Mechanical Properties of Concentrated Hydrogels of Agar-agar. III. Relaxation of Stress in Compression

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Introduction

In recent years, a number of papers have been published on the relaxation of stress in high polymers, reflecting its fundamental importance in rheological investigation of these substances. However, papers are still rather rare in the literature dealing with relaxation experiments on gel-systems. Some examples of the latter are the recent studies of Ferry and his co-workers on several important protein gels.(1) For agar-agar gel with which we have been concerned in this series of rheological studies, no information of stress-relaxation appears to have yet been reported, so far as the authors are aware. For this reason, we have carried out an experimental study of the relaxation of stress in agar-agar gel held at constant compression, and the results obtained are reported in this paper.

A cylindrical test piece was kept at constant compression between two parallel plates under relaxing stresses, and the process of decay of stress was followed autographically by means of a relaxometer which was constructed based on the principle of the chainomatic balance. Measurements were conducted at different temperatures from 9° to 70°C., and at different fairly small strains. Because of the complexity of the phenomenon, experiments were restricted only to a single agar-agar concentration of 4 g./100 cc.. However, it is hoped that we may have an opportunity in a forthcoming paper of this series to present data on the concentration effect along with data on other subjects left untouched in the present work.

Experimental

The agar-agar samples and the procedure of preparing the specimen gels used in the present work were, in all respects, identical with those which have been used in Part I(2) of this series; the specimen gel was shaped in a cylindrical column whose height and diameter were both about 3 cm. An autographic relaxometer was designed employing the principle of the chainomatic balance used by Dart and Guth(3) for the study of compression stress-relaxation in natural cork. A schematic diagram of the relaxometer is shown in Figure 1. To save space, the description of the mechanism and the procedures for practical use of this apparatus is omitted here; it will be published in a separate paper by one of the present authors.(4) The relaxometer was installed in an air oven made of wood and glass lined with thick layers of asbestos and cardboard cartons. Temperature control was attained by means of a bimetallic thermoregulator which was accurate to about ±0.25°C.. Humidity was maintained at an almost saturated state to prevent drying of the specimen gel as much as possible. In addition, with the same object, liquid paraffin was sufficiently applied on the surface of the specimen exposed to air. With these treatments, drying of the specimen was almost checked up to about 60°C., so that at temperatures below 60°C., it might be regarded that actual temperatures of the specimen during the course of a

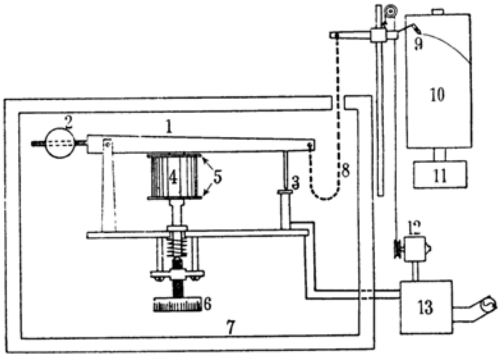

Fig. 1.—Schematic diagram of the relaxometer; 1: balance arm. 2: balancer. 3: point of contact. 4: test piece. 5: metal plates for compression. 6: screw gauge. 7: air oven. 8: chain. 9: recording pen. 10: rotating drum. 11: driving clock. 12: driving motor. 13: relay.

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(1) M. Miller, J. D. Ferry, F. W. Schremp and J. E. Eldridge, *J. Phys. and Colloid Chem.*, **55**, 1387 (1951).

(2) H. Fujita, K. Ninomiya and T. Homma, This Bulletin, **25**, 374 (1952).

(3) S. L. Dart, and E. Guth, *J. Appl. Phys.*, **17**, 314 (1946).

(4) K. Ninomiya, *J. Chem. Soc. Japan*, in preparation.

relaxation test were substantially equal to the temperatures of air in the oven. However, at temperatures higher than about 60°C., it was concluded, as a consequence of evaporation of the solvent from the specimen, that the gel reached thermal equilibria at temperatures somewhat lower than those of its surrounding air; and difference of these two temperatures was found to become more and more marked with the increase of the air oven temperature. In view of this finding, a preliminary experiment was carried out to determine this temperature difference as a function of the given temperature of the air oven. With the result thus obtained, when the relaxation test was made at temperatures higher than 60°C., we estimated the actual gel temperature from the experimentally given temperature of the air oven.

