

Some Rheological Properties of Molten Polytetrafluoroethylene*

G. AJROLDI, C. GARBUGLIO, and M. RAGAZZINI,
Montecatini Edison S.p.A., Centro Ricerche Bollate-Milano, Italy 20021

Synopsis

Measurements of melt viscosity on samples of polytetrafluoroethylene of different molecular weight were carried out at 360°C by means of tensile creep tests in the linear viscoelasticity range. The apparent activation energy for viscous flow in the range between 330° and 380°C was estimated to be 20 kcal/mole. A value of about 7,500 was also determined for the average molecular weight between entanglement points (M_e), from the equilibrium compliance (D_e). Melt viscosity data were compared with zero strength time (ZST) values and a linear correlation was found on a bilogarithmic scale. The dependence of ZST on the applied stress and temperature was also studied and the results are discussed on the basis of Bueche's theory on the creep at rupture above the glass transition temperature.

INTRODUCTION

The molecular weight determination of polytetrafluoroethylene (PTFE) cannot be done by the usual physicochemical methods, since the polymer is insoluble in all known solvents. The only quantitative estimates of molecular weight have been carried out by determining the concentration of endgroups by radioactive counting techniques.¹ However, in practice relative determinations were obtained by means of specific gravity,^{2,3} crystallinity,^{3,4} stress relaxation,⁵ zero strength time (ZST),^{6,7} and melt viscosity measurements.⁸

In this work melt viscosity of some commercial and experimental PTFE samples was determined by tensile creep experiments. Apparent activation energy for the viscous flow was determined. ZST measurements have also been carried out as functions of applied load and temperature and a correlation between ZST and η was found. ZST tests are discussed on the basis of the Bueche theory relative to break behavior of plastic materials above T_g .⁹

* Presented at the International Symposium on Macromolecular Chemistry, IUPAC, Toronto, Canada, September 1968.

EXPERIMENTAL

Materials

Both commercial and experimental samples of suspension-polymerized PTFE were used. The specimens for viscosity and *ZST* measurements were cut from disks sintered according to ASTM 1457-62T standard procedure.

Creep Measurements

The apparatus used to get creep measurements is shown in Figure 1. The sample (M) is held by the upper clamp (N) into the inner cavity of an iron cylinder 25 cm long and 7 cm of outer diameter. The load is applied at the lower end of a thin Duralumin rod connected with the lower clamp (O). The total weight of the lower clamp and rod is about 4.5 g. The deformation of the sample was determined by following a mark on the rod with a travelling microscope. Corrections for the thermal expansion of the sample and of metallic parts of the apparatus were taken into account. The temperature profile along the vertical axis was constant within $\pm 0.5^\circ\text{C}$ for

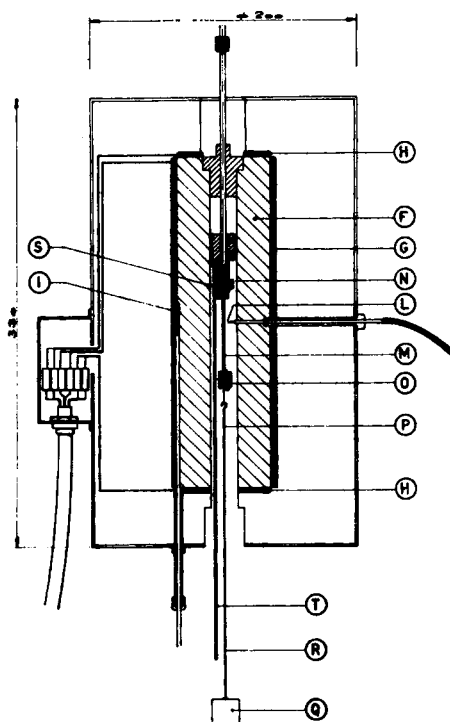


Fig. 1. Creep apparatus: (F) iron cylinder, $D_i = 2$ cm, $D_o = 7$ cm; (G) cylindrical heater; (H) top and bottom heaters; (I) 100-ohm platinum thermometer; (L) Ir-Cost thermocouple; (M) sample; (N) upper clamp; (O) lower clamp; (P) Duralumin rod; (Q) weight; (R) travelling microscope; (S) reference rod; (T) reference mark.

