes a biased motion of chain segments, both micro and macro Brownian movements being affected. Micro Brownian movement is the change in the shape of the molecule, while macro Brownian movement is the movement of the whole molecule in relation to its neighbors. The stress-biased micro Brownian movement appears as a retarded elastic response, while the stress-biased macro Brownian movement is true flow. Consequently, under an external stress the following mechanisms will contribute to the total elastic deformation: instaneous elasticity, configurational or retarded elasticity and viscous flow.

Ultimate strength, elongation at break and permanent set or residual elongation are the mechanical properties which are most easily determined and are commonly reported in studies of high polymeric materials. These, of course, are also dependent on the structural and configurational properties of the polymer.

An amorphous rubber in uncured state will exhibit low tensile strengths and will extend to several thousand percent of its initial length before rupture occurs. Under external stress, tangling and interchain forces are generally not sufficient to prevent slippage of whole chains past one another to result in rupture. However, in case of sufficiently high molecular weight where reasonably high tensiles are realized, polymers break largely by the rupture of primary valence chains in contrast with the slippage of chains for lower molecular weight polymers.

An elastomer can be cured or vulcanized by introducing primary or secondary valence forces between the neighboring chains. These valence forces prevent the extensive slippage of chains past one another on an application of a force. The cured state can be generally characterized by improved ultimate tensile strength, high modulus and low permanent set as compared to the gum specimen. Interchain forces can also be provided by reinforcement with fine particles of carbon black. Irreversible sorption of chains on the surface of the carbon particles is believed to be responsible for this reinforcement.

Crystallization is another extremely important structural consideration of the mechanical behavior of high polymers. Upon stretching linear polymers will become oriented and by mutual van-der Waals' interaction, the formation of crystallites for a number of them will take place. The existence of these crystallites will virtually eliminate longitudinal slippage of chains and yield the polymer strong even at uncured states. Synthetic rubbers which do not crystallize when stretched, generally exhibit low strengths, except when compounded with reinforcing pigment such as carbon black. Conversely, reinforcing pigments interfere with crystallite formation and in general do not improve the strength of stretch crystallizable materials.

2. Viscoelastic Properties.- Viscoelastic properties of a great number of the C-MA copolymer free films have been investigated by studying their creep behavior. These films include both gum specimens and cured films. From these experiments it was hoped to arrive at an understanding of structural effects as well as the effect of curing agents and aging characteristics.

The creep behavior was conveniently studied by applying a constant stress and recording the time dependent deformation of the films at constant temperature. Constant stress was achieved by using a hyperbolic tension bob, first described by Dahlquist, Hendricks and Taylor (13).The profile of this bob is such that when lowered into water, the buoyant force exactly compensates the increase in stress, due to the decrease in cross-sectional area. The equation of the bob is:

$$r = \frac{1}{L_0 + H}\sqrt{\frac{W_0 L_0}{\pi d}}$$

where $r$ is the radius at height H, $W_0$ is the total initial load, $L_0$ is the length of the test specimen, and d is the apparent density of the bob which is made equal to that of the liquid (water).

Deformation data were used to compute compliances (inverse moduli) which were generally plotted against the logarithm of the time. A number of such semi-log plots are depicted in Figure VIII. Corresponding linear presentation is given in Figure VII. An advantage of this semi-log presentation will become apparent in the theoretical considerations of the distribution of retardation times. These plots are also more convenient as the variations at short times are readily observed. Frequently almost linear compliance-log time relationship are realized.

In analyzing a set of creep data, and attempting to fit this data to the empirical model (Model E), one finds that at least four retarded elements are necessary to depict the total deformation of the specimen for the time-scale from one to several thousand minutes, where the linear compliance-time plot approaches a straight line. The following procedure was employed in fitting the experimental data to the empirical model.

The general creep function can be written in the following form:

$$\frac{\gamma}{S} = J_1^E + J_2^E\left(1 - e^{-t/\tau^E}\right) + \frac{1}{\eta^E}t$$

where the superscript E implies that the corresponding parameters belong to the empirical model.

The effective viscosity can be subtracted from the total compliance giving rise to $\phi(t)$ :

$$\phi(t) = \frac{\gamma}{S} - \frac{1}{\eta^E}t = J_1^E + J_2^E\left(1 - e^{-t/\tau^E}\right)$$

As t approaches infinity the term $e^{-t/\tau^E}$ will approach zero and thus we can define $\Phi(\infty) = J_1^E + J_2^E$

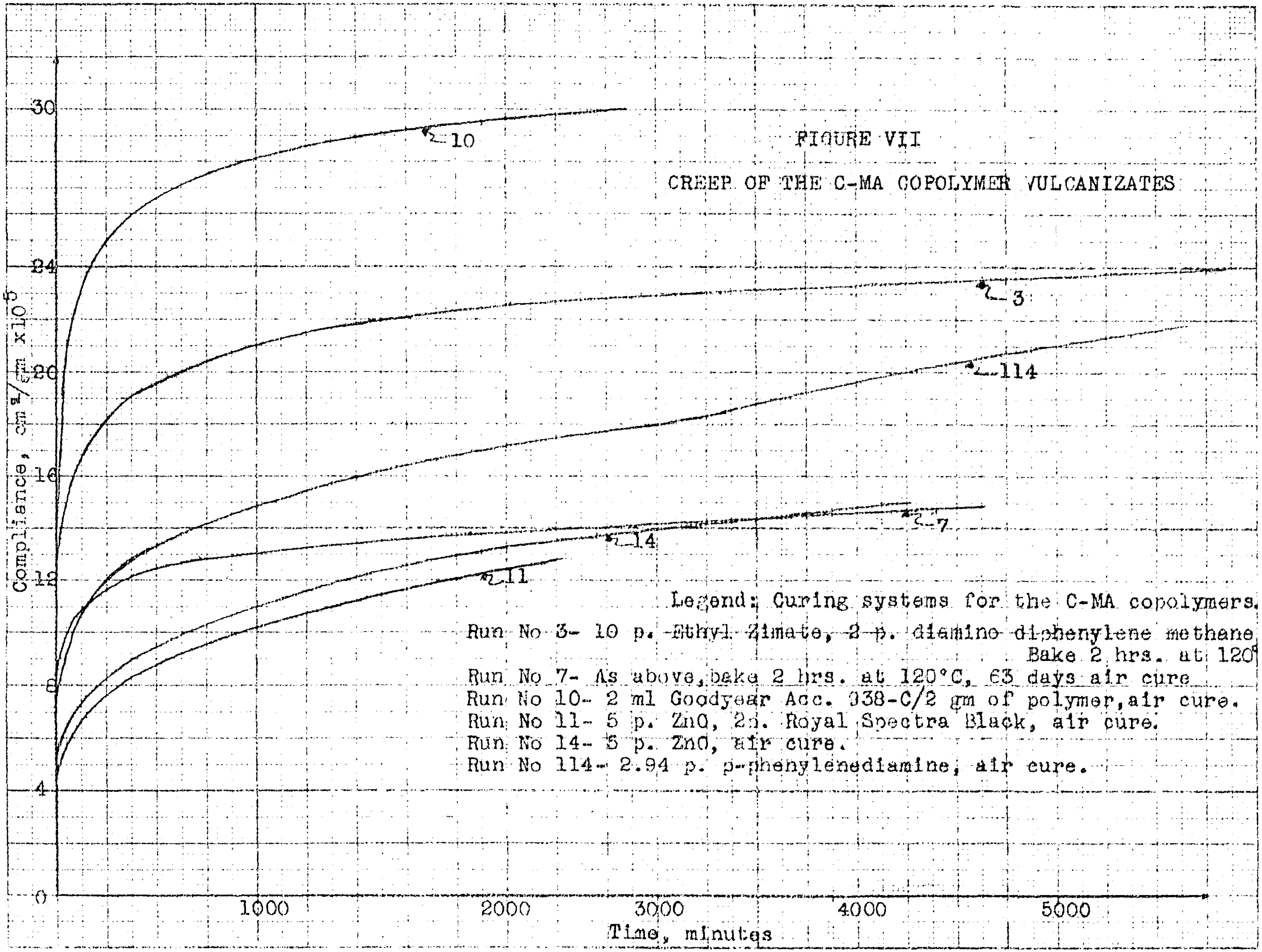


FIGURE VII

CREEP OF THE C-MA COPOLYMER VULCANIZATES

Legend: Curing systems for the C-MA copolymers.

Run No 3- 10 p. Ethyl Zimate, 2 p. diamino diphenylene methane
Bake 2 hrs. at 120°
Run No 7- As above, bake 2 hrs. at 120°C, 63 days air cure
Run No 10- 2 ml Goodyear Acc. 938-C/2 gm of polymer, air cure.
Run No 11- 5 p. ZnO, 2 p. Royal Spectra Black, air cure.
Run No 14- 5 p. ZnO, air cure.
Run No 114- 2.94 p. p-phenylenediamine, air cure.

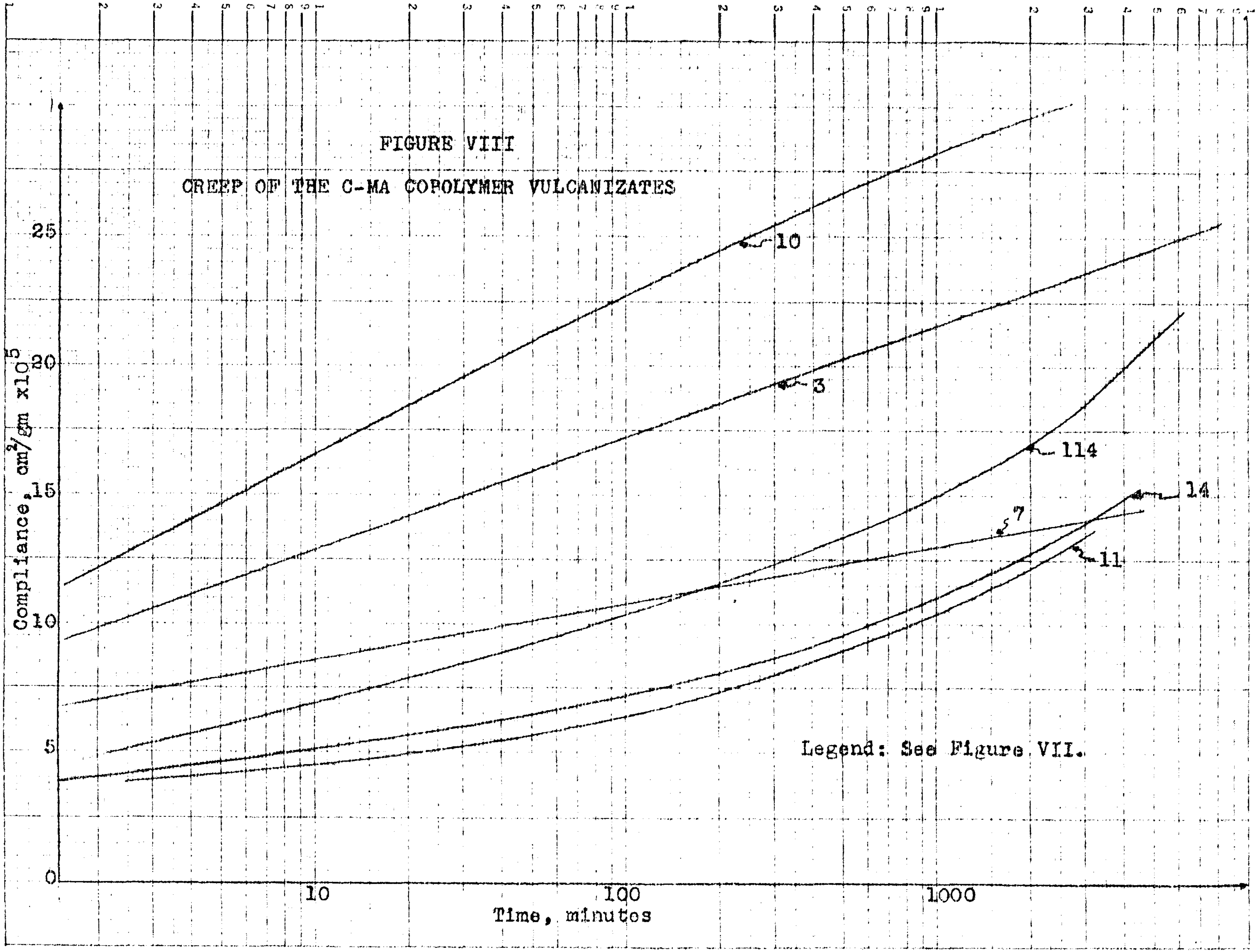


FIGURE VIII

CREEP OF THE C-MA COPOLYMER VULCANIZATES

$\Phi(t)$ can be now written as:

$$\Phi(t) = J_1^E + \left[ \Phi(\infty) - J_1^E \right] \left( 1 - e^{-t/\tau^E} \right)$$

and,

$$\frac{\Phi(\infty) - \Phi(t)}{J_2^E} = e^{-t/\tau^E}$$

As $J_2^E$ is constant for a given time-scale, it is apparent that the plot $\log\left[\Phi(\infty) - \Phi(t)\right]$ versus time will allow $\tau^E$ to be evaluated from the slope of the plot. The time-scale for this particular $\tau^E$ is determined by the extent of points falling to the straight line portion of this plot. The effective compliance, $J_2^E$, is readily calculated from the above expression. After subtracting the contribution of this retarded element, the procedure can be repeated and the parameters for a new retarded element determined. Additional retarded elements are determined until the entire creep curve is fitted. The C-MA copolymer (13.3% acid, 54% conversion), when cured with 10 parts Ethyl Zimate and 2 parts diamino diphenylene methane for 2 hours at 120° C, produced creep data, which could be represented by the following analytical expression:

$$J(t) = 3.98 \times 10^{-5} \left(1-e^{-t/1.77}\right) + 3.47 \times 10^{-5} \left(1-e^{-t/16.8}\right) +$$
$$3.53 \times 10^{-5} \left(1-e^{-t/100}\right) + 5.00 \times 10^{-5} \left(1-e^{-t/845}\right) + 3.09 \times 10^{-9} t$$

It is of interest to note that there is very little variation in the compliances belonging to various retarded elements. Time scales, corresponding to the determined retardation times are given in Table VI:

Table VI

Apparent Time Scales for Retardation Times.

| Retardation Time, min. | Time scale, Min. |
|---|---|
| 1.77 | 0.9 - 8 |
| 16.8 | 8 - 60 |
| 100 | 60 - 350 |
| 845 | 350 -2300 |

An approximate distribution function of retardation times has been derived according to the method employed by Andrews (6), who derives the corresponding relation for stress relaxation.

The approximate distribution of retardation times in terms of logarithmic time, $L(\log\tau)$, at any value of retardation time $\tau$, is equal to the slope of the creep curve plotted as $\gamma/S$ versus the logarithm of the time (logt) at the same value of t.

This approximation can be obtained in the following fashion. The total retarded elastic compliance for a continuous distribution of retardation times can be written as

$$J(t) = \int_0^\infty J(\tau)\left(1 - e^{-t/\tau}\right) d\tau$$

Using the substitution $L(\log_{10}\tau) = 2.3\tau J(\tau)$, we have

$$L(\log\tau)\, d\log\tau = J(\tau)\, d\tau$$

and substituting into J (t) one obtains

$$J(t) = \int_{-\infty}^{\infty} L(\log\tau)\left(1 - e^{-t/\tau}\right) d\log\tau$$

and

$$J(t) = \int_{\infty}^{-\infty} L(\log\tau)\, e^{-t/\tau}\, d\log\tau + C$$

Differentiating with respect to log t gives

$$\frac{dJ(t)}{d\log t} = \int_{-\infty}^{\infty} L(\log\tau)\left[\frac{2.303\, t\, e^{-t/\tau}}{\tau}\right] d\log\tau$$

If the distribution function is constant in a region, and since the remaining integral has a value of unity

$$I = \int_{-\infty}^{\infty}\left[\frac{2.303\, t\, e^{-t/\tau}}{\tau}\right] d\log\tau = 1$$

as

$$I = \int_{0}^{\infty} \frac{t\, e^{-t/\tau}}{\tau^2}\, d\tau$$

and if $\frac{1}{\tau} = x$, then

$$I = \int_{0}^{\infty} t\, e^{-tx}\, dx = 1$$

Thus we obtain the desired relation:

$$\frac{dJ(t)}{d\log t} = \left[L(\log\tau)\right]_{\tau=t}$$

According to this approximate presentation of the distribution function of retardation times, L (log τ) as determined from the straight line compliance - log t plot (Figure IX) is equal to 4.2 x $10^{-5}$ $cm^2/gm$, for the time-scale of one to several thousand minutes. To compare this constant value for the distribution,function with the previously determined compliance contributions of effective retarded elements, the following reasoning can be employed. The distribution of retardation times in terms of logarithmic time is related to the distribution in terms of linear time,

$$s = L(\log\tau) = 2.303\,\tau\, J(\tau)$$

where s is the slope of the compliance - logt plot.