Compressions adopted in the present work were from 0.6 to 8.6% at lower temperatures, and from 0.6 to 3.6% at higher temperatures. Within these limits of compression, the resultant stresses were varied almost linearly with strains. In dealing with experimental data on viscoelasticity in the light of the current theories for the mechanical behavior of high polymers, it is important to bear in mind that those theories are applicable only for materials, the elastic behavior of which follows closely the so-called Hooke's law.

Results and Discussion

Type of Stress-Relaxation Curves Obtained.—A typical example of relaxation data obtained is shown in Figure 2, which shows relaxation curves for different compressions at a constant temperature of 15°C. The fairly rapid decay of stress at this room temperature is a clear evidence of the lack of the primary network structure in agar-agar gels. This is in agreement with the current view for the structure of the majority of polymer gels that it consists of a three-dimensional network cross-linked with bonds of a secondary nature. The shape of the relaxation curves is apparently similar to that which would be observed in a viscoelastic body obeying a single Maxwell equation. However, as will be seen later on, a single Maxwell equation is not sufficient to describe these plotted curves but at least two Maxwell equations are required. It is important to note a characteristic behavior of our relaxation curves in the neighborhood of the zero stress base. In usual polymer solids which lack the primary network structure (e. g., polyisobutylene⁽⁵⁾), it is known that stress at constant deformation is relaxed to zero after an infinitely or sufficiently long run for all values of given deformation. Contrary to this, our relaxation curves for concentrated agar-agar gel are apparently lowered to zero after running certain finite intervals of time, which are apparently seen to be largely dependent on the given strain magnitudes. According to the data obtained at temperatures different from 15°C., the value of time interval at which stress is relaxed to zero is also a function of temperature. The reason why our relaxation curves for agar-agar gel are so markedly different in the manner of decaying to zero stress from those of other polymer solids has yet not been fully elucidated, but, as will be shown in a later part of this paper, there is a fairly reliable reason to believe that this is essentially due to the effect of syneresis which is characteristic of the majority of gel-systems.

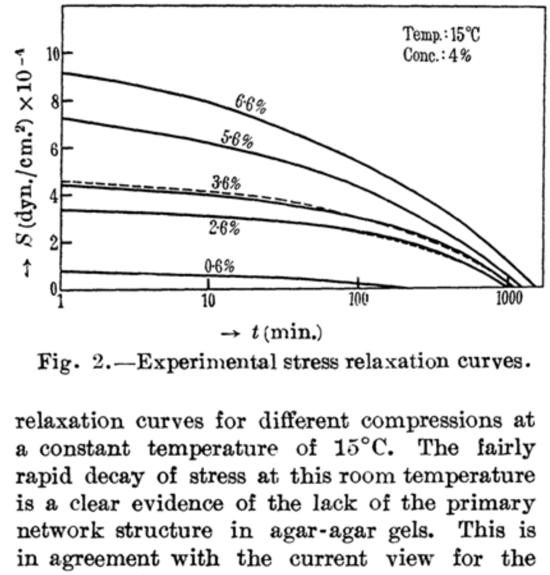

Fig. 2.—Experimental stress relaxation curves.

In Figure 2, results of duplicate experiments are also indicated with dotted lines for two strains of 2.6 and 3.6%. Stress magnitude is seen not always to be reproducible in these duplicate experiments. However, allowing for the sample variance, which is usually encountered in this kind of experiments dealing with natural substances, and for difficulty of precise determination of strain magnitude, the agreements of stress magnitude attained in these duplicate experiments must be regarded as rather satisfactory.

Analysis of Data.—In Part II⁽⁶⁾ of this series of papers, we have known as a result of the measurements of compression creep that agar-agar gel has a general tendency as a consequence of syneresis to contract spontaneously at a certain definite rate of deformation, which is dependent on the conditions of the particular experiment. Therefore, it is reasonable to suppose that when a cylindrical column of agar-agar gel is made to deform between two parallel plates under compressive load, the observed rate of decrease in the column height with time is the sum of the following two

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(5) R. D. Andrews, N. Hofman-Bang and A. V. Tobolsky, *J. Polymer Sci.*, **3**, 669 (1948).