15 cm. The temperature fluctuation of the oven at 360°C was kept within $\pm 0.1^\circ\text{C}$. The dimensions of the samples were $5 \times 1.5 \times 0.2$ cm. The specific applied stress was about 4×10^5 dynes/cm² and the maximum strain attained in the course of the measurements was always smaller than $2\text{--}3 \times 10^{-2}$. The viscoelastic behavior in this range of stress and strain was shown to be linear.

ZST Measurements

The experimental method and the apparatus used in the course of this work were similar to those previously described by Kaufman and co-workers.¹⁰ The dimensions of the specimens were $5.08 \times 0.320 \times 0.164$ cm; the cross-section at the notch was 0.119 cm wide by 0.164 cm thick and the notch angle was 90° . Standard tests were carried out at $360^\circ \pm 1^\circ\text{C}$ and the mean of at least five measurements was taken as a measure of *ZST*. The influence of the stress-concentration factor at the notch was also investigated carrying out *ZST* experiments on dumbbell-shaped specimens with the same cross-section area as the standard ones. No dependence on the shape of the specimens was found.

RESULTS AND DISCUSSION

Tensile creep experiments carried out above T_g in the terminal zone of the creep master curve are useful tools to estimate tensile viscosity of very high-viscosity materials.

From the general equation for the creep compliance¹¹

$$D(t) = D_g + \int_{-\infty}^{+\infty} [1 - \exp(-t/\tau)] L(\tau) d \ln \tau + t/\eta_t \quad (1)$$

where $D(t)$ is the creep compliance, D_g the glassy compliance, $L(\tau)$ the retardation spectrum, τ the retardation time, and η_t the tensile viscosity, it is easy to see that for a time of experience t greater than the maximum retardation time τ_m , the compliance $D(t)$ is only determined by the t/η_t term: the shear viscosity $\eta_t/3$ can be determined from the slope of the linear part of the creep curves plotted as $D(t)$ versus t .

Most of the creep compliance experiments were carried out at 360°C from 1 up to about 3×10^4 sec and the creep rate at long times was shown to be practically constant for most of the samples examined; for the highest viscosity samples small deviations were noted. In this case we could not rule out some residual contributions of retarded elasticity mechanisms also at the longest time investigated. This fact was confirmed by examining Tobolsky's stress relaxation data on PTFE.⁵ Tobolsky's data relative to samples Teflon 1 and Teflon 6, having 54,000 and 21,000 sec, respectively, as maximum relaxation times at 380°C, were reduced at 360°C and converted into creep data¹¹ by means of the equation

$$\int_0^t D(t - \tau) E(\tau) d\tau = t \quad (2)$$

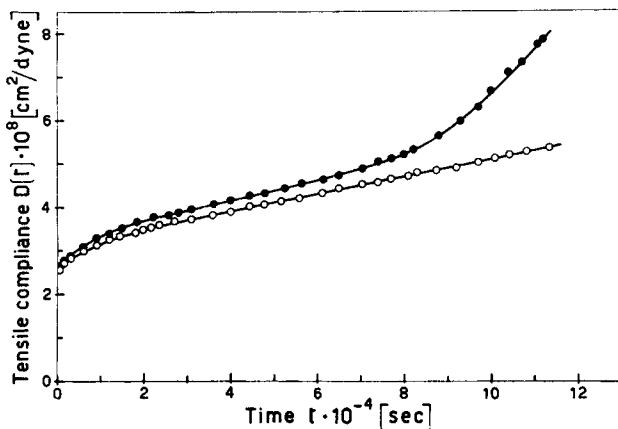


Fig. 2. Creep curves: (●) sample 1, (○) sample 2.

which states the relationship between the creep compliance $D(t)$ and the stress relaxation modulus $E(t)$. The calculation was carried out by means of the approximate method reported by Hopkins and Hamming.^{12,13} Viscosities of these samples, calculated from the obtained creep curves, were 1.55×10^{11} and 5.50×10^{11} poises, respectively. An extrapolation based on these data indicates that the steady-state flow is reached at $t \geq 10^4$ sec and at $t \geq 4-6 \times 10^4$ sec for samples of PTFE having $\eta = 10^{11}$ and $\eta = 10^{12}$ poises, respectively.