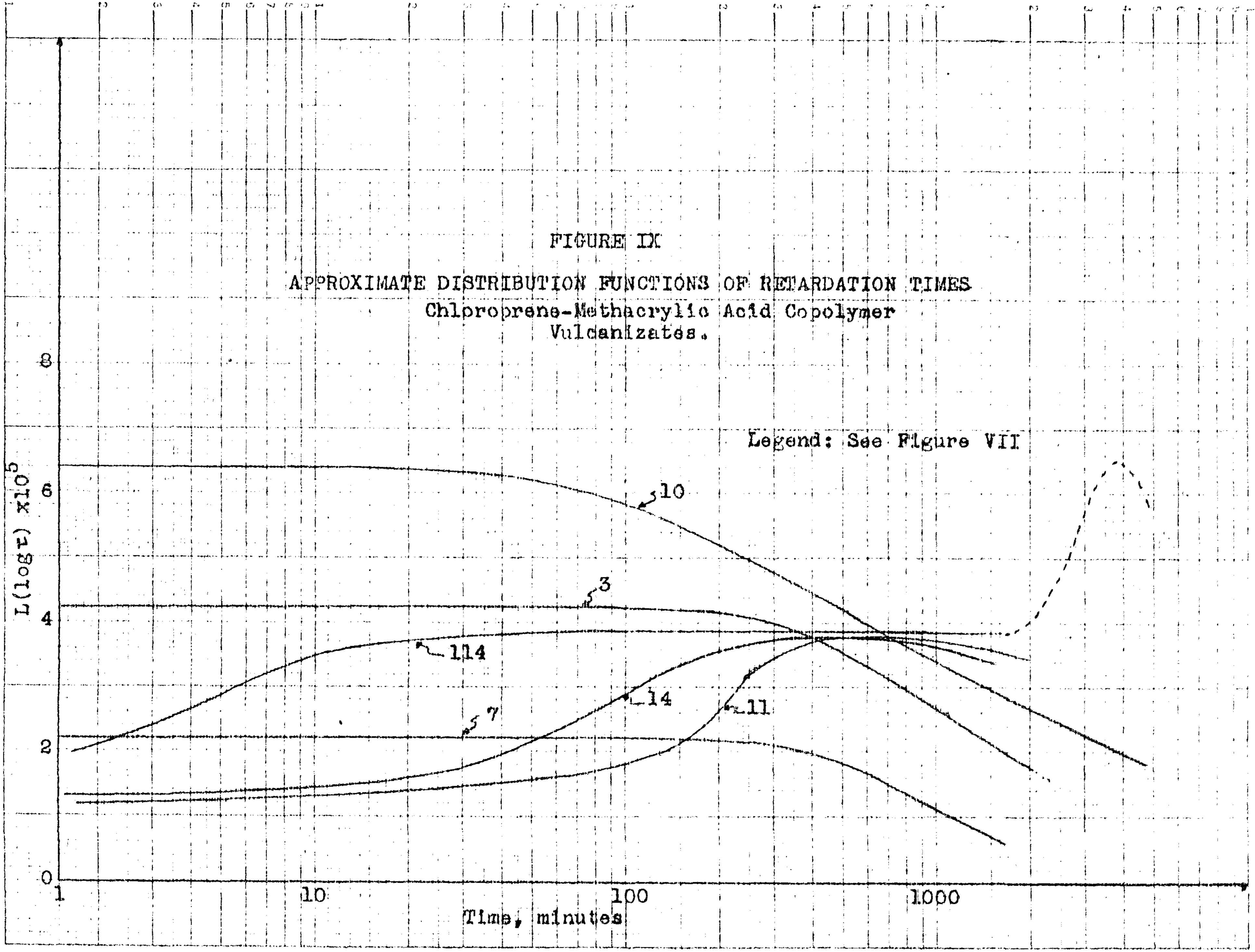


FIGURE IX

APPROXIMATE DISTRIBUTION FUNCTIONS OF RETARDATION TIMES
Chloroprene-Methacrylic Acid Copolymer
Vulcanizates.

Legend: See Figure VII

Accordingly,

$$J(t_1,t_2) = \int_{\tau_1}^{\tau_2} J(\tau)\,d\tau = \frac{S}{2.303}\int_{\tau_1}^{\tau_2}\frac{d\tau}{\tau}$$

In this particular case,

$$J(t_1,t_2) = \frac{4.2\times10^{-5}}{2.303}\,\ln\frac{\tau_2}{\tau_1} = 4.2\times10^{-5}\,\log\frac{\tau_2}{\tau_1}$$

The apparent values for $\tau_1$ and $\tau_2$ can be obtained from Table VI and J ( $t_1$, $t_2$) calculated. Results of this comparison are given in Table VII.

Table VII.

Distribution of Retardation Times by Linear and Logarithmic Method.

| Time Scale, min. | J ($t_1$, $t_2$)* cm$^2$/ gm x $10^5$ | J($t_1$, $t_2$) ** cm $^2$/ gm x $10^5$ |
|---|---|---|
| 0.9 - 8 | 3.98 | 3.99 |
| 8 - 60 | 3.47 | 3.67 |
| 60 - 350 | 3.53 | 3.22 |
| 350 - 2300 | 5.00 | -- |

* Retarded compliances from "effective model" treatment.
** Retarded compliances from the approximate distribution function.

It is apparent from Table VII that excellent agreement is obtained for relatively short time-scales; for long times the agreement becomes poorer. This is due to the difficulty in determining the exact time-scales involved . Also, after 350 minutes, L (log $\tau$ ), is not constant any longer. Consequently J ( $\tau$) is no longer proportional to 1/$\tau$ and the simple analytical treatment given above fails.

In Figure IX, are given the distribution function under consideration, and also a number of other typical distribution functions. These curves have been obtained from the compliance - log time plots after subtraction of the viscosity contribution. A fluidity of $3x10^{-9}$ $cm^2/gm$ has been used for all samples, a procedure which may be justified in the following manner. Table VIII gives a number of apparent fluidities, as determined from the runs carried out to sufficiently long times to have the compliance-time plots approach straight lines apparently within experimental error. Variation of these fluidities is from $2.2x10^{-9}$ to $2.08 \times 10^{-8}$ $cm^2/gm$. It is seen that if the compliances are determined after about 5000 minutes, higher fluidities are obtained, while after 8000 minutes, the variation is only from 2.2 to $3.5x10^{-9}$ $cm^2/gm$. It is shown that even though a "viscosity" term can be obtained from apparently straight lines at 5000 minutes, lower fluidities for the same experiment will result if determined after 8000 minutes (Table VIII).

## Table VIII

### Fluidity of the C-MA Copolymers

| Run No. | Cure | Time Scale, min. | Fluidity, $cm^2/gm$ |
|---|---|---|---|
| 113 | Phloroglucinol, 5p., air cure | 8000 | $3.5 \times 10^{-9}$ |
| 113 | " " " " | 5000 | $1.1 \times 10^{-8}$ |
| 114 | p-phenylenediamine, 4.3p, air cure | 6000 | $7.2 \times 10^{-9}$ |
| 90 | " " " " | 5000 | $1.76 \times 10^{-8}$ |
| 49 | " " " " | 4000 | $2.08 \times 10^{-8}$ |
| 23 | Zinc oxide, 5p. air cure | 4000 | $9.12 \times 10^{-9}$ |
| 3 | Ethyl Zimate 10p diamino diphenylene methane, 2p., 2 hrs., at 120°C | 10000 | $3.09 \times 10^{-9}$ |
| 7 | Ethyl Zimate 10p diamino diphenylene methane, 2p., 2 hrs., at 120° C.+ 13 days air cure | 11000 | $2.20 \times 10^{-9}$ |

It may be concluded that fluidities determined at 5000 minutes still include some long time retarded response. While this may be to a lesser extent true of fluidities determined at 8000 minutes, any error introduced by using the smaller fluidites will be correspondingly less. Since the 8000 minute fluidities do not differ appreciably for the various samples, a value of $3 \times 10^{-9}$ $cm^2/gm$ was chosen as representing a most reasonable estimate. It should also be borne in mind that the true flow contribution need not be Newtonian, since intermolecular attractions would be affected by orientation during stretching. Thus, it is not likely that any further differentiation in fludities of the various samples would be justified at all.

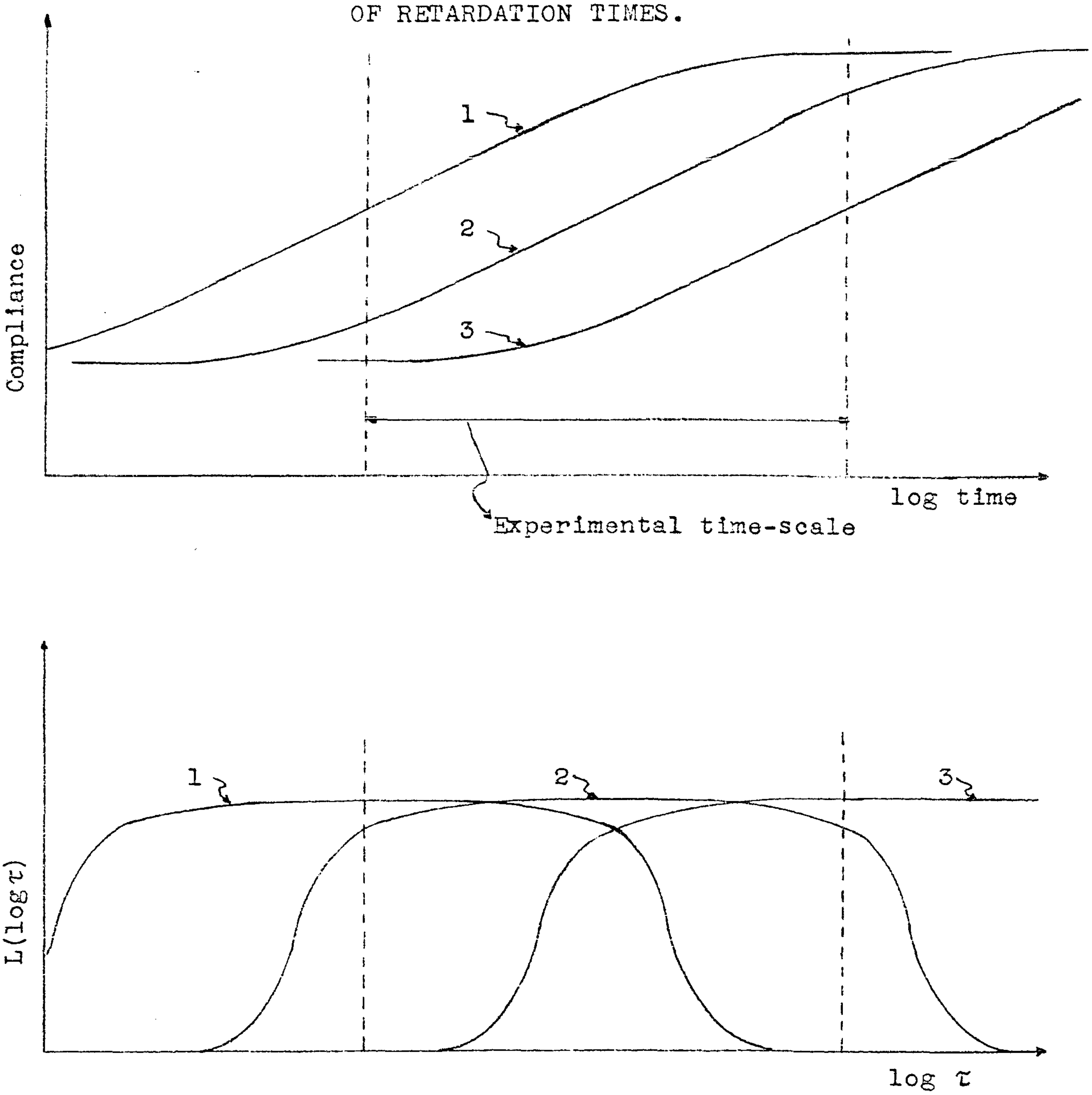
The distribution curves obtained seem to fall generally into two classes; one in which the curve shows an increase in compliance with longer time and one in which the opposite is observed. Since all such distribution curves would be expected to exhibit a maximum and to fall off on either side it appears as if each curve were only a portion of a total "bell-shaped" distribution function, resulting from a sigmoid compliance-log plot (41).

In Figure X, a number of hypothetical distribution functions have been plotted, resulting from creep curves shifted only in time scale. This illustration shows that if a creep study were to be conducted in a limited range of time three different types of creep curves would be obtained after flow contribution has been subtracted, i.e. apparent straight lines, convex and concave compliance-log t plots. This is exactly what is found in the case of C-MA copolymers vulcanized by various types of curing agents. The portion of the distribution functions derived from such creep curves, of course, also have the required shape.

The total area under the distribution curves represent the total compliance. The position of the maximum, however, gives information regarding the retardation time, at which the bulk of this compliance is effective. The curves which have their peaks at short times are consequently lively rubbers which quickly respond to the applied stress. Of course, uncured rubber is associated with very high total compliance and can be considered as lively, but it also exhibits considerable flow. When a polymer is vulcanized the total compliance will be reduced, i.e. the distribution curves become flatter. However, Figure IX shows another interesting effect, namely that the compliance peaks are shifted to various positions on the time-scales. This shift is obviously a function of cure which will be discussed at a later point.

FIGURE X

HYPOTHETICAL SHIFT OF CREEP CURVES AND ITS EFFECT ON THE APPROXIMATE DISTRIBUTION FUNCTION OF RETARDATION TIMES.



Reproducibility of the creep experiments has been found to be satisfactory. Results of four creep experiments of 60 minute duration (ca 500% elongation) on the C-MA gum films (11.8% acid, 53% conversion) are summarized in Table IX. These films were cast from lacquers with cyclohexanone, methyl isobutyl ketone solvent and were air-dried for 28 days and finally subjected to vacuum at room temperature for 5 days. Accordingly, changes in compliances due to the presence of solvent in films are assumed to be neglible. Also, employed stresses were sufficiently close to produce no significant variation in compliances. These four creep experiments were carried out in the course of 9 days. As it will be seen elsewhere, some aging i.e. reduction in compliance can be assumed to occur in this interval. Compliance for short times are least dependent on structural variations and aging, as only short retardation times are involved. Accordingly, best reproducibility of the creep experiments was realized with one minute compliances, as compared with compliances measured at 10 and 50 minutes.

Table IX

Repreducibility of Creep Experiments.

| Stress | Compliance $cm^2/gm \times 10^4$ | | |
|---|---|---|---|
| $kg/cm^2$ | 1 min. | 10 min. | 50 min. |
| 6.61 | 1.22 | 3.16 | 7.65 |
| 7.23 | 1.21 | 2.76 | 6.80 |
| 7.19 | 1.23 | 2.94 | 7.08 |
| 7.10 | 1.23 | 2.96 | 6.56 |

The effect of stress on creep behavior has been studied for stresses ranging from 2.96 to 12.53 $kg/cm^2$. These variations in stress were brought about by utilizing specimens of various thickness and width. The data, summarized in Table X, seem to point to small increase in compliance on increasing stress. Accordingly, approximately four-fold difference in stress produced one minute compliances varying from 3.02 to 3.95 x $10^{-4}$ $cm^2/gm$, corresponding elongations ranging from 89 to 495 percent. A similar trend prevails for ten minute compliances.

Table X

Effect of Stress on Creep

| Width of specimen, in. | Stress kg/cm$^2$ | 1 min. |  | 10 min. |  |
|---|---|---|---|---|---|
|  |  | Compliance, cm$^2$/gm x $10^4$ | Elongation, % | Compliance, cm$^2$/gm x $10^4$ | Elongation, % |
| 3/8 | 2.96 | 3.02 | 89 | 9.34 | 276 |
| 1/4 | 4.68 | 3.32 | 155 | 12.38 | 579 |
| 3/8 | 5.08 | 3.49 | 177 | 12.30 | 622 |
| 1/4 | 6.87 | 3.51 | 241 | - | - |
| 3/8 | 12.53 | 3.95 | 495 | - | - |

3. **The Effect of Cure and Aging on Viscoelastic Properties.-** Creep experiments have found to be useful in studying the changes of viscoelastic properties of the C-MA copolymers, due to the introduction of various curing systems, and also due to aging. Both curing agents and aging have been found to change significantly the viscoelastic properties of the C-MA copolymer films. Accordingly, these creep experiments yield useful information for critical evaluation of polymeric films, whether used for coating applications or elsewhere. Creep data was supplemented with tensile strengths to yield more information about the state of cure and aging. Generally aging was considered to occur if the reduction in compliances was accompanied with considerable reduction in tensiles. Conversely, if reduction of compliance was accompanied with improvement

in tensiles, the curing process was assumed to be continuing.

In this investigation, air cures have been given major attention, since heat cures are not practically feasible in coating application. However, before investigating various curing agents in detail, the effect of heat on the creep behavior of the C-MA copolymer gum specimens will be discussed.

(a) Effect of heat.- The effect of heat on the C-MA copolymer gum specimens was briefly investigated to obtain some information for comparison of heat and air cures. Results of the creep experiments are summarized in Table XI and Figure XI.

Table XI

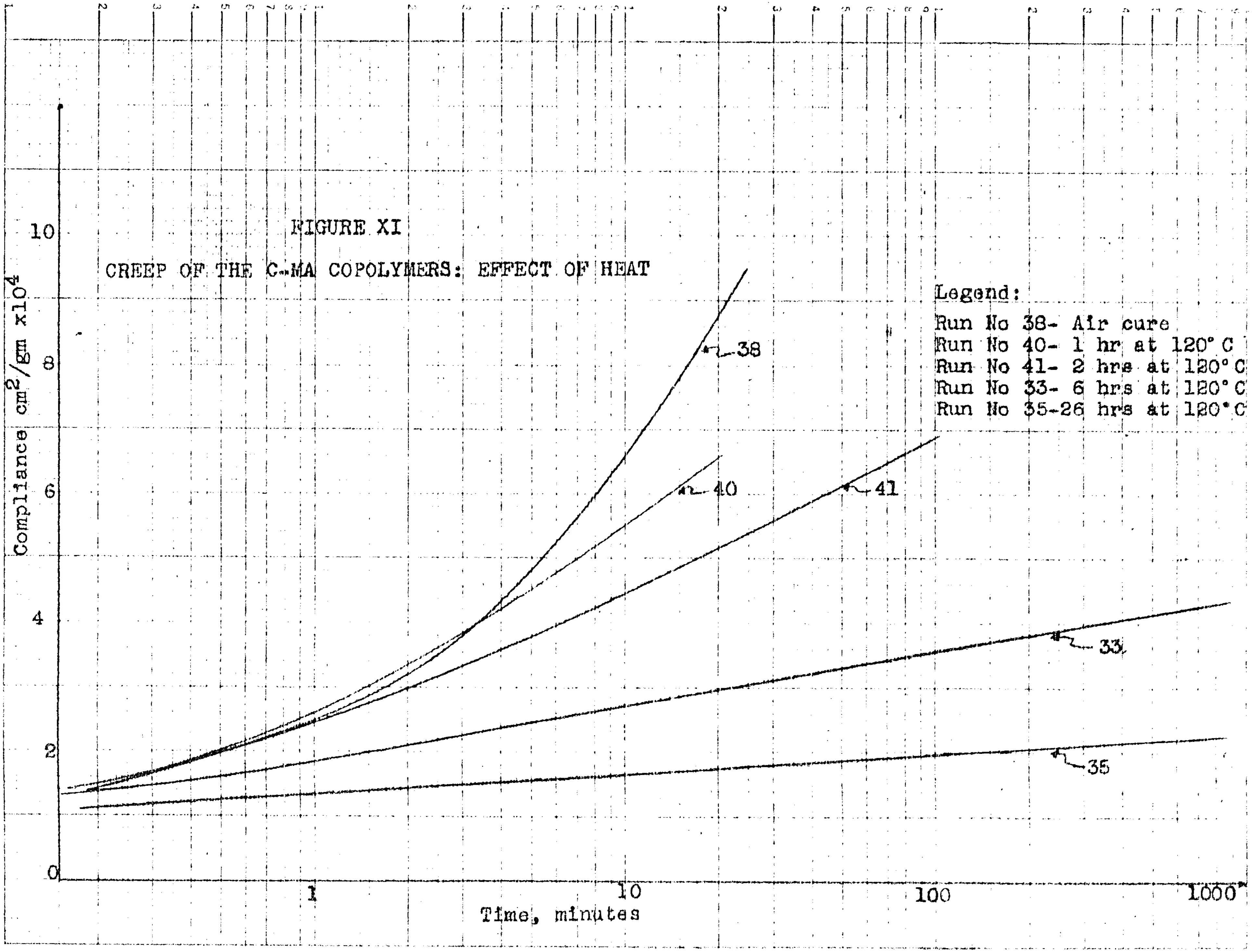
Effect of Heat on Creep

| Run No. | Cure | Stress kg/cm$^2$ | Compliance, cm$^2$/gm x $10^4$ 1 min. | 10 min. |
|---|---|---|---|---|
| 38 | 14 days, air cure | 6.58 | 2.43 | 6.45 |
| 40 | 1 hr. 120° C. | 8.66 | 2.54 | 5.51 |
| 41 | 2 hrs. 120° C. | 8.45 | 2.41 | 4.50 |
| 33 | 6 hrs. 120° C. | 8.97 | 1.85 | 2.72 |
| 35 | 26 hrs. 120° C. | 8.37 | 1.38 | 1.68 |

The anticipated polymer stiffening on heating was apparent from decrease in compliance, especially when determined at times exceeding 5 minutes. Accordingly, one minute compliances exhibited an insignificant change in the range of customary curing conditions (not more than 2 hours at 120° C.) Consequently, heating from 1 to 26 hours at 120° C. produced a "straightening out" effect of the compliance-log time plots, and was accompanied by a decrease of slope. For one hour cure L (log$\tau$) was 2.3 x $10^{-4}$ cm$^2$/gm as compared to 3.1 x $10^{-5}$ cm$^2$/ gm for a 26 hour bake.