(6) H. Fujita, K. Ninomiya and T. Homma, This Bulletin, **26**, 20 (1953).

rates of deformation, one of which is that due to molecular structural flows caused only by the action of the external load, and another of which is that due to the spontaneous contraction of the cylinder as a whole.

To formulate this consideration, we shall assume that the relaxation mechanisms contained in an agar-agar gel whole solid can be represented by two Maxwell mechanical elements connected in parallel. Since, in this mechanical model, the individual relaxation elements are equally subjected to compression resulting from the self-contraction, the rate of change in strain with time, $d\gamma/dt$, for each element is written as:

$$\frac{d\gamma}{dt}=\frac{1}{E_1}\frac{dS_1}{dt}+\frac{S_1}{\eta_1}+f, \qquad (1)$$

$$\frac{d\gamma}{dt}=\frac{1}{E_2}\frac{dS_2}{dt}+\frac{S_2}{\eta_2}+f, \qquad (2)$$

and for the total stress S, we have

$$S=S_1+S_2, \qquad (3)$$

where f stands for the rate of deformation resulting from the self-contraction, and S_i, E_i, and η_i denote the partial stress, the elastic constant of the spring, and the viscosity of the dash-pot, of the ith element, respectively $(i=1, 2)$.

To solve the above set of equations for any given condition of stress or strain, it is necessary to know the mathematical expression for f corresponding to that condition. However, unfortunately, we have hardly had information available on this point. It has been revealed in Part II that when the external stress is absent, and moreover, when the environmental conditions are kept constant, f takes a constant value for a long period of time. If, as has been stated by Ferry,(7) syneresis in gel-systems is produced as a result of the progressively closer binding of the network strands, the rate of change in volume with time thereby resulting would be much less modified even if the material is subject to external stress. If this view be true, it may be assumed as a first approximation that the value of f remains unchanged even under stressed condition so far as the stress magnitude is sufficiently small as was the case with the present relaxation tests. This assumption is the same as saying that the f value is constant over a long interval of time at any stress condition. We shall here presume this assumption to be justifiable and denote the constant value to be assigned to f by C.

Introducing the condition that $f=C$ into Eqs. (1) and (2), and solving the resultant set of equations for S with the condition of relaxation experiment at constant strain, we obtain the following solution:

$$\begin{aligned}S=&\gamma_0(E_1e^{-t/\tau_1}+E_2e^{-t/\tau_2})\\&-C\{\eta_1(1-e^{-t/\tau_1})+\eta_2(1-e^{-t/\tau_2})\}, \qquad (4)\end{aligned}$$

where γ_0 is the strain at which the specimen is held fixed, and τ_i is the Maxwellian relaxation time of the ith element as defined by the so-called Maxwell relation:

$$\tau_i=\frac{\eta_i}{E_i}. \qquad (5)$$

Our main object in what follows is to determine the numerical values of parameter, E_i and τ_i, as functions of temperature by fitting Eq. (4) to experimental data. For this purpose the following procedure of fitting is employed:

Firstly, from the relaxation data for different strains at constant temperature, we construct a system of plots between S and γ_0 with t as parameter. According to Eq. (4), if the parameter, E_i and τ_i, are constants characteristics of the material concerned, the plots thus obtained should be linear and their inclinations to the γ_0 axis should give the values of the quantity Q defined by

$$Q=E_1e^{-t/\tau_1}+E_2e^{-t/\tau_2}. \qquad (6)$$

It was found for all the relaxation data

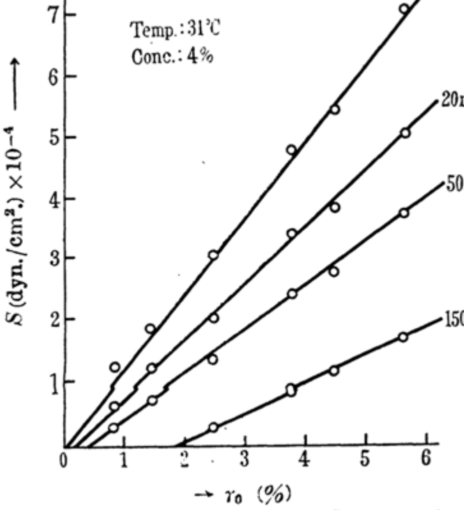

Fig. 3.—An example of the S vs. γ_0 plot.