On this basis some creep experiments were extended up to 1.5×10^6 sec in order to attain the pure flow region, but some degradation phenomena seem to arise for some samples when the experience time is longer than 5×10^4 sec. Typical results for a degrading and a nondegrading polymer are reported in Figure 2. The upward curvature above $5-6 \times 10^4$ sec shown by sample 1 can be accounted for by an irreversible degradation process.

In order to check the reliability of our data, we applied also the extrapolation method suggested by Ninomiya¹⁴ for determining the viscosity from the terminal part of the creep curves. Dividing eq. (1) by t and going to the limit $1/t \rightarrow 0$ it can be easily shown that

$$\lim_{1/t \rightarrow 0} D(t)/t = 1/\eta \quad (3)$$

and also

$$\lim_{1/t \rightarrow 0} mD(t)/t = 1/\eta \quad (4)$$

where, in eq. (4), $m = d \log D(t)/d \log t$. $D(t)/t$ and $mD(t)/t$ were plotted against $1/t$ and viscosity values were obtained from the intercept. Viscosity values obtained both from this method and from the slope of the creep curves in the range between 15,000 and 25,000 sec are fairly close, also for the samples with the highest molecular weight.

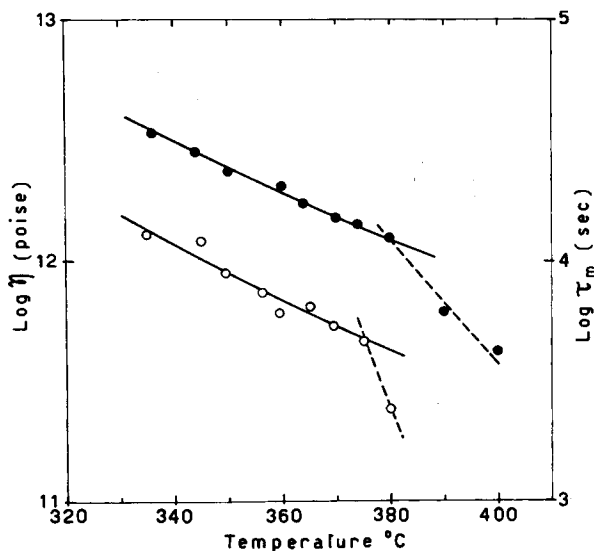


Fig. 3. Experimental dependence of the melt viscosity η (O) (this work) and maximum relaxation time τ_m (●) (Tobolsky¹⁷) on the temperature and predicted by the WLF equation (full lines).

In conclusion, our results show that the error due to the contribution of residual elasticity does not affect our viscosity data by more than about 10% for the highest molecular weight samples, while it is clear that the Nishioka and Watanabe viscosity data,⁸ obtained in a more restricted time range, are certainly underestimated.

The pseudoequilibrium compliance D_e can also be obtained from the creep curve and it is given by the intercept of its linear part.

From the value of D_e and on the basis of the rubber elasticity theory,¹¹ the molecular weight between entanglement points M_e was also calculated. The obtained value of $M_e = 7,500$ fairly well agrees with the value of 6,600 reported by Tobolsky¹⁵ on the basis of stress relaxation experiments.

The viscosity dependence on the temperature was also determined for one sample between 335° and 380°C. The results are plotted in Figure 3 as $\log \eta$ against T . Experimental points can be represented by the well-known WLF equation¹¹:

$$\log \eta = \log \eta_{T_g} - \frac{(B/2.303f_g)(T - T_g)}{f_g/\alpha_f + T - T_g} \quad (5)$$

where B is an empirical constant of the order of unity, f_g is the fractional free volume at T_g , α_f is the thermal expansion coefficient of the free volume, and T_g is the glass transition temperature. The so-called "universal values"¹¹ of $f_g = 0.025$ and $\alpha_f = 4.8 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ were used and the best fit was obtained by assuming $T_g = 120^\circ\text{C}$. The same value was obtained by us for the α -maximum of the damping factor Δ from low-frequency, dy-

namic-mechanical measurements and it is close to that of 127°C found by McCrum¹⁶ for the same kind of test and to the value of 110°C found by Tobolsky from stress relaxation experiments.¹⁷ Maximum relaxation times obtained by Tobolsky are also plotted in Figure 3 as a function of temperature. These data and our viscosity data do not fit the WLF equation above 380° and 375°C, respectively. According to Case,¹⁸ the deviation from the theoretical curve should be attributed to the beginning of random scission of the molecular chain.^{18,19} We also calculated an apparent activation energy for the viscous flow of 20.1 kcal/mole in the range of 335° to 375°C, which is in good agreement with the value of 18.2 kcal/mole found by Tobolsky in the same temperature range. The value of 25 kcal/mole found by Case,¹⁸ who used the viscosity data of Nishioka and Watanabe, is fairly higher.