FIGURE XI

CREEP OF THE C-MA COPOLYMERS: EFFECT OF HEAT



It was of interest to note that no appreciable change in tensile strength was realized on heating. Elongation at break and ASTM set decreased with an increase in bake. These data are summarized in Table XII.

### Table XII .

### Effect of Heat on C-MA Copolymer

Gumstock

| Run No. | Cure | Tensile, psi. | Elongation at break, % | ASTM set, % |
|---|---|---|---|---|
| 38 | 14 days, air cure | 1565 | 1420 | 74 |
| 40 | 1 hr., 120°C | 1700 | 1360 | 45 |
| 41 | 2 hrs.,120° C | 1680 | 1210 | 35 |
| 33 | 6 hrs.,120°C | 1670 | 1060 | 15 |
| 35 | 26 hrs.,120°C | 1350 | 890 | 8 |

(b) Effect of Metal Oxides. - Magnesia and zinc oxide, which are customarily used in combination for neoprene vulcanizates have both exhibited excellent curing characteristics for the C-MA copolymers (1,23). Both heat and air cures have produced favorable results; air cures, of course, have required a period of one to several weeks to exhibit a full cure. However, the use of magnesia has hot been fully satisfactory, as the addition of magnesia slurry to lacquers produces gelation in a relatively short time (1,23). Accordingly, zinc oxide was chosen as a more desirable metal oxide for the C-MA copolymer cure.

Creep experiments were conducted on the C-MA copolymer films, containing up to 10 parts of zinc oxide. Concurrent tests on tensile strength were also performed. These tests were conducted on vulcanizates containing 1,5, and 10 parts of zinc oxide after about a month of air cure and were repeated after some seven months of storage. Results of these experiments are summarized in Tables XIV and XV and in Figure XIII.

Table XIV

Creep Behavior of the C-MA copolymer*; Effect of Zinc Oxide

| Run No. | Curing Agent, parts ZnO | Air cure, days | Stress kg/cm$^2$ | Compliance cm$^2$/gm x $10^5$ 1 min. | 10 min. | 100 min. |
|---|---|---|---|---|---|---|
| 25 | - | 28 | 8.50 | 29.8 | 70.2 | - |
| 82 | - | 150 | 8.24 | 24.1 | 43.8 | - |
| 24 | 1 | 22 | 9.89 | 14.6 | 23.2 | 32.9 |
| 100 | 1 | 232 | 10.28 | 9.66 | 13.1 | 17.3 |
| 23 | 5 | 20 | 10.10 | 4.28 | 5.91 | 7.88 |
| 112 | 5 | 239 | 10.90 | 2.71 | 4.28 | 6.05 |
| 22 | 10 | 19 | 10.00 | 1.59 | 2.93 | 4.95 |
| 92 | 10 | 226 | 9.50 | 0.70 | 1.42 | 2.68 |

*/ C-MA copolymer 11.8 % acid, 53% conversion.

Table XV

The C-MA Copolymer Properties*; Effect of Zinc Oxide.

| Curing Agent, parts ZnO | Air Cure, days | Tensile, psi. | Elongation at break, % | ASTM set, % |
|---|---|---|---|---|
| - | 14 | 1570 | 1420 | 74 |
| 1 | 10 | 3660 | 900 | 27 |
| 5 | 20 | 6980 | 700 | 11 |
| 5 | 239 | 6240 | 460 | 13 |
| 10 | 19 | 7510 | 630 | 30 |
| 10 | 226 | 7380 | 320 | 38 |

*/ C-MA copolymer 11.8% acid, 53% conversion.

Gradual decrease in compliance and increase in tensile strength upon increasing the amount of zinc oxide is apparent from these data. Corresponding decrease in elongation at break and fluctuation in permanent set are also of interest.

The changes in creep behavior illustrated by Figure XII are seen to be of considerable magnitude. These changes are not realized from the ultimate tensile strength and elongation data. These creep curves can also be used to visualize the changes in the approximate distribution functions for retardation times. Up to times of more than 100 minutes, when the flow contribution from the assumed fluidity ($3 \times 10^{-9}$ $cm^2/gm$ ) is neglible, the slope of the creep curves can be taken at various points to represent the corresponding points at the distribution curve. With one part zinc oxide, $L(\log\tau)$ is equal to $9.5 \times 10^{-5}$ $cm^2/gm$ over the range from a few minutes to above one hundred minutes, indicating that the plateau of the distribution curve is reached in a few minutes. Five and 10 parts of zinc oxide produce distribution functions of different character; the total compliance being less and the peak of the distribution curve is apparently shifted to longer times. However, there is no appreciable difference between 5 and 10 parts of zinc oxide curves; $L(\log\tau)$; at 1,10, and 100 minutes for the two amounts of zinc oxide are 1.6, 1.1; 1.7, 1.7; and 2.1, $2.0 \times 10^{-5}$ $cm^2/gm$ respectively. There is a reduction in total compliance on increased amount of zinc oxide, but the peak of the distribution curve does not seem to be shifted appreciably.

When the zinc oxide cure specimens were stored up to eight months, a considerable decrease in compliance has taken place. This is apparent from Figure XII and also from Figure XIII where some four creep curves have been run with specimens (some

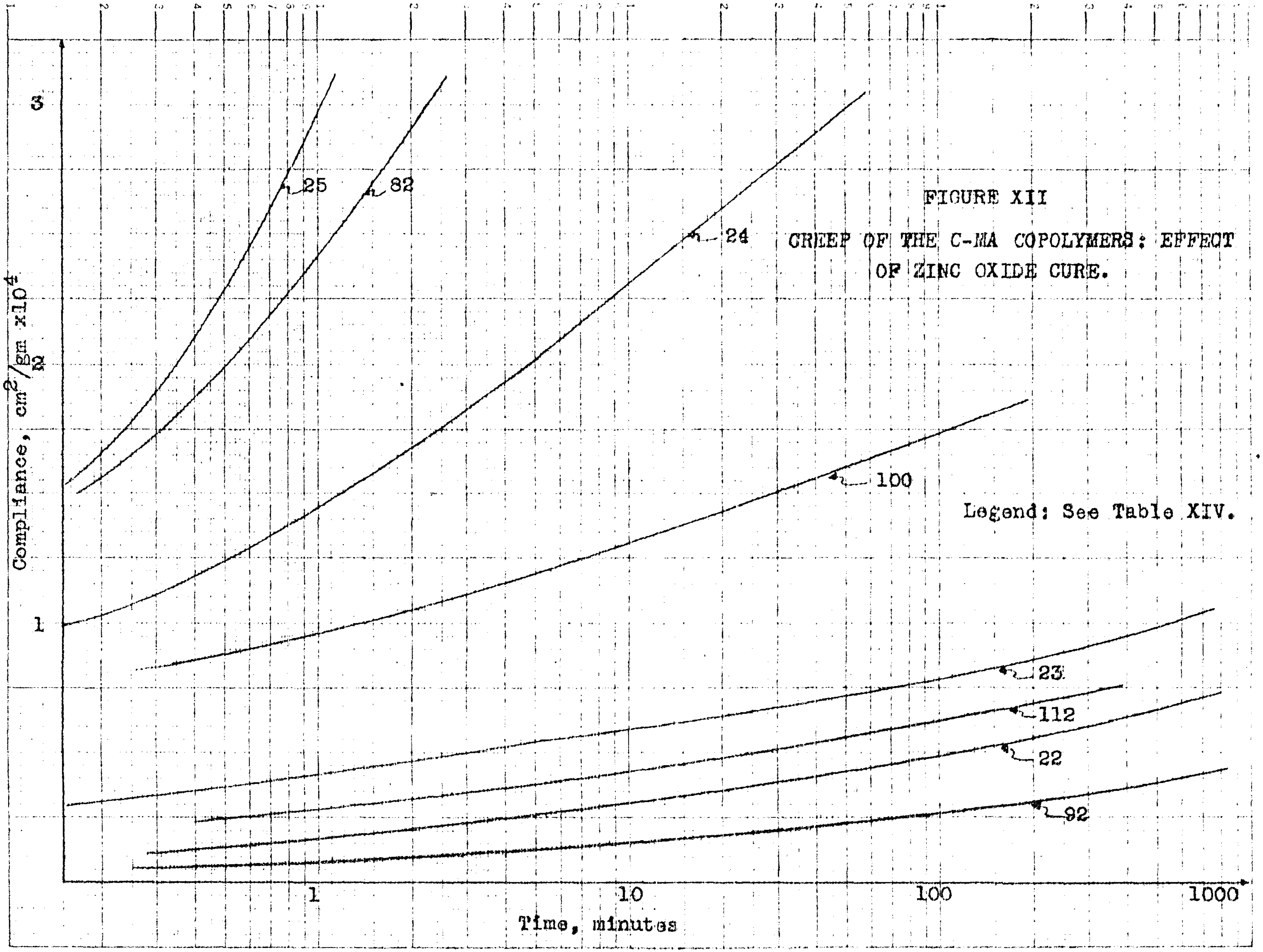


FIGURE XII

CREEP OF THE C-MA COPOLYMERS: EFFECT OF ZINC OXIDE CURE.

Legend: See Table XIV.

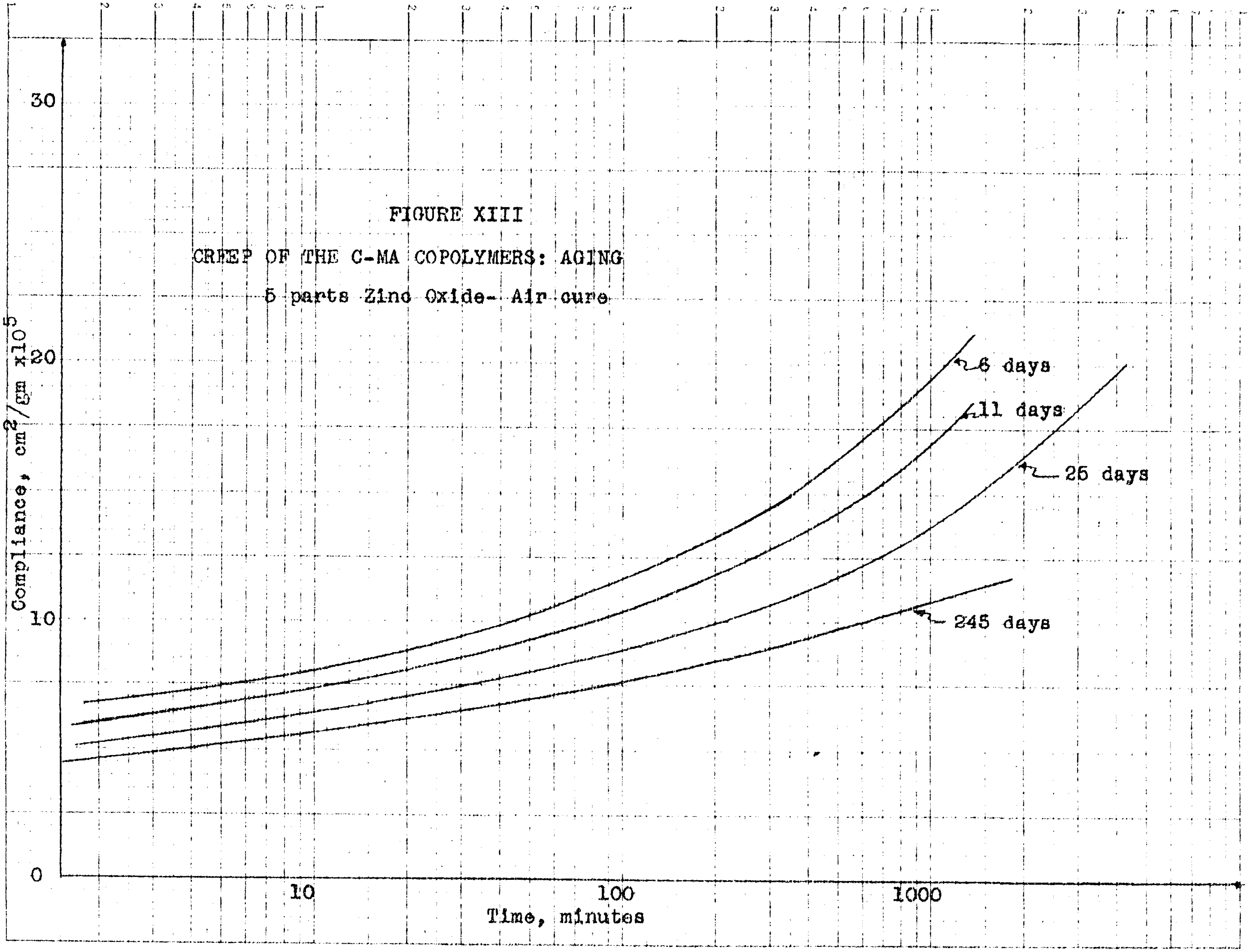


FIGURE XIII

CREEP OF THE C-MA COPOLYMERS: AGING

5 parts Zinc Oxide- Air cure

gel present) cured with 5 parts zinc oxide, after 6,11,25 and 245 days. These experiments are also summarized at Table XVI, and the concurrent changes in tensile strength and elongation are given in Table XVII. Reduction of tensile from 7040 to 6240 psi and of elongation from 650 to 460 percent prevails for the time period mentioned. Similar small decrease in tensile and reduction in elongation is apparent for the experiments described in Table XIV and XV.

On aging, as on increase of zinc oxide content the reduction in total compliance is apparent, as evidenced by the successive decrease in the slope of the creep curves. In general it can be said that 5 and 10 part zinc oxide cures result in rubbers of a small degree of "liveliness", i.e. their response to an applied stress is slow as compared to some other curing agents, which are discussed elsewhere, However, with zinc oxide cures the C-MA copolymers have exhibited the highest tensile strengths (7500 psi. - 10 parts zinc oxide).

In many applications, this stiffening of polymer films would be of utmost importance and therefore these relatively simple creep experiments would be of considerable value in such evaluations.

## Table XVI

Creep Behavior of the C-MA Copolymers* ; Aging.

| Run No. | Air Cure, days | Stress kg/cm$^2$ | Compliance, cm$^2$/gm x $10^5$ 1 min. | 10 min. | 100 min. |
|---|---|---|---|---|---|
| 19 | 6 | 9.56 | 5.93 | 8.14 | 11.98 |
| 20 | 11 | 9.53 | 5.52 | 7.43 | 10.40 |
| 21 | 25 | 9.45 | 4.66 | 6.51 | 8.97 |
| 99 | 245 | 7.29 | 4.10 | 5.73 | 7.55 |

*/ C-MA copolymer - 11.8% acid, 53% conversion; cure - 5 parts ZnO.

## Table XVII

The C-MA Copolymer Properties *, Aging.

| Air Cure, days | Tensile, psi. | Elongation at break, % | ASTM Set, % |
|---|---|---|---|
| 6 | 7040 | 650 | 12 |
| 11 | 7010 | 600 | 12 |
| 25 | 6730 | 490 | 13 |
| 245 | 6240 | 460 | 13 |

*/ C-MA copolymer - 11.8% acid, 53% conversion; cure - 5 parts ZnO.

(c) Effect of Organic Compounds. - Due to the desirability of air cures in coating application and also to obtain lacquers of improved stability and homogeneity as compared to those cured with metal oxides, a number of organic compounds of varying nature were investigated as curing agents for the C-MA copolymer. The compounds under investigation included conventional rubber accelerators and stabilizers, aromatic diamines and polyhydroxybenzenes.

When cured with 5 parts curing agent per 100 parts of polymer the results from the creep experiments (Table XVIII) seem to divide the organic compounds tested into two categories; first, compounds which promote varying degrees of cure and second, compounds which act as effective plasticizing agents. With aromatic diamines a most effective air-cure was obtained in 14 days as evidenced by considerable reduction in compliances, when compared to the gum-stock, and also by considerable increase in the tensile strength (Table XIX). Somewhat lesser degrees of cure in 14 days were obtained with polyhydroxybenzenes, like phloroglucinol, and also with diphenylquanidine. The rest of the compounds did not exhibit any curing action but increased the compliances as compared to those of the gum-stock. The corresponding tensile strengths were also impaired. Captax, Altax, Du Pont Accelerator 808, Ethyl Selenac, phenyl beta naphthylamine and para toluidine were representatives of this group.

It is interest to note that in case of aromatic amines, at least two functional groups are necessary for effective cure. This becomes apparent in comparing the results of p-phenylenediamine and p-toluidine cures; the latter acts as an effective plasticizing agent while p-phenylenediamine is the most effective curing agent of the compounds tested.

The creep experiments and the tensile tests were repeated after more than 4 months of storage. These results are also summarized in Tables XVIII and XIX. A number of typical creep experiments are also shown in Figure XIV. It is obvious that generally the reduction of compliances, accompanied by a "straightening out" of the semi-log compliance time plots has taken place on continued air cure.

This observation indicates the reduction in total compliance, and also shows that the distribution of retardation times over a wider time range has taken place. The slopes of the creep curves of the specimens cured with polyhydroxybenzenes and aromatic diamines after being stored for more than 4 months become quite small and the variations in slopes become difficult to determine, Accordingly no attempt has been made in this connection to determine the distribution functions and to locate their possible peaks. It can be noticed, however, that phenolic type cures will produce straight line creep plots in a much shorter time of air cure than by aromatic diamine cures. At first, with phenolic cures, the distribution function has its peak at relatively short times as compared to diamine cures, and will therefore respond more quickly to applied stresses. On aging this distinction becomes less apparent. It is of interest to note that even with phenyl beta naphthylamine, which is customarily used as an antioxidant, the reduction in compliance results on continued storage.