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(7) J. D. Ferry: "Advances in Protein Chemistry", IV, Academic Press, Inc., Publishers, New York, 1948, Chapt. I, pp. 1-78.

obtained that this linearity between S and γ_0 was approximately realized; a typical illustration of this is given in Figure 3, where to avoid confusion of the diagram only several representative lines are plotted. That the straight lines drawn visually to give the best fit to the experimental points do not pass through the origin of coordinates is apparently to be ascribed to the contribution from the term involving C. It is now possible to evaluate Q as a function of time t. A typical graph of this function in the form of $\log Q$ plotted against the linear time t is shown in Figure 4. Seeing this graph, one can at once expect that the plotted curve may nicely be fitted by an expression of the form of Eq. (6).* This prediction was satisfactorily confirmed for all temperatures studied except for the two cases mentioned below, and thus we could determine the required values of E_i and τ_i ($i=1, 2$) with sufficient accuracy. The two exceptional cases were the temperatures as low as 9° and 15°C., at which Eq. (6) proved somewhat insufficient to represent the plots precisely at small values of t. Thus, in these cases, it had to be modified as:

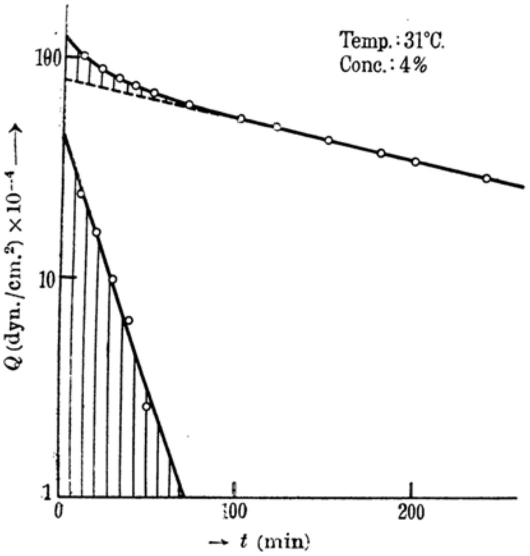

Fig. 4.—An example of the log Q vs. t plot.

$$Q = E_1 e^{-t/\tau_2} + E_2 e^{-t/\tau_2} + E_3 e^{-t/\tau_3}.$$

Accurate determination of the numerical values of the newly introduced parameters, E_3 and τ_3, was, however, rather prohibitive, so we had to be content with obtaining their rough values.

In this way, the results tabulated in Table 1 have been determined, in which the figures enclosed by brackets are somewhat doubtful. E represents the sum of E_i's, so that it is nothing but the overall modulus of elasticity in compression of the agar-agar gel investigated. In passing, it is of interest to note that the above method of analysis has an advantage in that, on its application, no allowance needs to be made for actual value of C.

Table 1

Temperature (°C.)	Elastic constants (dyn./cm.^{2}) $\times 10^{-5}$				Relaxation times (min.)	
	E_1	E_2	E_3	$E = \Sigma E_i$	τ_1	τ_2
9.0	(7.5)	(4.1)	(1.4)	(13.0)	(700)	(32)
15.0	8.0	4.7	1.1	13.8	625	43
21.0	8.9	3.9	(1.0)	(13.8)	380	32
26.0	8.8	3.9	—	12.7	314	30
31.0	7.9	4.3	—	12.2	246	19
37.0	7.6	2.4	(0.5)	(10.5)	(191)	15
49.0	6.8	3.1	—	9.9	90	9
56.0	4.0	2.2	—	6.2	52	6
64.0	2.4	0.5	—	2.9	30	3
70.0	2.0	—	—	2.0	16	—

We shall next consider the temperature dependencies of the relaxation times, τ_1 and τ_2, in the light of the Arrhenius equation of the form:

$$\tau = A \exp(U/RT),$$

where τ is the relaxation time, A is the so-called "frequency factor," U is the activation energy for stress-relaxation, and R and T are the gas constant and absolute temperature, respectively. For this purpose, we plot the logarithms of τ_1 and τ_2 against $1/T$, the resultant plots being shown in Figure 5. It is seen that both relaxation times, though they differ markedly in numerical values, vary with temperature following an almost similar process. Up to about 40°C., the plots are regarded as linear and approximately parallel each other, indicating that in this temperature region, the activation energies U_1 and U_2