ZST Data

An easy and useful method to determine the relative molecular weight of PTFE is the measure of the time required to break the specimen under an applied load above the melting point.

While for other polymers like polychlorotrifluoroethylene¹⁰ and polyethylene²⁰ some relationships were found between *ZST* and properties

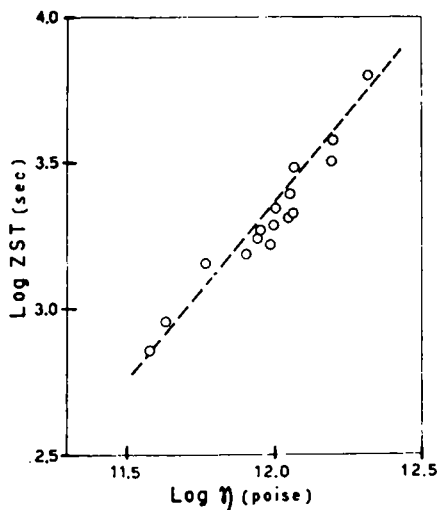


Fig. 4. Relationship between melt viscosity η and *ZST*.

such as solution viscosity, dependent on the molecular weight, no such a correlation was reported for PTFE, to our knowledge. We carried out parallel measurements of melt viscosity η and *ZST* with a standard constant load of 200 g at 360°C. The results for a large number of samples are reported in Figure 4 on a log-log plot; a linear correlation is evident. It must be pointed out that some scatter of experimental points could be

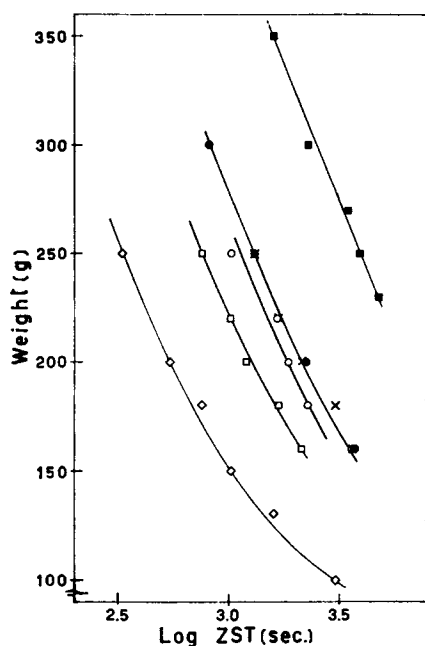


Fig. 5. Dependence of ZST on the applied load at 360°C for samples A-F: (\diamond) A, $\eta = 3.80 \times 10^{11}$; (\square) B, $\eta = 9.20 \times 10^{11}$; (\circ) C, $\eta = 9.0 \times 10^{11}$; (\bullet) D, $\eta = 1.01 \times 10^{12}$; (\times) E, $\eta = 1.16 \times 10^{12}$; (\blacksquare) F, $\eta = 2.09 \times 10^{12}$.

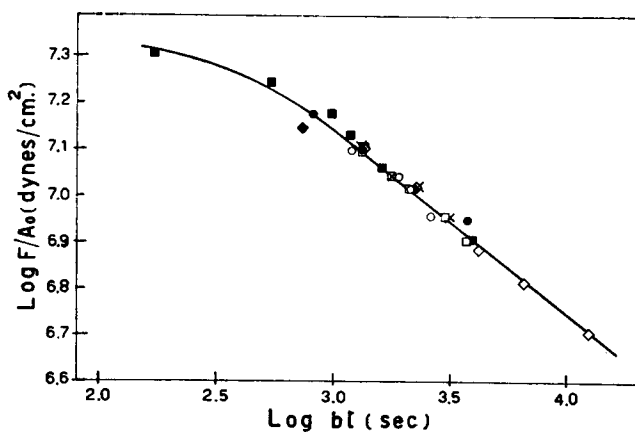


Fig. 6. Master curve $\log F/A_0$ vs. reduced ZST $\log bt$ resulting from the superposition of the curves reported in Figure 5; $T = 360^{\circ}\text{C}$.

attributed to different void content, particle size, and morphology of the samples.