Ultimate tensile strengths also yield useful information in regard to cure and aging (Table XIX). Maximum tensile strengths of 5340 psi. have been obtained with 5 parts of p-phenylenediamine as a curing agent. With polyhydroxybenzenes, phloroglucinol exhibited 2700 psi. as the best result. Organic compounds which were not effective curing agents as determined from the creep data, have shown tensile strengths which are generally less than that of the C-MA gum-stock, 1570 psi. with these compounds, on storage further reduction in tensiles has occured, even though reductions in compliance are evident.

Prolonged storage has generally little effect on the tensile strengths of the C-MA copolymer which had originally been vulcanized with diamine and polyhydroxybenzene type curing agents With aromatic diamines on prolonged storage most compounds produce some increase and generally approach 5000 psi., initially exhibited by p-phenylenediamine cure. Accordingly benzidine, dianisidine and diamino diphenylene methane have shown an increase from the initial 3770, 2660, and 2620 psi. to 5000, 3890 and 4410 psi. respectively on prolonged air cure. If p-phenylenediamine is used in equimolar quantities to benzidine it is of interest to note that also originally almost identical tensile strengths of 3840 and 3770 psi. are realized.

With polyhydroxybenzene cures, an interesting trend becomes apparent. The compounds used can be lined up in their decreasing order of effectiveness as curing agents; phloroglucinol, resorcinol and catechol. Hydroquinone has to be omitted as it is not completely compatible with the C-MA copolymer. The above order has been reduced from the creep experiments and also from the tensile data. It appears that the spacial availability the hydroxyl groups to produce interchain linkages determines the effectiveness of these curing agents.

## Table XVIII

Creep Behavior of the C-MA Copolymers*; Air Cure with Organic Compounds.

| Run No. | Curing agent, 5 parts | Air Cure, days | Stress, kg/cm$^2$ | Compliance cm$^2$/gm x $10^4$ | | |
|---|---|---|---|---|---|---|
| | | | | 1 min. | 10 min. | 100 min. |
| 28 | - | 14 | 6.58 | 2.43 | 6.45 | - |
| 28b | - | 150 | 8.24 | 2.41 | 4.38 | - |
| 49 | p-phenylenediamine | 14 | 8.40 | 0.94 | 1.54 | 2.41 |
| 49b | | | | | | |
| 64 | " " | 135 | 8.48 | 0.51 | 0.66 | 0.86 |
| 50 | benzidine | 14 | 8.51 | 1.30 | 2.50 | 4.45 |
| 50b | " | 167 | 9.52 | 0.62 | 0.77 | 0.95 |
| 46 | phloroglucinol | 14 | 9.51 | 1.84 | 3.19 | 4.69 |
| 46b | " | 140 | 9.75 | 1.01 | 1.25 | 1.45 |
| 44 | dianisidine | 14 | 9.11 | 1.53 | 3.03 | 5.56 |
| 39 | diamino diphenylene methane | 14 | 8.59 | 1.27 | 2.31 | 1.25 |
| 63 | resorcinol | 14 | 8.15 | 2.28 | 4.95 | - |
| 63b | " | 137 | 8.82 | - | 2.06 | 2.74 |
| 45 | diphenylquanidine | 14 | 9.33 | 2.04 | 4.93 | - |
| 43 | o-amino phenol | 14 | 9.61 | 2.60 | - | - |
| 43b | " " | 141 | 8.32 | 1.64 | 2.95 | - |
| 42 | catechol | 14 | 10.85 | 3.10 | - | - |
| 42b | " | 134 | 9.18 | 1.55 | 2.45 | - |
| 32 | Thionex | 14 | 8.63 | 2.58 | 6.44 | - |
| 32b | " | 188 | 9.94 | 2.07 | 4.08 | - |
| 48 | phenyl beta naphthylamine | 14 | 8.68 | 3.45 | - | - |
| 48b | " " | 122 | 7.65 | 2.23 | 4.46 | |
| 51 | beta nitroso naphthylamine | 14 | 9.42 | 3.82 | - | - |
| 37 | Ethyl Selenac | 14 | 7.25 | 3.01 | - | - |
| 29 | Accelerator 808-10 parts | 14 | 5.65 | 3.90 | 11.50 | - |
| 29b | " " | 162 | 7.91 | 3.65 | 5.86 | - |
| 52 | p-toluidine | 14 | 9.73 | 4.17 | - | - |
| 52b | " " | 128 | 9.35 | 2.58 | 5.43 | - |
| 30 | Captax | 14 | 8.62 | 4.30 | - | - |
| 30b | " | 192 | 10.79 | 4.40 | - | - |
| 31 | Altax | 14 | 8.78 | 4.82 | - | - |
| 31b | " | 191 | 10.60 | 4.25 | - | - |
| 62 | hydroquinone | 14 | 9.26 | 2.20 | 4.92 | - |
| 62b | " | 133 | 8.54 | 1.54 | 2.48 | 3.61 |

*/ C-MA Copolymer 11.8%acid; 53% conversion.

## Table XIX

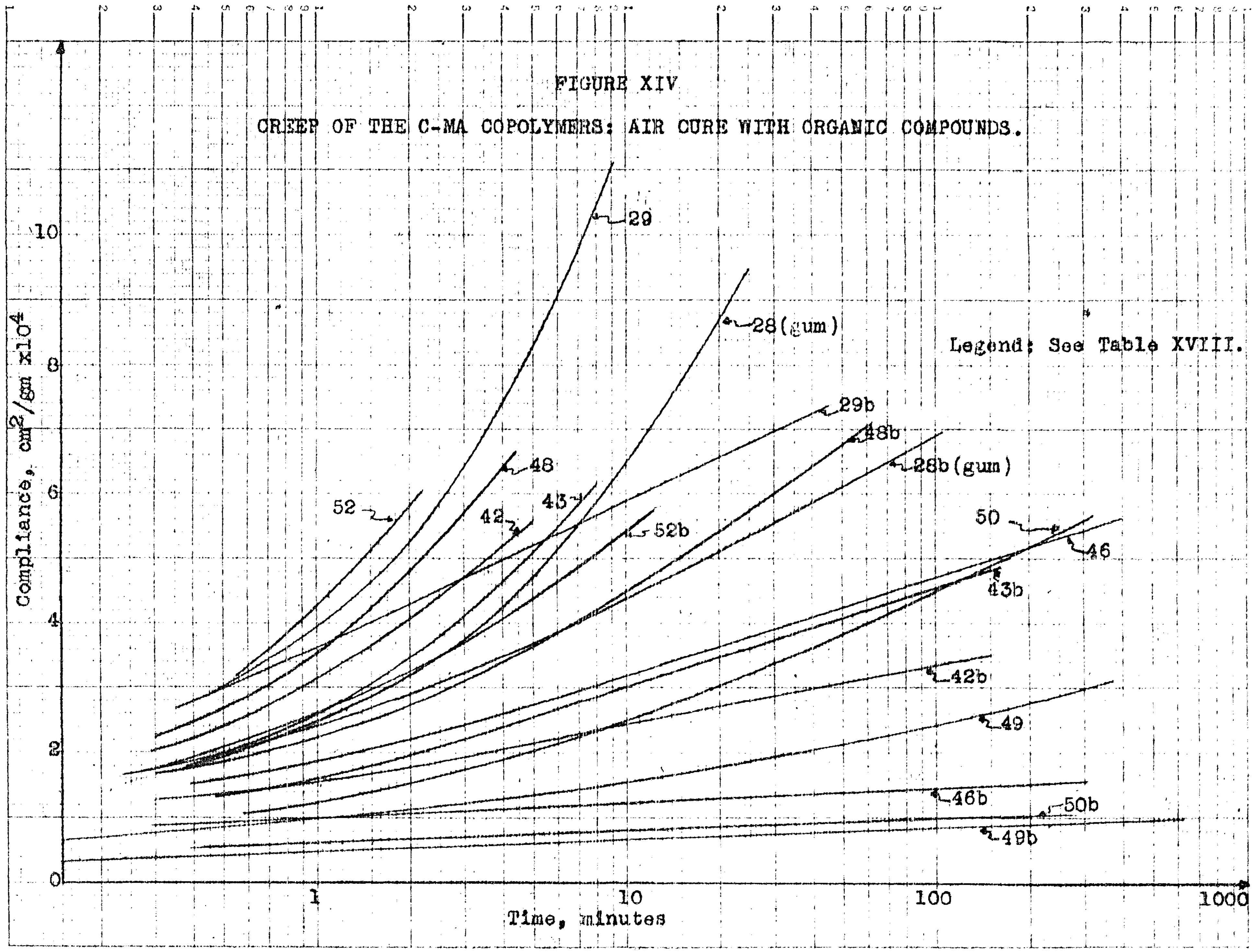
The C-MA Copolymer Properties *; Air Cure with Organic Compounds

| Run No. | Curing agent, 5 parts | Air cure, days | Tensile psi. | Elongation at break % | ASTM set, % |
|---|---|---|---|---|---|
| 28 | gum | 14 | 1570 | 1420 | 74 |
| 49 | p-phenylenediamine | 14 | 5430 | 990 | 26 |
| 49b | " " | 135 | 5320 | 660 | 12 |
| 64 | " " 2.94p. | 14 | 3840 | 960 | 28 |
| 50 | benzidine | 14 | 3770 | 1020 | 35 |
| 50b | " | 167 | 5000 | 750 | 9 |
| 46 | phloroglucinol | 14 | 2700 | 1240 | 45 |
| 46b | " | 140 | 2760 | 830 | 9 |
| 44 | dianisidine | 14 | 2660 | 1260 | 44 |
| 44b | " | 139 | 3890 | 750 | 11 |
| 39 | diamino diphenylene methane | 14 | 2620 | 1170 | 36 |
| 39h | " " | 133 | 4410 | 710 | 8 |
| 63 | resorcinol | 14 | 2330 | 1120 | 45 |
| 63b | " | 137 | 1930 | 1000 | 23 |
| 45 | diphenylguanidine | 14 | 2240 | 1160 | 64 |
| 45b | " | 140 | 1360 | 980 | 32 |
| 43 | o-amino phenol | 14 | 1720 | 1300 | 68 |
| 43b | " " | 141 | 1650 | 990 | 32 |
| 42 | catechol | 14 | 1630 | 1300 | 69 |
| 42b | " | 134 | 1750 | 1065 | 27 |
| 32 | Thionex | 14 | 1570 | 1500 | 65 |
| 32b | " | 188 | 1040 | 1150 | 43 |
| 48 | phenyl beta naphthylamine | 14 | 1900 | 1400 | 65 |
| 48b | " " " | 122 | 1050 | 1120 | 44 |
| 51 | Beta nitroso naphthol | 14 | 1500 | 1240 | 70 |
| 51b | " " " | 136 | 1690 | 960 | 43 |
| 37 | Ethyl Selenac | 14 | 1450 | 1420 | 72 |
| 37b | " " | 180 | 1320 | 1020 | 27 |
| 29 | Accelerator 808-10 parts | 14 | 1490 | 1580 | 57 |
| 29b | " " " " | 162 | 670 | 1150 | 33 |
| 52 | p-toluidine | 14 | 1800 | 1300 | 64 |
| 52b | " | 128 | 1020 | 1080 | 48 |
| 30 | Captax | 14 | 1370 | 1550 | 83 |
| 30b | " | 192 | 820 | 1330 | 90 |
| 31 | Altax | 14 | 1350 | 1650 | 78 |
| 31b | " | 162 | 930 | 1300 | 91 |
| 62 | hydroquinone | 14 | 1290 | 1200 | 50 |
| 62b | " | 133 | 1750 | 1020 | 33 |

*/ C-MA Copolymer 11.8% acid, 53% conversion.

FIGURE XIV

CREEP OF THE C-MA COPOLYMERS: AIR CURE WITH ORGANIC COMPOUNDS.



Legend: See Table XVIII.

(d) Further Evaluation of Aromatic Diamine and Polyhydroxybenzene Cures. - The results of the preliminary study on organic curing agents have warranted a more thorough investigation of diamine and polyhydroxybenzenes cures. Phloroglucinol and p-phenylenediamine were used as representative compounds in equimoler quantities (5 parts phlorglucinol). To gain further insight into the nature of these cures, creep behavior, tensile strength and the amount of extractable materials (with methanol) were determined after 11, 26 and 50 days of air cure. Also the weight loss of free films was determined in a two month period of air drying. To possibly gain further information on cure, commercial Neoprene AC lacquers were tested concurrently with the C-MA copolymer films.

Results of the creep experiments on the C-MA films are shown in Figure XV and Table XX. For the C-MA gum specimens relatively little decrease in compliance was observed on standing for 50 days. With phloroglucinol, the specimens exhibited a noted decrease in compliance on continued air cure, accompanied with a spreading of retardation times over a wider time scale. Corresponding compliances were less for p-phenylenediamine cures, and accompanying spreading of retardation times was also less as evidenced by creep curves of more concave character than those resulting from phloroglucinol curves.

Table XX

Creep of the C-MA Copolymers*; Phloroglucinol and p-Phenylenediamine Cures.

| Curing agent | Air cure, days | Compliance $cm^2/gm \times 10^4$ | | |
|---|---|---|---|---|
| | | 1 min. | 10 min. | 100 min. |
| - | 11 | 2.00 | 6.20 | - |
| - | 25 | 2.03 | 5.59 | - |
| - | 50 | 1.91 | 4.41 | - |
| phloroglucinol, 5 parts | 11 | 1.27 | 2.57 | 5.39 |
| " | 25 | 1.00 | 1.69 | 2.59 |
| " | 50 | 0.86 | 1.26 | 1.67 |
| p-phenylenediamine 4.29p | 11 | 0.84 | 1.70 | 3.17 |
| " | 25 | 0.70 | 1.26 | 2.19 |
| " | 50 | 0.45 | 0.68 | 1.04 |

*/ C-MA copolymer 12.7% acid; 55% conversion.

In Figure XVI a few of the previously discussed creep experiments are plotted on an exaggerated scale of compliance; these runs were also carried to a longer experimental time scale. Quite an abrupt change in slope of the creep curves during the experiment is apparent, resulting in creep curves represented by two straight line portions of different slopes on the compliance-log t plot. This sort of observation has been also made by Hahn and Gazdik (22) in their creep study of Neoprene E.

Determination of the approximate distribution functions, L(log τ), becomes associated with some difficulties in interpretation as a second maximum would be realized if a constant viscosity contribution is subtracted,(Figure IX). Presumably a change in viscous flow is associated with the change in the slope of the creep curve. Also the distribution function of a more "normal" shape would result if the new flow contribution is taken into account.