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* Assuming preferentially $\tau_1 > \tau_2$, Eq. (6) indicates that for large values of time the logarithm of Q, when plotted against t, provides a straight line whose inclination is τ_1 and whose interception on the $\ln Q$-axis is $\ln E_1$. A good illustration of this relation is given in Figure 4. If this relation proves to hold, Eq. (6) further predicts that the logarithm of $Q - E_1 e^{-t/\tau_1}$ should also become linear with t and that the straight line obtained allows to evaluate the values of τ_2 and E_2 respectively from its inclination and its intercepti on the ordinate axis. A fairly good establishment of the latter straight line is also illustrated in the lower portion of Figure 4 (the shadowed triangle).

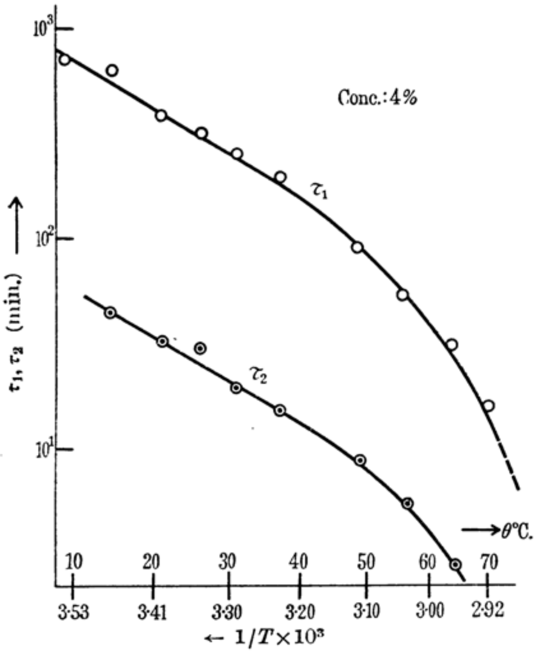

Fig. 5.—Relaxation times, τ_1 and τ_2, as functions of temperature.

corresponding to these two elements are constant and take nearly equal values, the average of which is estimated at 9 kcal./mole. This value of the energy of activation for relaxation is in good harmony with the view that polymer gels usually consist of a three-dimensional network structure whose strands are cross-linked at points of contact of a secondary strength. Above 40°C., the plotted lines have curvatures, being deviated more and more from linearity and appearing to fall rapidly in the neighborhood of 90°C. This result is that which should be expected a priori, because agar-agar gels usually have their melting points in the vicinity of 90°C. It would be reasonable to suppose that the increasing deviations of the plotted curves from linearity are chiefly associated with the decrease in the frequency factor (or probably, the increase in entropy for relaxation) accompanying the increase in temperature.

We are not yet in a position to have molecular theoretical interpretation of mechanical model constants obtained above for agar-agar gel. However, it may be of some interest to infer, referring to Ferry's view,(8) that τ_1, the longer relaxation time, corresponds to slippage at points of contact of the network strands, and τ_2, the shorter relaxation time, to rotation of the individual strands over the potential barrier into the next position of minimum energy.

Solving Eqs. (1), (2) and (3) under the conditions that $S=\text{constant}\equiv S_0$ and $f=C$, we obtain the creep equation in the form:

$$\gamma=\frac{S_0}{E_1+E_2}+B\left(1-e^{-\frac{1+\frac{E_2\tau_2}{E_1\tau_1}}{1+\frac{E_2}{E_1}}\frac{t}{\tau_2}}\right)+\left(\frac{S_0}{\eta_1+\eta_2}+C\right)t \tag{7}$$

where B is an indeterminable constant. This equation is exactly the same in form as the empirical creep equation presented in Part II of this series of papers, in which the term $\eta_1+\eta_2$ in the above equation has been represented by a symbol η. In that study, the values of η were evaluated at different temperatures by fitting that empirical creep equation to data of compression creep tests therein conducted. On the other hand, individual values of η_i can readily be calculated from the results listed in Table 1 by use of the Maxwell relation (5). Thus, it is now possible to examine if the values of η from the creep measurement can be reproduced as the sum of the individual viscosity values η_i from the present relaxation test. In Fig. 6, the result of this examination is indicated in the form of $\log \eta$ plotted against $1/T$, from which we see that all plotted points approximately fall on a single curve. This agreement