A more detailed analysis was performed on six samples (A to F) of different melt viscosity in the range 4×10^{11} to 20×10^{11} poises at 360°C by examining the dependence of ZST on the applied load W . The curves

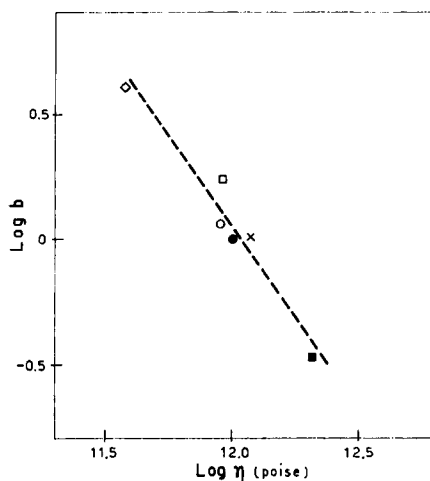


Fig. 7. Experimental shift factor b vs. melt viscosity η .

W versus $\log ZST$ are plotted in Figure 5. All of these can be easily superimposed by shifting them along the time axis, to give the master curve shown in Figure 6, where the force for the original cross-section area $\log F/A_0$ is plotted against the reduced ZST , i.e., $\log bt$. The chosen reference curve was that of polymer D; the experimental shift factor b is reported against melt viscosity η in Figure 7 on a log-log plot; a linear correlation is clearly shown. Therefore, the empirical correlation between ZST and η found for standard load is valid over the whole range of loads investigated, which makes it suitable for useful measurements. Moreover, since the melt viscosity is generally related to the molecular weight M by means of the well-known relationship²¹

$$\eta = KM^{3.4}, \quad (6)$$

a linear correlation could be expected between the logarithms of ZST and molecular weight. Smilek²² obtained this kind of relationship between ZST and M for polychlorotrifluoroethylene, while Kaufman and co-workers reported for polychlorotrifluoroethylene¹⁰ and polyethylene²⁰ exponential relationships between ZST and specific, reduced viscosity and between ZST and M_n , respectively.

A more comprehensive explanation of the relationship found for PTFE can be conveniently put forward on a molecular basis if we consider the ZST experiments as a creep-at-rupture test above T_g .

This kind of experiment was treated theoretically by Bueche.⁹ His starting assumption was that high molecular weight uncrosslinked polymers must show a short-time behavior similar to that of the crosslinked ones because entanglements act as temporary crosslinks. On this basis a theory was developed and a universal relationship between ultimate strength and the time at rupture was predicted. In the rubbery plateau

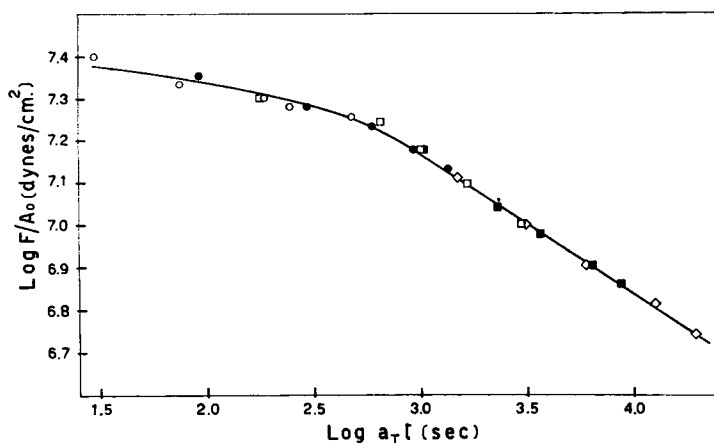


Fig. 8. Master curve $\log F/A_0$ vs. reduced $ZST \log a_{\tau}t$ for sample D (of Fig. 5) obtained from data at different temperatures; $T = 360^{\circ}\text{C}$: (\circ) 330°C ; (\bullet) 345°C ; (\square) 360°C ; (\blacksquare) 370°C ; (\diamond) 380°C .