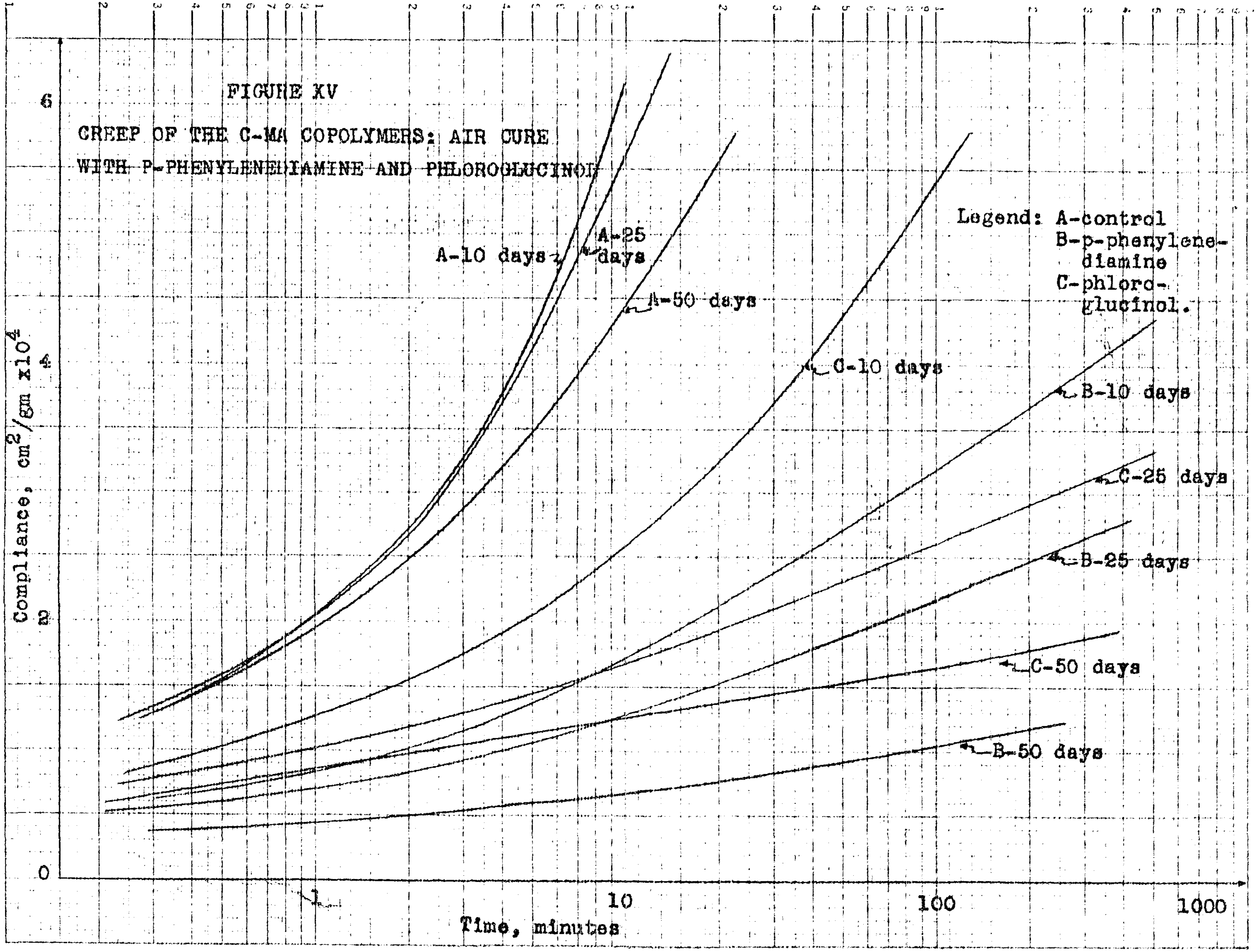


FIGURE XV

CREEP OF THE C-MA COPOLYMERS: AIR CURE WITH P-PHENYLENEDIAMINE AND PHLOROGLUCINOL

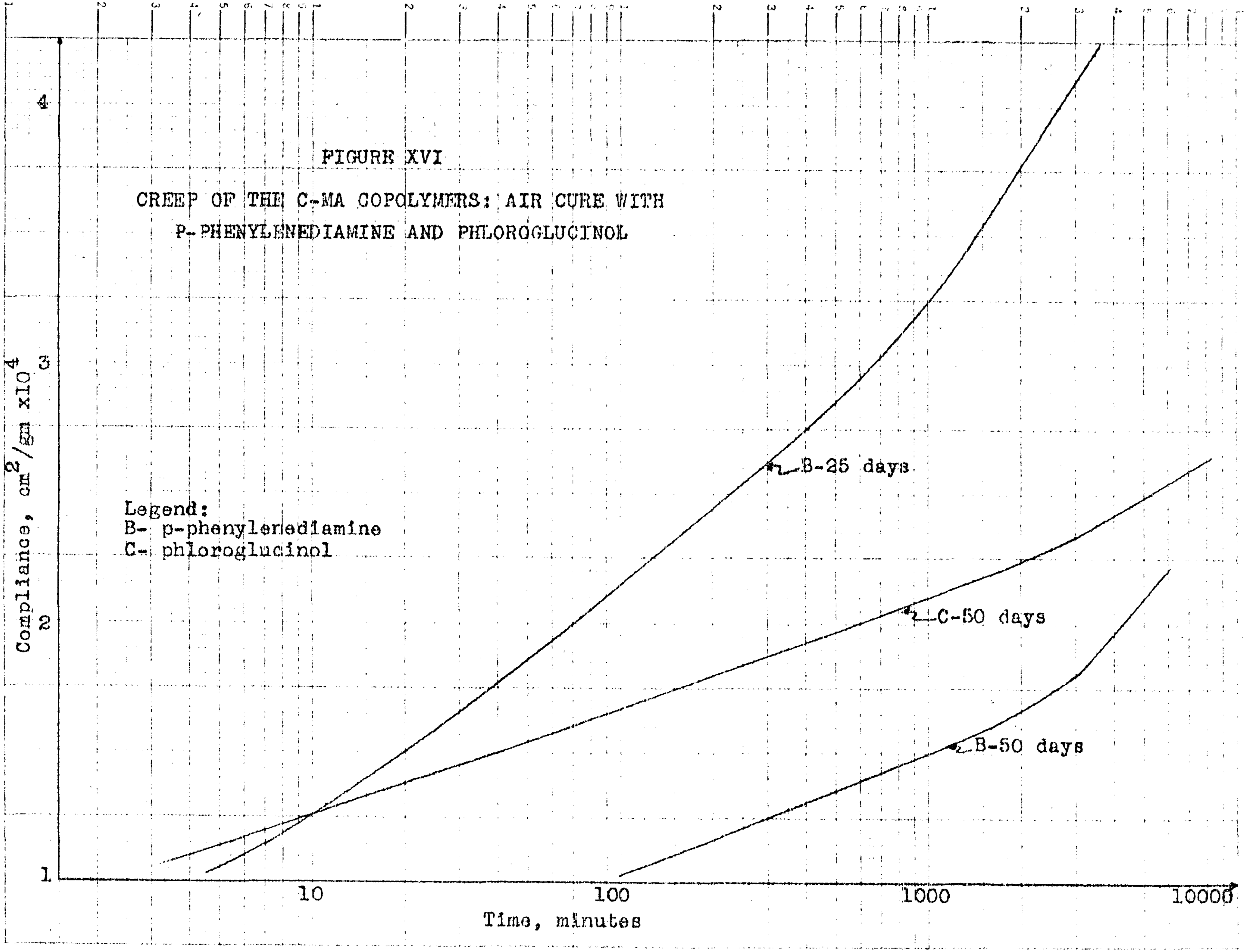


FIGURE XVI

CREEP OF THE C-MA COPOLYMERS: AIR CURE WITH
P-PHENYLENEDIAMINE AND PHLOROGLUCINOL

No satisfactory creep experiments could be carried out with Neoprene AC. It was similar in its behavior to a sample of Goodyear's Neoprene coating, by showing no appreciable creep with a stress of some 10 kg/cm$^2$ but which exhibit large creep and necking under larger stresses.

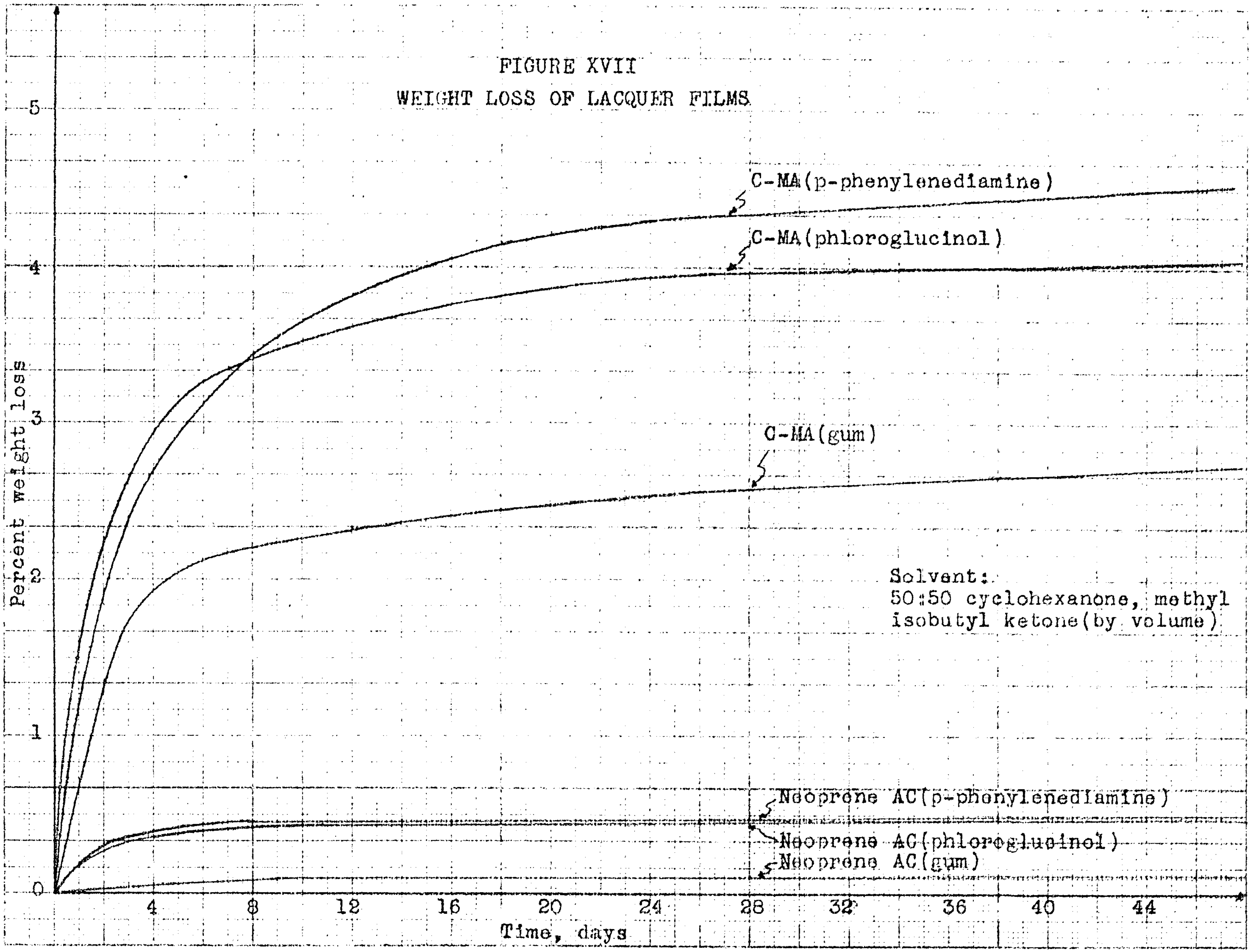
Tensile strength, elongation at break and ASTM set are summarized in Table XXIfor these experiments. Tensile strengths for the C-MA copolymer show improvement on incorporation of curing systems and also on standing with phloroglucinol cure; the tensile of 1790 psi., determined after 11 days of air cure improved to 2890 psi. as measured at 50 days. With p-phenylenediamine cure a maximum tensile 4320 psi. was achieved after 26 days. Neoprene AC gum specimen had a tensile of 4630 psi. after 11 days, increasing to 5250 psi. for 50 days of air cure. These high tensiles for the gum specimens were not unexpected, as Neoprene AC is in high state of crystallinity especially when stretched. Upon incorporation of phloroglucinol, the tensile was reduced to 3600 psi., and very little change was noted on standing. Para phenylenediamine produced improved tensiles (5300 psi.), which also showed no significant change on standing.

Results of the Soxhelt extractions of the C-MA copolymer films are summarized in Table XXII. Methanol was chosen as a solvent because phloroglucinol, p-phenylenediamine and ketonic solvents are all soluble in it. The C-MA gum films were about 10 percent extractable ; the gum specimens of Neoprene AC did not yield more than 7.5 percent extractable material. Extractions for the cured specimens show no more than12.5 percent extractable material for the C-MA copolymer and 10.5 percent for Neoprene AC vulcanizates. In comparison with the control these results imply that a part of the curing agent is firmly bound to the polymer to yield it non-extractable. In testing the gum extracts with 2,4 dinitrophenylhydrazine, a positive test for the carbonyl group resulted, being less distinct for that of Neoprene AC. The retention of solvent in the films on storage seems to be a necessary conclusion. Extractions after 26 days of air cure resulted in less distinct tests for the carbonyl group. Extracts from p-phenylenediamine cured specimens gave also a test for primary amines with nickel chloride and 5-nitrosalicylaldehyde.

As retention of ketone solvents in the C-MA copolymer films has been suggested by several observations, the weight loss of free polymer films has been determined in the course of two months, followed by drying to constant weight _in vacuo_. The percent weight loss of approximately 2 gram free films was recorded periodically after 4 days of air cure on glass plates. These data are shown in Figure XVII. The weight loss of Neoprene AC specimens did not exceed 0.5 percent in a 50 day period, while the weight loss for the cured C-MA films was approximately 4 percent. The carboxyl group in the C-MA copolymer is apparently effective in trapping some of the ketone solvent by association. It is of interest to note that for gum samples of both C-MA copolymer and Neoprene AC, considerably less weight loss occured than for specimens with curing agents. This seems to indicate that some more solvent is associated with the curing agent and remains in the films for some time. After 50 days of air drying these free films were dryed to constant weight _in vacuo_

FIGURE XVII

WEIGHT LOSS OF LACQUER FILMS



at 50° C. Additional small decrease in weight occured, ranging from 0 percent for Neoprene AC gum sample to 0.97 percent for Neoprene AC, cured with phloroglucinol.

## Table XXI

Phloroglucinol and p-Phenylenediamine as Curing Agents for the C-MA Copolymer* and Neoprene AC.

| Polymer and Curing Agent | Amount, % | Tensile, psi. After Air cure, Days | | | Elongation at Break % After Air Cure, days | | | ASTM set, % After Air Cure, Days | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 11 | 26 | 50 | 11 | 26 | 50 | 11 | 26 | 50 |
| C-MA | – | 1325 | 1750 | 1590 | 1030 | 950 | 960 | 70 | 57 | 54 |
| Neoprene AC | – | 4630 | 5150 | 5250 | 890 | 820 | 880 | 35 | 24 | 28 |
| C-MA, phloroglucinol | 5 | 1790 | 1860 | 2890 | 1000 | 840 | 830 | 49 | 30 | 21 |
| Neoprene AC, phloroglucinol | 5 | 3600 | 3520 | 3710 | 810 | 850 | 830 | 33 | 34 | 28 |
| C-MA, p-phenylene-diamene | 4.29 | 3140 | 4320 | 4120 | 870 | 880 | 870 | 51 | 38 | 39 |
| Neoprene-AC, p-phenylenediamene | 4.29 | 5300 | 5320 | 5080 | 900 | 860 | 860 | 35 | 36 | 42 |

*/ C-MA copolymer 12.7% acid; 55% conversion.

## Table XXII

Extraction of the C-MA Copolymer Films with Methanol.*/

| Film | Extracted Film |  | Extract |  |
|---|---|---|---|---|
|  | Wt. Loss, gms | % Wt. loss | dry wt., gms. | Corresponding Wt. loss, % |
| **After 11 days air cure.** |  |  |  |  |
| C-MA - gum | 0.1894 | 9.05 | 0.1528 | 7.31 |
| Neoprene AC-gum | 0.1592 | 7.55 | 0.1605 | 7.57 |
| C-MA, phloroglucinol | 0.2777 | 12.58 | - | - |
| Neoprene AC " | 0.2189 | 9.65 | - | - |
| C-MA, p-phenylenediamine | 0.2567 | 11.24 | 0.2363 | 10.35 |
| Neoprene Ac " | 0.2289 | 10.35 | 0.2033 | 9.20 |
| **After 26 days air cure.** |  |  |  |  |
| C-MA - gum | 0.1976 | 9.47 | 0.1980 | 9.48 |
| Neoprene AC-gum | 0.1509 | 7.03 | 0.1456 | 6.79 |
| C-MA, phloroglucinol | 0.2665 | 12.2 | 0.2463 | 11.3 |
| Neoprene AC " | 0.2115 | 9.45 | 0.1822 | 8.15 |
| C-MA, p-phenylenediamine | 0.2787 | 12.2 | 0.2601 | 11.38 |
| Neoprene AC " | 0.2033 | 9.19 | 0.1870 | 8.47 |

*/ C-MA copolymer 12.7% acid; 55% conversion, 0.1 gm. phloroglucinol and 0.0858 gms p-phenylenediamine used in each film.

4. Reinforcement. - The possibility to reinforce the C-MA copolymer with various carbon blacks and hydrophobic silica was investigated. The results, summarized in Table XXIII indicate that generally no appreciable reinforcement is obtained, rather loadings up to 20 and 40 parts carbon black result in impaired tensile strengths, reduced elongations and increased permanent sets. Hydrophobic silica loadings of 10 and 20 parts have effected some improvement as compared to the control. However, permanent set has increased as in the previous case. Reduction in compliance has also taken place when going from 10 to 20 parts hydrophobic silica, as evidenced by the creep tests depicted in Figure XVIII.

As the C-MA copolymer is acidic in its nature, it was of interest to determine the effect of basic and acidic carbon blacks as loading materials. Huber HX, a channel black and Philblack O, high abrasion furnace black were chosen as representative materials, exhibiting comparable surface areas. There was some increase in gum tensile strengths, while with cured samples (p-phenylenediamine ) no improvement was realized. However, in both cases there was an increase in permanent set on loading. The creep experiments conducted on these samples showed that there was no reduction in compliance for gum specimens as compared to the control. With cured samples, loading affected a noticeable reduction in compliance. There was no data to indicate basic differences between the two carbon blacks. This presumably implies the lack of participation of the carboxyl groups on carbon black sorption.

These results are in conformity with the anticipated tendencies of the C-MA copolymer as a stress crystallizable rubber.

## Table XXIII

The C-MA Copolymer Properties: Effect of Loading.

| Polymer | Load, parts (3) | Tensile, psi | Elongation at break, % | ASTM set, % |
|---|---|---|---|---|
| 15.7% acid, 66% conv. (1) | R.S., 2 | 5370 | 610 | 19 |
| " " " " | P-33,2 | 5200 | 605 | 18 |
| " " " " | P-33,20 | 4700 | 590 | 28 |
| " " " " | P-33,40 | 3310 | 530 | - |
| 13.2% acid,59% conv. (1) | R.S.,2 | 5660 | 660 | 14 |
| " " " " | E.P.C.,2 | 5740 | 710 | 12 |
| " " " " | E.P.C.,20 | 4650 | 530 | 13 |
| " " " " | E.P.C.,40 | 4330 | 440 | 15 |
| 11.8% acid, 53% conv. (2) | - | 3990 | 900 | 20 |
| " " " " | Hydrophobic silica, 10 | 4670 | 870 | 25 |
| " " " " | Hydrophobic silica,20 | 4530 | 790 | 37 |

(1) Cure: One part MgO - 2 hours at 120° C.

(2) Cure: 10 parts Ethyl Zimate, 2 parts diamino diphenylene methane- 2 months air drying.

(3) R.S. - Royal Spectra - color Black
E.P.C. - Easy Processing Channel Black.

## Table XXIV

The C-MA Copolymer Properties (1); Effect of Acid and Basic Carbon Blacks.

| Curing Agent | Load, parts (3) | Tensile, psi. | Elongation at break % | ASTM set, % |
|---|---|---|---|---|
| (2) - | - | 1750 | 950 | 57 |
| - | HuberHX ,10 | 2490 | 880 | 110 |
| - | Philblack 0,10 | 2500 | 890 | 98 |
| (2) p-phenylenediamine, 4.3p | - | 4320 | 880 | 38 |
| p-phenylenediamine, 4.3p | Huber HX,10 | 4000 | 710 | 52 |
| " " | Philblack 0,10 | 4040 | 730 | 46 |

(1) C-MA copolymer 12.7% acid, 55% conversion. Tested after two weeks of air cure.

(2) Tested after 26 days of air cure.

(3) Huber HX - pH= 4.4; surface area 78 $m^2/gm$, partical size 365Å.

Philblack O - pH= 9.0; surface area 84 $m^2/gm$, partical size 347Å.

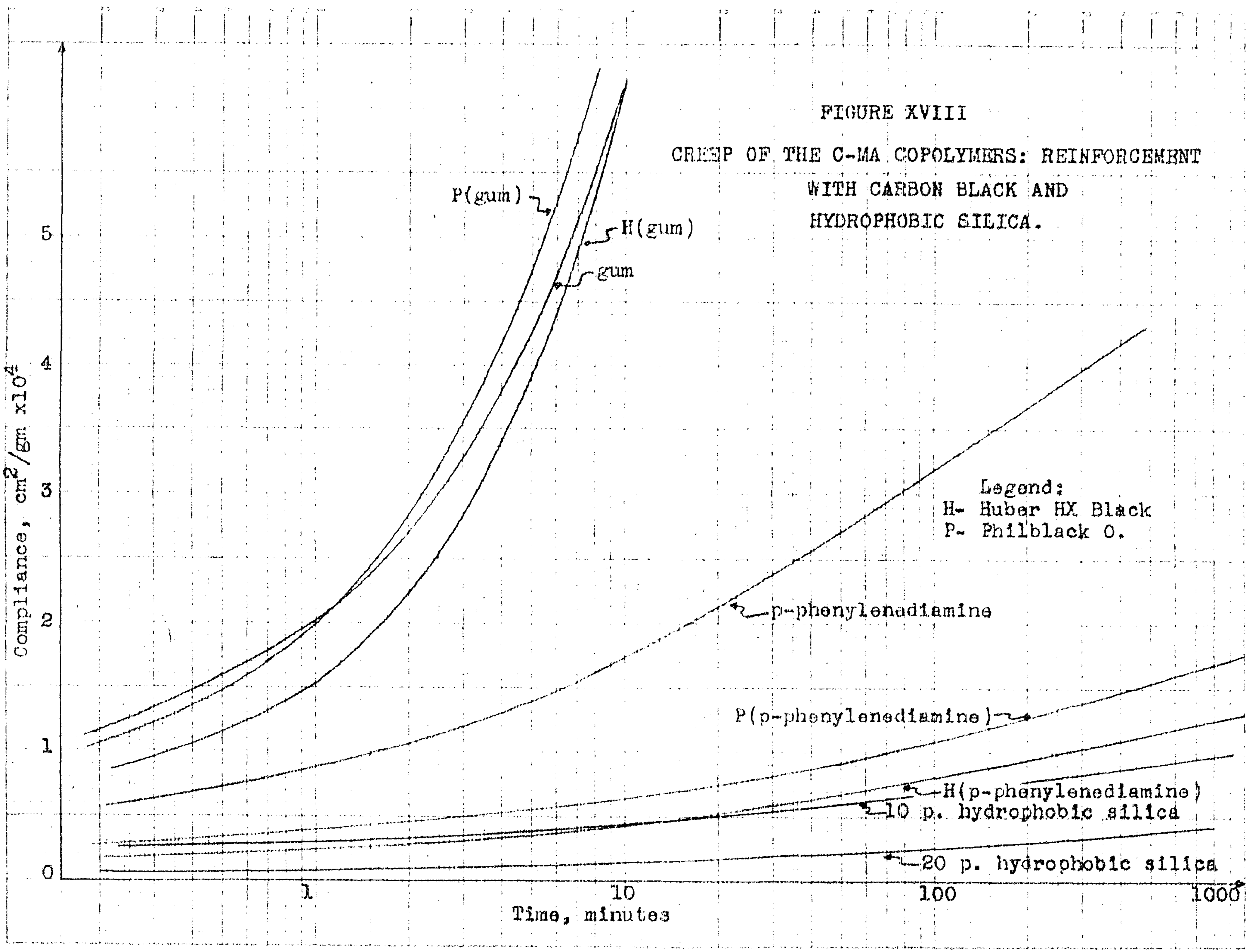


FIGURE XVIII

CREEP OF THE C-MA COPOLYMERS: REINFORCEMENT WITH CARBON BLACK AND HYDROPHOBIC SILICA.