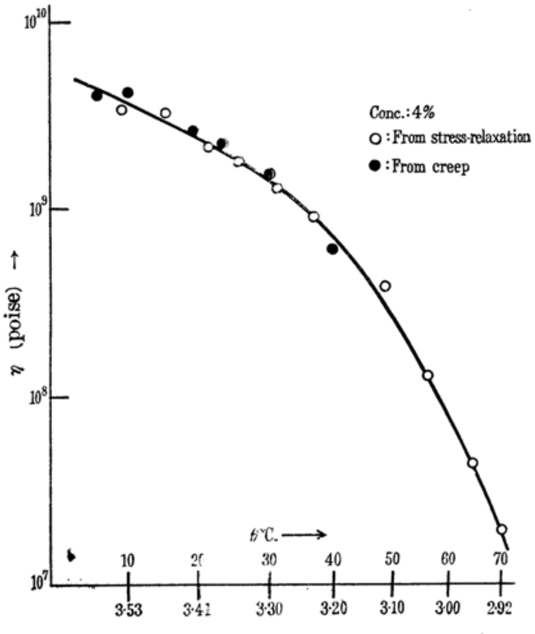

Fig. 6.—Overall viscosity as a function of temperature.

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(8) J. D. Ferry, W. M. Sawyer and J. N. Ashworth, *J. Polymer Sci.*, **2**, 593 (1947); especially, p. 611.

between the viscosity values from different sources of data suggests that our mechanical model set forth above is sound as a consistent basis for describing the static viscoelastic behavior of concentrated agar-agar gels.

In the foregoing lines we have remarked that relaxation curves of agar-agar gel in compression fall across zero stress after running a certain finite interval of time, differing from those in other polymers which lack the primary network structure. This behavior can now be interpreted adequately in the light of Eq. (4). It proves readily that the right-hand side of Eq. (4) vanishes at a certain positive value of t if C is positive, and that it vanishes only at infinitity if C is identically zero. This result implies that when and only when self-contraction of the material is operative, stress at constant compression should be relaxed completely after a finite interval of time has elapsed, just as has been demonstrated in the present relaxation study on agar-agar gels.

Summary

As the third report of the series of papers concerning the viscoelastic behavior of concentrated hydrogels of agar-agar, the results of an experimental investigation of the relaxation of stress in an agar-agar gel of a concentration 4 g./100 cc. have been presented, which are summarized as follows:

(1) The general type of the relaxation curves obtained may be seen in Figure 2, in which particular attention must be drawn to the behavior that the plotted curves fall across the zero stress base after running certain finite intervals of time. An adequate interpretation of this has been presented in the last section of the text.

(2) As was illustrated in the second paper of this series, an agar-agar gel block decreases spontaneously and gradually its volume under the experimental conditions adopted in this series of experiments. Taking into account he spontaneous volume contraction, a system of equations for representing the viscoelastic deformation of an agar-agar gel column subject to compressive load has been presented, in which as a mechanical model of the material two Maxwell relaxation elements connected in parallel have been assumed.

(3) All the data of relaxation obtained have been considered in the light of this set of equations. In this way, the numerical results listed in Table 1 have been obtained.

(4) The activation energy for relaxation has been calculated for each individual mechanical element by the use of the Arrhenius equation. It has been found that the activation energies so calculated are constant below about 40°C. for both elements, amounting to nearly equal values, the average of which is estimated at about 9 kcal./mole. Above 40°C., for both relaxation elements, deviations from the Arrhenius equation appeared, which are gradually marked with increase in temperature. We have ascribed these deviations to the decrease in the frequency factor in the Arrhenius equation.

(5) Finally, the set of equations presented above has been solved for the case of compression creep under constant load, resulting in a creep equation coinciding exactly in form with the empirical creep equation derived in the previous paper II of this series. In addition to this formal agreement of the present theoretical and the previous empirical creep equations, quantitative agreement of them has been demonstrated by showing that the viscosity values from the previous creep test can be well reproduced by the sum of the individual viscosity values obtained from the present relaxation test.

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