zone, i.e., for experiments carried out above T_g , the theory predicts an asymptotic trend parallel to the time axis. However, deviations from this behavior should be expected for linear polymers when the experience time is sufficiently long. The material indeed can show viscous flow due to the slippage of entanglement points; in this case there is an apparent increase of the stress due to the reduction in the cross-sectional area. Such a behavior was noted by Bueche himself when examining high molecular weight poly(butyl methacrylate) at different temperatures. It follows that polymers with different molecular weights should deviate from Bueche's master curve at different times according to their melt viscosity. This hypothesis is clearly confirmed by our data plotted in Figure 5. The master curve at short time tends toward a plateau, as predicted by the theory, and its value is that expected from the above calculated value of M_e . It is also to be noted, according to Bueche's theory, that our master curve (Fig. 6) is only valid in the time range where the flow is allowed.

The trend of the master curve was even confirmed by examining the dependence of PTFE ZST on both load and temperature for the sample D . The time-temperature superposition was applied to the curves obtained at five different temperatures between 330° and 380°C and a master curve $\log F/A_0$ against reduced $ZST \log a_{\tau}t$ was obtained. This master curve, shown in Figure 8, can be fairly well superimposed on that reported in Figure 6. Therefore melt viscosity appears to be the determining factor of the behavior of the universal breaking curve in the terminal zone.

The results of this work indicate that the ZST test can be interpreted on the basis of the molecular theory of viscoelasticity and, as a further insight of Bueche's theory, it was shown that the creep at rupture of macromolecular systems above T_g can be suitably explained only if the influence of molecular weight is considered.

We are grateful to Mr. M. Fumagalli and P. Sfondrini for their help in the experimental work.

References

1. K. L. Berry and J. H. Peterson, *J. Amer. Chem. Soc.*, **73**, 5195 (1951).
2. R. D. Dobran, A. C. Knight, J. H. Peterson, and C. A. Sperati, 130th Meeting of ACS, Atlantic City, 1956.
3. C. A. Sperati and H. W. Starkweather, *Adv. Polym. Sci.*, **2**, 465 (1961).
4. R. E. Moynihan, *J. Amer. Chem. Soc.*, **81**, 1045 (1959).
5. A. V. Tobolsky, D. Katz, and A. Eisenberg, *J. Appl. Polym. Sci.*, **7**, 469 (1963).
6. A. Nishioka, *J. Polym. Sci.*, **26**, 107 (1957).
7. A. Nishioka, K. Matsumae, M. Watanabe, M. Tajima, and M. Owaki, *J. Appl. Polym. Sci.*, **2**, 114 (1959).
8. A. Nishioka and M. Watanabe, *J. Polym. Sci.*, **24**, 298 (1957).
9. F. Bueche, *J. Appl. Phys.*, **26**, 1133 (1955).
10. H. S. Kaufman, C. O. Kroncke, and C. R. Giannotta, *Mod. Plast.*, **32**(2), 146 (1954).
11. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.
12. I. L. Hopkins and R. W. Hamming, *J. Appl. Phys.*, **28**, 906 (1957).
13. G. Ajroldi, C. Garbuglio, and G. Pezzin, *Ing. Chim. Ital.*, **4**, 1 (1968).
14. K. Ninomiya, *J. Phys. Chem.*, **67**, 1152 (1963).
15. A. V. Tobolsky and M. Takahashi, *J. Appl. Polym. Sci.*, **7**, 1341 (1963).
16. N. C. McCrum, *J. Polym. Sci.*, **34**, 355 (1959).
17. A. V. Tobolsky, D. Katz, and M. Takahashi, *J. Polym. Sci. A*, **1**, 483 (1963).
18. L. C. Case, *J. Appl. Polym. Sci.*, **3**, 254 (1969).
19. L. C. Case, *J. Polym. Sci. B*, **1**, 345 (1963).
20. H. S. Kaufman and C. O. Kroncke, *Mod. Plast.*, **33**(7), 167 (1956).
21. T. G. Fox and V. R. Allen, *J. Chem. Phys.*, **41**, 344 (1964).
22. P. Smilek, *Chem. Prum.*, **13**, 498 (1963).

Received May 13, 1969

Revised July 31, 1969