5. Rain Erosion Tests and Creep Behavior. - Creep studies were originally undertaken to learn more about the mechanical behavior of the C-MA vulcanizates and on that additional information base some correlation with the rain erosion behavior. The lack of rain erosion data, however, has hindered this correlating program. Only one series of Cornell rain erosion test films , prepared in this laboratory (1), have concurrently been tested for their viscoelastic behavior. These results are summarized in Table XXV and Figure XIX. It is apparent that there is no obvious correlation between the two tests. Goodyear's and Gates' neoprene coatings have thus far exhibited most desirable rain erosion resistance characteristics, and both have exhibited extremely low compliances, as compared with those of the C-MA vulcanizates. However, the general reduction in compliance has not necessarily resulted in improved rain erosion resistance. Zinc oxide vulcanizates have been shown of being inferior to organic curing agents. The best organic curing system consisted of diaminadiphenylene methane and Goodyear's Accelerator 983-C; this system would be expected to exhibit relatively low compliance . Cures with Goodyear's Accelerator 983-C produced second best results, but exhibited varied creep behavior (Figure XIX). It seems that at the present state of knowledge the effects of cure, pigmentation, fillers, and smoothness of the coating are all important to resulting in a satisfactory rain erosion resistant coating.

It has been reported that there is some "bubbling" with the C-MA copolymer specimens during the rain erosion test. It was believed that this might result from some solvent which has been trapped by the coating. Accordingly, in addition to previously described weight losses of free films, creep experiments were run on the C-MA copolymer when cast from three different solvent combinations of cyclohexanone, methyl isobutyl ketone, toluene and xylene, and after identical air-cure (24 days). Varied creep behavior resulted (Figure XX). The 50:50 mixture by volume of cyclohexanone, methyl isobutyl ketone produced the creep curve of highest compliance. The 50:50 mixture of methyl isobutyl ketone, toluene and 25:37. 5:37.5 mixture of methly isobutyl ketone, toluene and xylene yielded almost identical creep curves. The first solvent mixture of cyclohexanone and methyl isobutyl ketone was expected to remain longest in the lacquer films as cyclohexanone is the highest boiling of the solvents used, and therefore, yields the highest compliance. The other two solvent mixtures demonstrate that toluene and xylene both are largely lost during this period. It is probable that ketones in general may be expected to remain longer in copolymer films due to association with the carboxyl groups. This assumption is consistent with the creep data.

## Table XXV

Rain Erosion Performance Versus Creep Behavior of the C-MA Copoylmer

| Specimen | Polymer | Load parts | Cure | Primer(6) | Timeto erode through,min. | Air Cure days | Stress kg/cm$^2$ | Compliance cm$^2$/gm x $10^5$ 1 min. | 10 min. |
|---|---|---|---|---|---|---|---|---|---|
| 9a | C-MA[1] | 2 pts.R.S. | 5 pts. ZnO,R.T. | Bostik | 20 | 10 | 8.12 | 3.6 | 4.7 |
| 9b | C-MA[2] | None | 10 pts. Zimate[3]<br>2 pts. DADPM[4], 1 hr. at 120°C. | C-MA | 30 | 20 | 5.89 | 7.2 | 9.9 |
| 9c | " | 2 pts. R.S. | 2 mls.Accel 983-C[5] per 2 gms polymer, R.T. | " | 10 | 23 | 5.63 | 16.5 | 35. |
| 9d | " | None | 5 pts. ZnO, R.T. | Bostik | 10 | 14 | 7.63 | 3.5 | 5.3 |
| 9e | " | " | 2 mls Accel.983-C per 2 gms polymer, R.T. | Bostik | 30 | 18 | 8.81 | 10.5 | 16.7 |
| 9e | " | " | 2 mls Accel.983-C per 2 gms polymer, R.T. | C-MA | 40 | 20 | 8.32 | 16. | 30. |
| 9g | " | 5 pts. Hydrophobic Silica | 5 pts. ZnO, R.T. | Bostik | 20 | - | - | - | - |
| 9h | " | None | 1 pt. MgO, R.T. | C-MA | 20 | - | - | - | - |
| 9j | " | None | 2 mls. 983-per C/2 gm polymer - 4 pts. DADPM, R.T. | Bostik | 60 | - | - | - | - |
| 9j | " | None | 2 mls 983-C/2gm polymer - 4 pts. DADPM - 2 pts. ZnO, R.T. | Bostik | 20 | 19 | 9.45 | 7.4 | 10.3 |
| - | Gates | - | 6.3 ml Acc. N-300-9 per 100 gms of lacquer, R.T. | Bostik | 60 | 7 | 3.38 | 1.15 | 1.3 |
| - | Goodyear | - | 8.4 ml Acc. 983-C per 100 gm of lacquerR.T. | Bostik | 80 | 6 | 33.1 | 0.15 | 0.22 |

1) C-MA copolymer 12.7% acid, 55% conversion
2) C-MA " 11.8% acid, 53% conversion
3) Zinc diethyl dithiocarbamate
4) Diamino diphenylene methane
5) Goodyear Accelerator 983-C
6) C-MA primer, 21% acid, 80% conversion 5% $MgCO_3$ as curing agent. Bake: 4 hrs. at 120°C.

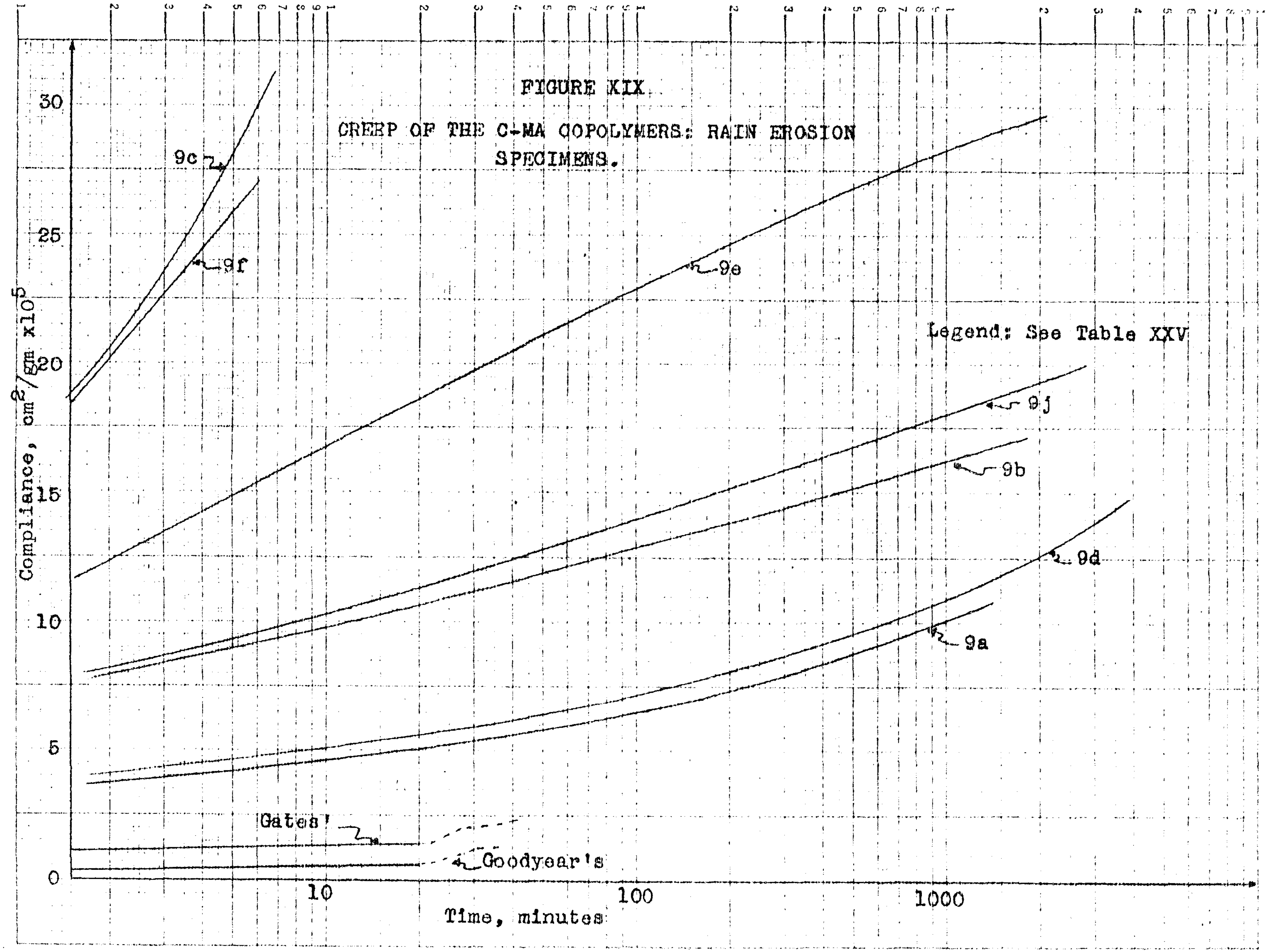


FIGURE XIX.

CREEP OF THE C-MA COPOLYMERS: RAIN EROSION SPECIMENS.

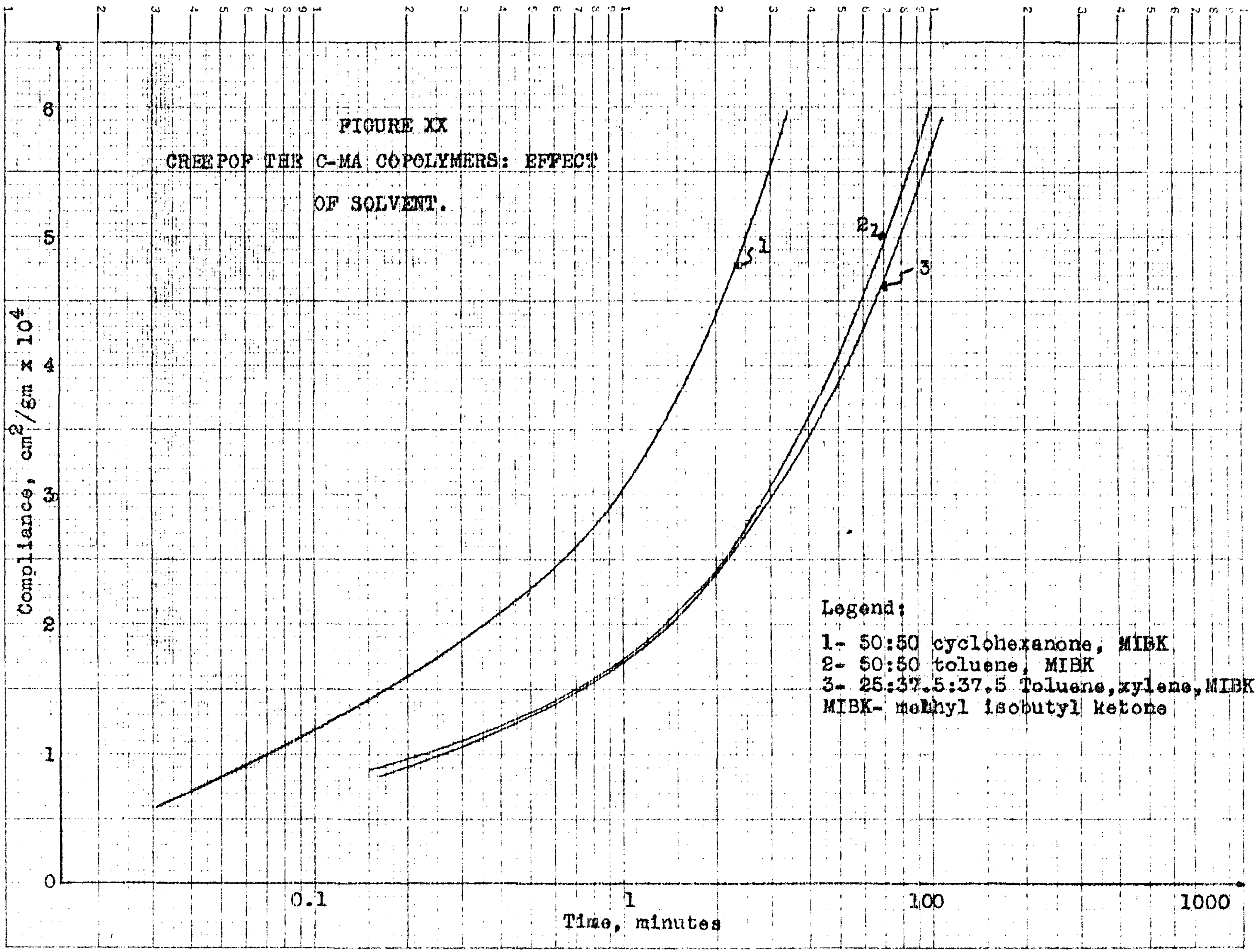


FIGURE XX

CREEPOF THE C-MA COPOLYMERS: EFFECT OF SOLVENT.

6. **Effect of Composition and Conversion on Creep Behavior.-** Due to gradually increasing intermolecular forces when increasing the methacrylic acid content in the copolymer, one would expect a gradual reduction in compliance. Reduction in compliance is also anticipated on increased conversions. A series of the C-MA copolymers of acid content varying from 6.4 to 21 percent and of conversions varying from 29 to 55 percent were tested for their creep behavior and tensile properties (Tables XXV and II).

Table XXVI

Creep Behavior of the C-MA Copolymers*; Effect of acid Content and Conversion.

| Polymer | | | | Compliance $cm^2/gm$ x $10^4$ | | |
|---|---|---|---|---|---|---|
| Acid, % | Conversion, % | Curing agent, parts | Stress, $kg/cm^2$ | 1 min. | 10.min. | 100 min. |
| 6.4 | 23 | - | 8.93 | 4.66 | - | - |
| 15 | 29 | - | 7.60 | 2.10 | 6.92 | - |
| 15 | 55 | - | 8.64 | 1.29 | 3.24 | - |
| 21 | 33 | - | 8.33 | 1.27 | 3.02 | - |
| 21 | 48 | - | 9.22 | 1.04 | 2.21 | - |
| 21 | 48 | phloroglucinol,5 | 10.82 | 0.86 | 1.62 | 3.91 |
| 21 | 48 | p-phenylene-diamine,4.29 | 8.18 | 0.81 | 1.46 | 2.92 |

*/ Four parts of tetramethyl thiuram disulfide milled in to attain complete solubility. Films air-dried for 20 days before testing.

Creep behavior of these copolymers is also shown in Figure XXI, indicating that the predicted trend prevails. It is of interest to note that the two C-MA copolymers of 15 and 21 percent acid resulted in almost identical creep curves, but exhibited conversion of 55 and 33 percent respectively. Apparently, molecular weight of the higher conversion polymer is such that to cause the two copolymers to show similar creep behavior.

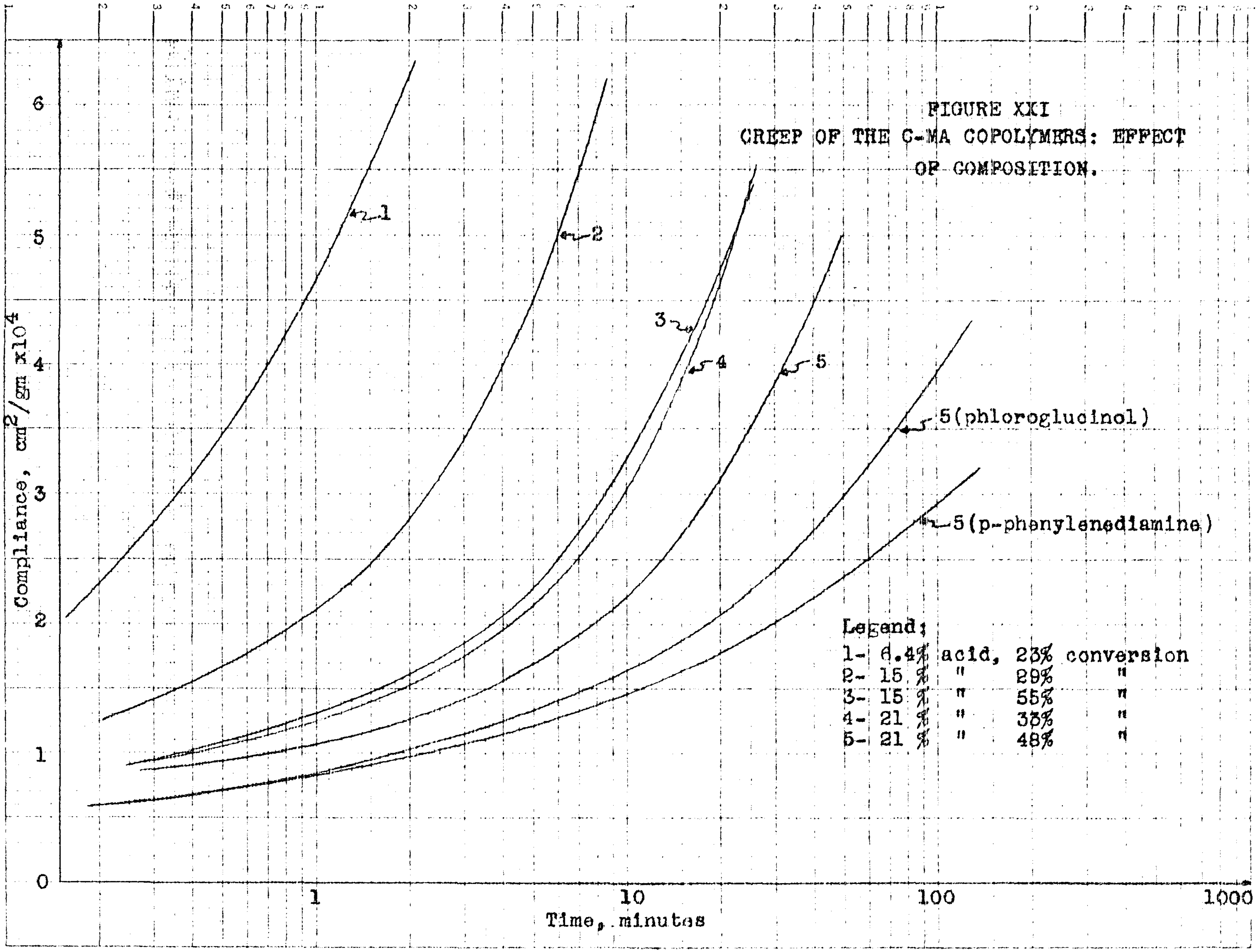


FIGURE XXI
CREEP OF THE C-MA COPOLYMERS: EFFECT OF COMPOSITION.

The C-MA copolymer of 21 percent acid and 48 percent conversion was also cured with 5 parts phloroglucinol and 4.29 parts p-phenylenediamine, to observe the effect of higher acid content on these cures, previously described in detail for a copolymer of 12.7 percent acid. It was of considerable interest to note that in this case phloroglucinol cure resulted in a tensile of 4580 psi. (set-29%) while that of p-phenylenediamine cure was only 3160 psi.(set 38%). The diamine cure still exhibits a lower compliance than that shown by phloroglucinol cures but the difference has become considerably less as compared to similar runs in Figure XV for a copolymer of 12.7 percent acid.

As a result of this data and that of Neoprene AC vulcanizates, it seems plausible to assume that the C-MA copolymers are air-cured mainly through chloroprene units with p-phenylenediamine, while through carboxyl groups with phloroglucinol.

## IV EXPERIMENTAL

### A. Copolymer Preparations.

1. Emulsion Polymerization.- Monomeric chloroprene was obtained as a 50 percent inhibited xylene solution from I.E. du Pont de Nemours and Company. Glacial methacrylic acid containing 0.1 percent hydroquinone as an inhibitor was obtained from Rohm and Haas Company. Chloroprene was fractionated under reduced pressure (220 and 280 mmHg) immediately prior to use; methacrylic acid was fractioned at about 5 mmHg and it could be stored under refrigeration for several weeks prior to use.

Polymerizations were carried out in 6 ounce citrate bottles fitted with crown caps. The bottles were charged by first introducing emulsifier solution, prepared from redistilled water and Triton X-301 ( a 20% aqueous emulsion of an alkyl aryl polyether sulfate, obtained from Rohm and Haas Company). Methacrylic acid was introduced to the previously cooled emulsion and the mixture frozen solid. Distilled chloroprene and sulfur were added and the reaction vessel shaken vigoriously to effect a complete dispersion of sulfur in chloroprene. Potassium persulfate catalyst was added just before capping the bottle. Polymerizations have been carried out both under nitrogen atmosphere, and without attempts to eliminate air from the reaction vessel. No apparent effect on rate or polymer properties has been observed because of some air which may remain in the reaction vessel. For polymerization, the bottles were rotated end-over-end at 30 rpm in a constant temperature water bath. Immediately after the discontinuation of the reaction, the latices were short-stopped with an emulsion containing 5.8 parts hydroquinone, 5.8 parts tetramethyl thiuram disulfide, 5.3 parts Triton X-301 and 100 parts of distilled water. The short-stop was prepared by passing the mixture several times through a colloid mill. One cubic centimeter of the short-stop was added for each 5 gms of monomer charged.

2. Coagulation and Drying.- The short-stopped latices were usually coagulated with saturated solution of sodium chloride or sodium sulfate at room temperatures. Latices from polymerizations carried out to high conversions at 50°C. were coagulated at elevated temperatures (up to 70° C) to obtain washable coagulates. When coagulated at room temperature polymers in a form of fine powders resulted. Latices were also coagulated by freezing at dry-ice temperature; easily washable products resulted from this latter procedure. The coagulated polymers were torn into small pieces and washed thoroughly with distilled water until there was no acid in the washings. The polymers were dried to constant weight in vacuo at 40° to 50° C. Drying required 24 to 72 hours, and was facilitated by passing the polymer through a rubber mill to expose new surface.

The dry polymer was plasticized by adding 2.5 parts tetramethyl thiuram disulfide on a cooled rubber mill. One part phenyl beta naphthylamine was added concurrently to serve as an anti-oxidant.

3. Bulk Polymerization.- Bulk polymerizations were carried out to obtain data for the relative reactivity determination. As in the emulsion system, the polymerization was carried out in 6 ounce citrate bottles. At room temperature, methacrylic acid and chloroprene were weighed accurately into the reaction bottles, which were

previously flushed with nitrogen. Immediately before capping, 0.5 percent benzoyl peroxide was added as an initiator. Polymerization was carried out in the constant temperature water bath at 30°C. Conversions ranging from 5 to 24 percent were obtained for polymerization times of 43 to 68 hours. Upon discontinuation of the polymerization no short-stop was added, because of the low rate of polymerization. Immediately, the contents of the reaction bottles was emptied into 500 cc of water and using an aspirator subjected to reduced pressure to eliminate the unreacted chloroprene. The torn polymer was carefully washed with distilled water until there was no acid in the washings. The polymers were dried to constant weight *in vacuo* at 50° C

4. *Compounding and Cure.-* Pigments were incorporated to the polymer by using a rubber mill. Minimum amount of time, to get complete mixing, was employed. No curing agents were added at this stage.

Ten to fifteen percent lacquers in cyclohexanone or in mixed cyclohexanone and methyl isobutyl ketone were prepared by ball milling with flint balls. Usually two to seven days ball milling was sufficient to obtain apparently gel free lacquers.

Before the application of a lacquer, the curing system was incorporated. Organic curing agents were dissolved in a minimum of solvent and added to the lacquers shortly before use. Metal oxides were prepared as 0.5 to 2 percent slurries by ball milling in the same solvent as used in the lacquer. These slurries were added to the lacquers immediately before use.

5. *Preparation of Films for Test Purposes.-* Mechanical

testing of the C-MA copolymers was conducted on free films, generally 4 to 6 mills in thickness, obtained from polymer lacquers. These films were obtained by pouring the lacquers on 4x6 inch glass or tin plates, placed on carefully levelled steel plates to result in films of uniform thickness. In case of gum specimens or those for air cure, the films were removed from the plates after they were allowed to air dry a minimum of 72 hours. This removal was affected by immersion of the glass panels in water for a few minutes. The resulting films were dusted with talcum powder to prevent sticking. Films from oven cures, usually for 2 hours at 120°C, were removed from glass plates in the same fashion, while those from the tin plates by amalgamating the tin.

Generally the films were cut into 1/4 inch strips for mechanical testing. For tensile measurements, the thickness of the films was determined with a dial-gauge micrometer. The average cross-sectional area of the creep specimens, however, was calculated directly from the weight, density, and length of the specimen. Density of a representative C-MA film (12.4% acid, 55% conversion) was determined according to ASTM procedure (5), and was found to be 1.235.

B. Analytical

1. Copolymer Analysis.- The percentage conversion of the monomers into polymer was calculated from the dry polymer weight and the monomer charge.

(a) Acid Titration.- To determine the composition of the copolymer, the amount of unreacted acid in a 10 cubic centimeter latex sample was determined. The washing water of the coagulated sample was saved and the amount of unreacted acid determined by titration of aliquot portions with 0.1 N sodium hydroxide solution. The weight of methacrylic acid polymerized was thus known and the percent acid in copolymer could be calculated. This method was subject to errors due to some physical losses. Accordingly the precision of the method was not entirely satisfactory. However, it was generally more satisfactory than direct titration of the polymer itself in view of solubility difficulties.

(b) Chlorine Analysis by Sodium Peroxide Fusion.- Sodium peroxide fusion of the polymer was carried out in a Parr bomb. A finely divided 0.15 gram sample was fused with 15 gms sodium peroxide using 0.1 gm sucrose and 0.5 gm benzoic acid as initiator. Flame ignition was found to produce substantially complete fusion (21). The fusion mixture was dissolved in 200 cc of distilled water and acidified with nitric acid. Chlorine was determined by Volhard titration.

Chlorine analysis has been reported to be consistently 2 percent low for pure polychloroprene (21,3). Consequently, the consistent error in analysis has been properly corrected from the titrated chloroprene content. Precision of this method has found to be quite satisfactory.

2. Copolymer Extraction.- Standard Soxhlet extractions with methanol, petroleum ether and ether have been carried out on gum samples and on polymer films. Films were cut into 1/4 inch squares and were extracted for 48 hours with 350 cc solvent. Both the extracted films and the resulting extracts have been dried to constant weight in vacuo at 50°C. With extracts from free films, 2 cc portions were tested with 2,4 dinitrophenylhydrazine for carbonyl compounds

i.e. for ketone solvents and with nickel chloride and 5-nitrosalicylaldehyde for primary amines in case of diamine cures.

3. Loss of Solvent from Films.- The polymer films were prepared as described elsewhere, and stripped four days after preparation. Periodically the weight change was determined on an analytical balance and the percent weight loss was computed, based on the initial film weight (ca. 2 gms).

## C. Testing

1. Creep Apparatus.- The creep apparatus, clamp assembly and the tension bob have been depicted in Figures XXII to XXVII. In this apparatus, the polymer specimens were deformed under constant stress in glass tubes (1.39 inches outside diameter,) which were placed vertically into a constant temperature water bath (24x12x12 inches). Insertions for the glass tubes, and the holes for the clamp assembly were drilled into the slate bottom, and the tubes cemented in place with a commercial sealing compound, "Gasket-Goo" No.1., made by Pep Manufacturing Company. Temperature control was achieved by means of a mercury thermal regulator in connection with a mercury relay, both manufactured by The American Instrument Company. The water in the bath was circulated by a vertical immersion pump. (Schaar and Company.)

The specimens were held in the glass tubes with two specially designed aluminum clamps (Figure XXV)to prevent slippage. The inner surfaces of the clamps were corrugated in such a fashion that uniform pressure was exerted by the clamps, even though the specimen was

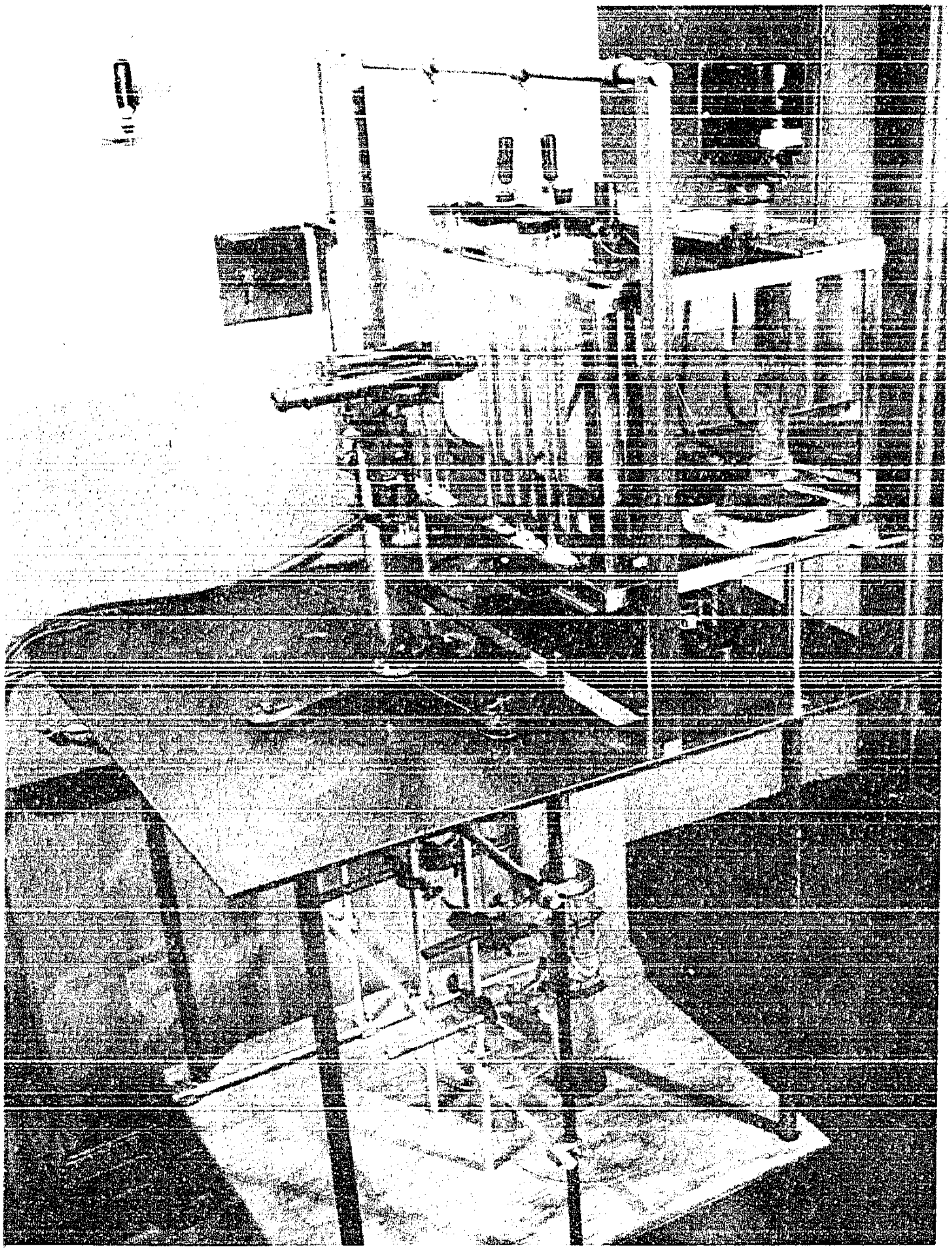


FIGURE XXII

CREEP APPARATUS

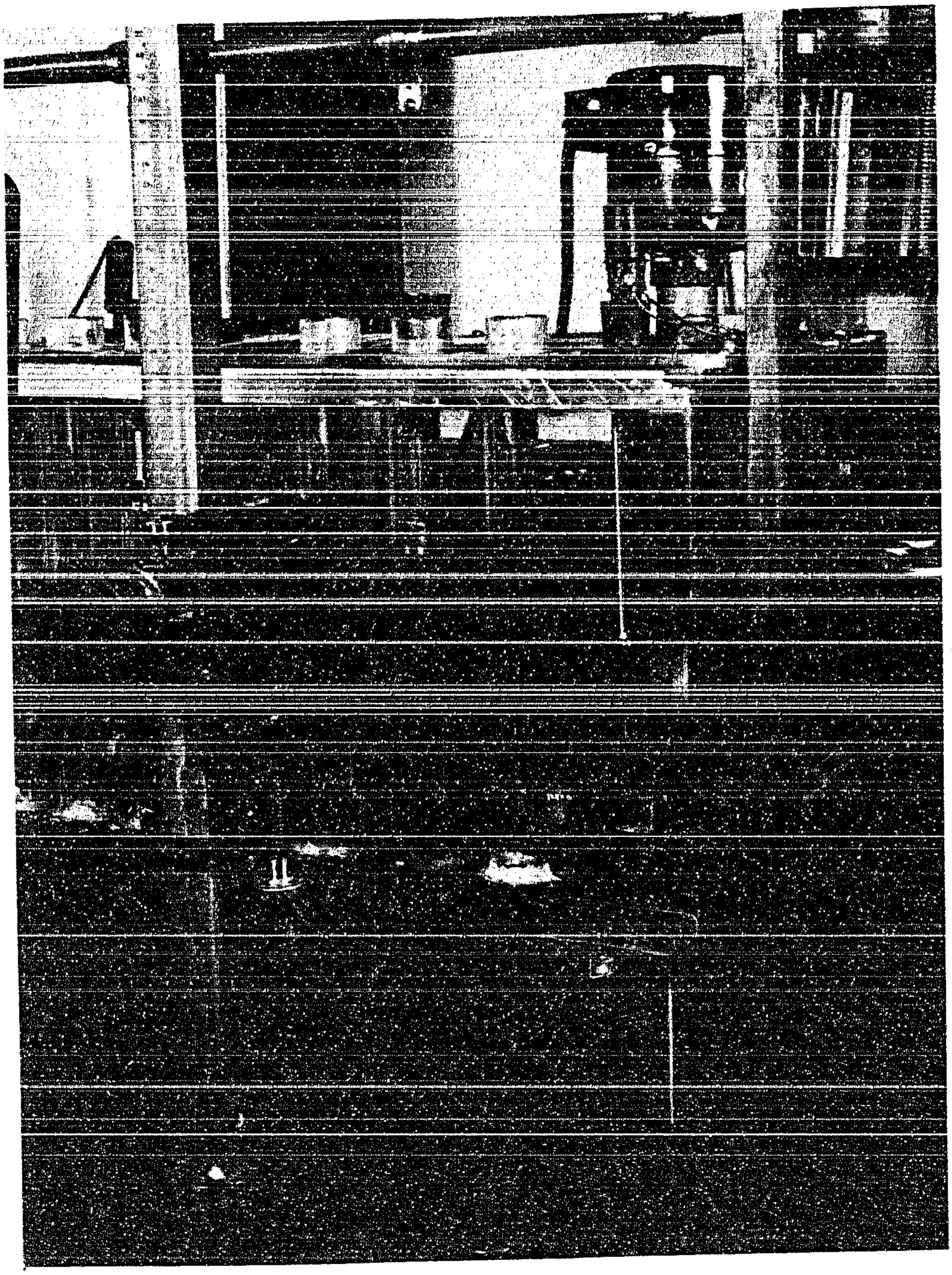


FIGURE XXIII

DETERMINATION OF DEFORMATION

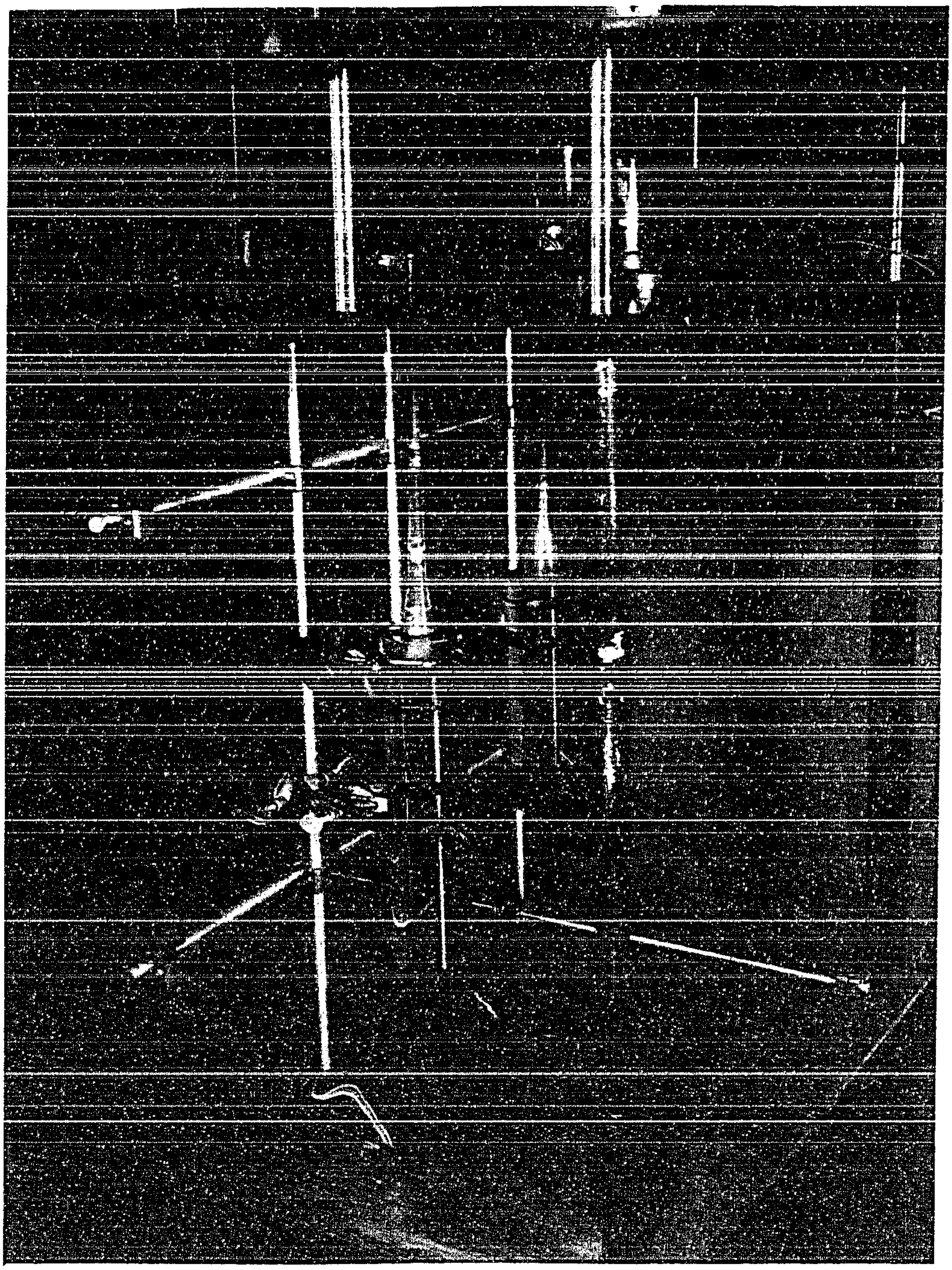


FIGURE XXIV

APPLICATION OF CONSTANT STRESS

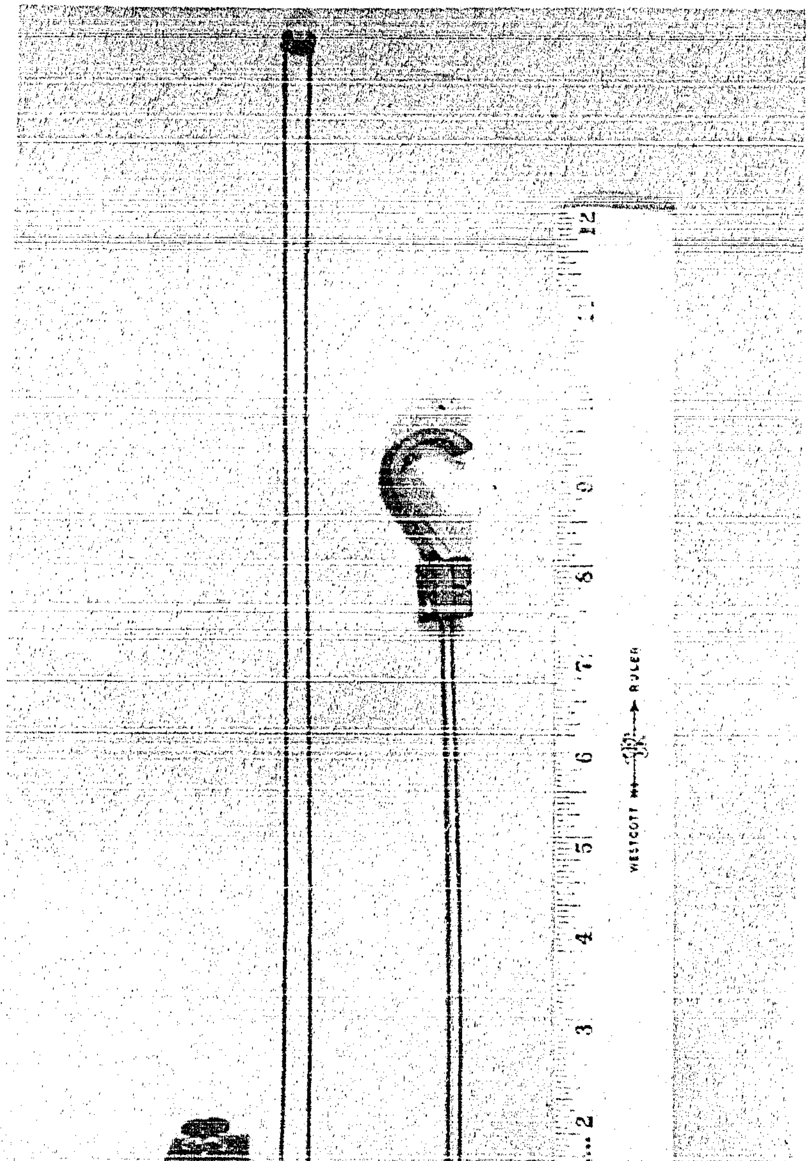


FIGURE XXV

CLAMP ASSEMBLY

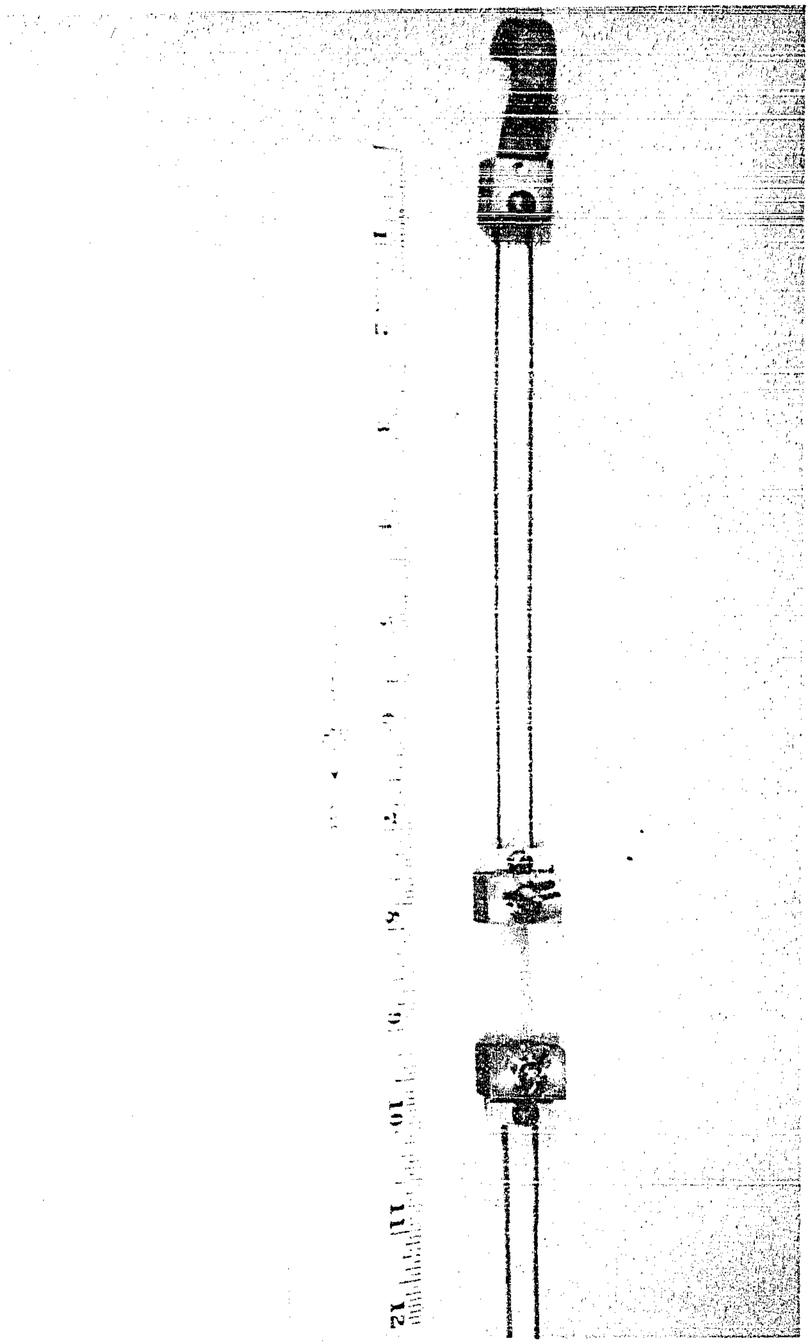


FIGURE XXVI

CLAMPED SPECIMEN

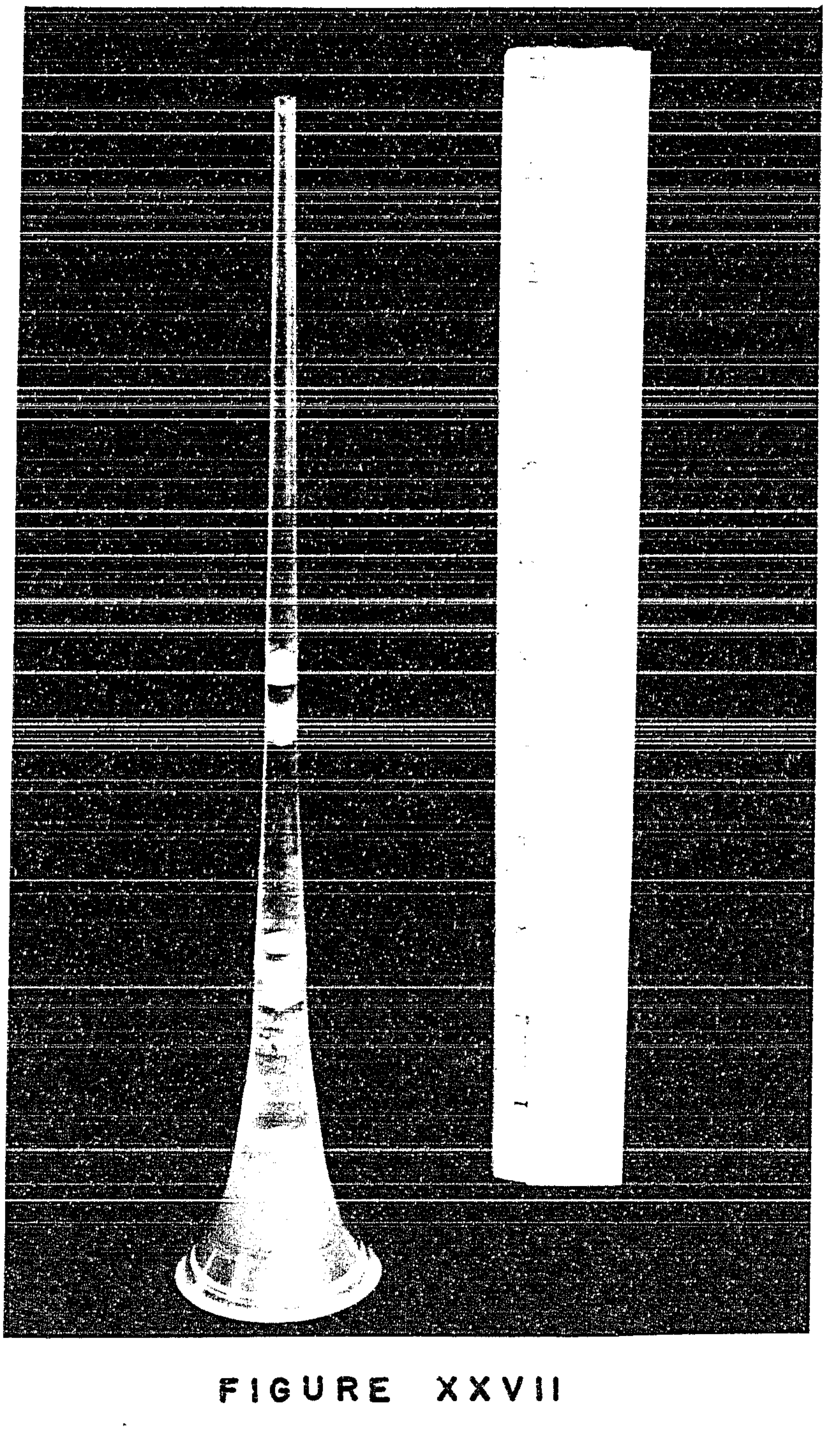


FIGURE XXVII

TENSION BOB

distorted to a wavy shape.. No apparent slippage was encountered by using these clamps. The upper clamp was held stationary by two pieces of 0.025 inch diameter piano wire and a termininating hook, which was fastened to a 3/4 inch stainless steel crossbar. The hook was held in place by two adjustable collars on the crossbar. The initial length of the specimen was 3 cm, i.e. the distance between the two clamps. The lower clamp was connected by two piano-wires to the tension bob. Prior to the application of the stress to the specimen, the base of the bob touched the surface of the water.

The shape of the tension bob was determined by the expression, discussed earlier. At first, Formica Gauge-Wood was machined into the required shape, and the mean density of the bob adjusted to that of water by drilling a proper size hole in the bottom of the bob and covering the opening. Formica Gauge-Wood was not a satisfactory material, however, as the laminating layers absorbed some water and caused a distortion and weight increase of the bob. A satisfactory bob was made by machining three appropriate sections out of Lucite rods, which then were fused together to yield a dimensionally stable bob. (Figure XXVII).

A short focal length (5 cm) cathetometer was used to determine the deformation of the specimen.

2. <u>Procedure for Creep Determinations.-</u> The specimens for the creep determinations were prepared according to the method described previously. To detect any possible defects or flaws, the specimens were carefully checked under microscope. After weighing and determining the exact length of the specimen for cross-sectional area calculations, the gauge marks were placed on the sample with Cel-flex elastic white printing ink. The gauge marks

were of "V" shape and approximately 2.9 cm apart to yield readily observable marks of reference for cathetometer readings. The marked creep specimen was carefully fastened between the clamps (3 cm apart), and a thin piece of wire (4 mil diameter) bound around the assembly to just support the weight of the lower clamp. The specimen was conditioned in the apparatus for at least 15 hours before the creep experiment was carried out. At zero time the piece of wire was cut with dissecting scissors to transfer the stress from the wire to the specimen and the stopwatch started. First readings could conveniently be made approximately 0.1 minute after the start of the experiment. Subsequent readings were made as subscribed by the nature of the specimen. Also the mark at the upper clamp had to be followed occasionally, and any change was extrapolated to intermediate times.

In creep experiments, it is customary to report the change in compliance versus time. Compliances were calculated, utilizing the following formula:

$$J = \frac{\Delta l . A}{S l_o}$$

Where J is the compliance, $\Delta l = l_t - l_o$ , i.e. the length of specimen at time, t, minus the original length; A is the cross-sectional area of the specimen and S is the load.

3. Tensile Testing.- Ultimate tensile strength was determined with a Scott I P 4 inclinded plane tensile machine. The tensiles were computed on the initial cross-sectional area, averaging ten determinations.

Before test the specimens were conditioned for at least 24 hours at 21° C and 65 percent relative humidity. Because of considerable slippage, elongation at break was determined by pulling marked strips to rupture by hand. The final elongation was determined visually with a steel ruler, graduated to one one-hundreths of an inch. Permanent set was measured according to ASTM procedure (4), which required elongation to 300 percent for 10 minutes, followed by free recovery for 10 minutes. The residual elongation was defined as permanent set. Elongation and permanent set were recorded as an average of three determinations.

## V SUMMARY

(1) Copolymers of chloroprene and methacrylic acid have been prepared in persulfate initiated emulsion systems at 30°C, utilizing sulfur modification. Subsequent treatment with tetramethyl thiuram disulfide rendered the copolymer soluble in ketones, particularly in cyclohexanone and methyl isobutyl ketone, and also in dioxane.

(2) The chloroprene - methacrylic acid copolymers have been investigated over a range of composition from 5 to 25 percent methacrylic acid. The optimum properties were achieved with copolymers containing 12 to 16 percent acid and of conversions between 50 to 60 percent. Satisfactory cures were obtained with metal oxides, aromatic diamines, and polyhydroxybenzenes. Best tensile strength of 7500 psi. has been obtained with copolymers air cured with ten parts of zinc oxide. No reinforcement was realized with carbon black.

(3) Relative reactivity ratios have been determined for both emulsion and bulk polymerization. The results are as follows: in emulsion at 30°C, $r_C=5.9\pm0.5$, $r_{MA}= 0.14 \pm 0.05$; in bulk at 30°C, $r_C= 1.4\pm 0.5$, $r_{MA}=0.16\pm 0.07$. The difference in these ratios between the bulk and emulsion systems is attributed to the water solubility of methacrylic acid. The bulk copolymer is more homogeneous than the emulsion copolymer.

(4) The viscoelastic properties of the chloroprene-methacrylic acid copolymers have been studied by creep experiments. These studies included the investigation of creep behavior upon incorporation of various curing agents and also on prolonged air cure. Effective

cures resulted in reduced total compliance as compared to the gum specimens. On prolonged air cure, reduction in compliance was also realized. When compliance is plotted versus the logarithm of the time, creep curves are mostly of concave or straight line character. Upon addition of various curing systems, the shape of the creep curves is affected.

The approximate distribution function of retardation times, in terms of logarithmic time, L (log $\tau$ ), at any value of retardation time, $\tau$ , is given by the slope of the compliance-log t plot at any time t. Accordingly, the spectrum of retardation times is appreciably changed on incorporating various curing systems and on aging. In addition to the change in total compliance, shift in the bulk of the retardation times is affected.

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