STRESS RELAXATION in FILAMENTOUS MATERIALS the EFFECT of HUMIDITY, TEMPERATURE and STRAIN on MAN-MADE FIBRES and SILK

by

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ABSTRACT

The relaxation of tension in strained filaments of Terylene, Perlon, Grilon, nylon 66, nylon 610, polyethylene, polypropylene and silk has been studied at strains up to 4% extension, at constant relative humidity of 65% and with humidity fluctuating between 35% and 90% r.h., and at constant humidity with the temperature varied from 20° to 50°C.

Single unit and six unit stress relaxometers are described together with the necessary auxiliary equipment for maintaining constant conditions of humidity and temperature.

Comparison of the rates of relaxation under standard conditions of 65% r.h. and 20°C with extensions of 1, 2, 3 and 4% showed that Terylene had the slowest rate of relaxation, that of Perlon was slightly higher. The highest rate of relaxation was shown by polypropylen In general, there was no effect of magnitude of strain on the rate of relaxation.

Repeated variation of the relative humidity from 35% to 90% at a constant temperature of 25°C accelerated the rate of decay of tension. The sensitivity of the tension in the different materials to fluctuating humidity has been satisfactorily explained. The result of the experiments with fluctuating humidity are of considerable practical importance.

The effect of temperature on stress relaxation under strains of 1, 2 and 3% at constant humidity were used to produce master curves using Ferry's reduced variable method. The success achieved in applying this method to partly crystalline polymers has enabled the tension that would remain at very long times to be predicted from short time measurements at elevated temperatures.

Experiments have also been made on viscose rayon in the bone dry condition over a wide range of extensions and from the resulting master relaxation curve it has been possible to calculate the number of hydrogen bonds which relax simultaneously according to Nissan's theory of the role of the hydrogen bond in determining the modulus of hydrogen bonded solids.

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* See footnote of Table 7.

CHAPTER I

INTRODUCTION

A very large class of substances, e.g. textile fibres, rubbers, muscles, tissues, etc., composed of large molecules exhibit viscoelastic properties that are qualitatively similar, thus reflecting the overall similarity in the molecular structure. These substanc contain long chain molecules linked together by strong primary bonds at certain points and at other points by secondary, comparatively weaker bonds, e.g. Van der Waa forces (as in regions of local crystallinity), dipole bonds, etc. The effective network structure of a poly is due to primary bonds. Between cross-linkages there may be coiling and twisting of the molecular chains, segments of which can move relative to one another. T interesting viscoelastic properties of fibres depend mainly on the amorphous regions in which relative movem of the chain molecules can take place with the lapse of time.

Time is a dimension to be reckoned with any stu of the physical properties of matter, especially the kinds of matter of which good textile fibres and filamentous materials are composed. The time study gives the manifestation of the structure of the materia According to Professor E.C. Bingham[1], the founder of mod rheology, the time dependent mechanical properties, especially creep and relaxation, are of much importance in the rheology of polymers, i.e. the association betwe the molecular structure and the properties of polymers. General reviews of viscoelastic properties have been given in books of Meredith,[2] Alfrey,[3] Tobolsky and Mark,[4,] Zener,[6] Meyer[7] and Ferry.[8]

When the deformation in a viscoelastic body is kept constant, the stress decays with the elapse of tim and this phenomenon is called "stress relaxation". On the other hand, if the stress or force is kept constant the deformation will increase with time and this behavi is known as "creep". Creep and stress relaxation are grouped as static viscoelastic property measurements, because the applied deformation or force is independent of time.

Creep measurements are easier from a practical point of view, but stress relaxation measurements, thoug not so easy to obtain practically, are simplest to interpret theoretically, because the external geometry of the specimen remains unchanged[9] throughout the test. In the case of stress relaxation, the earlier portion of a relaxation curve may be difficult to obtain owing to rise in temperature in the specimen during the sudden stretching: this changes the relaxation behaviour durin the early stages. Also, inaccuracy of the tension measuring system at very high rates of extension of specimen hinders the early stage study of stress relaxation.

There is no theoretical limit to the duration of a stress relaxation test, but in practice the duratio of any relaxation experiment is governed by the difficul of maintaining accurately, controlled temperature and humidity over very long periods and by the limit to the patience of the observer. However, the time-temperatur superposition principle suggested by Tobolsky[10] and reduced variable method of Ferry[11] have enabled the investigator to obtain a very long duration master stres relaxation behaviour, covering years on the log time scale, for amorphous polymers. This can be obtained at room temperature by horizontal shift of curves at differ temperatures to the relaxation curve at room temperature

Theoretical interpretations between stress relaxation and dynamic complex modulus or compliance of amorphous polymers have been successfully studied by various workers.[12,13] The molecular structure and deformat mechanisms in crystalline polymers depend in a complex w on temperature.[14] Thus, it is difficult to obtain maste stress relaxation curve to correlate their static and dynamic properties.

Some workers[15,16,17] have made attempts to obtain master stress relaxation curves for crystalline polymers, to correlate static and dynamic properties. They have bee successful up to only small strains, but that also is no conclusive. The present work also includes some of such investigations considering the possibility of obtaining master stress relaxation curves as obtained recently by Yoshitomi, Dunell and their co-workers[19,20] on crystalline polymers.

The stress relaxation measurements about to be described provide not only data to test the applicability of the time-temperature superposition principle to semi-crystalline polymers but also information of direct practical importance to certain users of the materials investigated.

One of the objects of the experiments to be described is the comparison of the rates of relaxation of stress of a number of different synthetic fibres with that of silk and the measurement of the influence of humidity and temperature on these rates of relaxation. The investigation originated from the observation that when nylon is used for sieve covers in place of the traditional silk, the sieve becomes slack after a period of time in use, in which the humidity and temperature of the surrounding air may fluctuate over a considerable range in a random manner. Direct measurement of the tension in sieve cloths of nylon and silk mounted in a stretched condition on frames gave somewhat variable results owing to lack of control of temperature and humidity. It was, therefore, decided to make measurements under controlled conditions of humidity and temperature on monofilaments already used in the construction of the sieve cloths and to include in the investigation other synthetic fibre materials which migh possibly give a better overall performance.

Sieve cloths remain in position for long periods, e.g. two years. It is impracticable to carry out laboratory measurements under closely controlled conditi for such long periods, but if one can predict the stress remaining after a long time at normal temperatures from the stress present after a comparatively short time at a higher temperature by Ferry's reduced variable method,[11] then the problem is solved. As described above, such prediction is possible for amorpho polymers, but the evidence available on crystalline fibrous polymers is small,[19,20] so a further objective is to test the superposition of stress relaxation curves observed at different temperatures with a view to establishing any similarities in the rheological behaviour of amorphous and partially crystalline fibrous polymers.

CHAPTER II

LITERATURE SURVEY

1. Stress Relaxation in fibrous and filamentous materials

In the field of textile fibres, Speakman[21] first studied the stress relaxation behaviour of wool in 1928. From his experimental results he found that the rate of stress decay increased with increase of relative humidit Relaxation of stress in wool in water was explained as due to hydrolytic changes associated with polypeptide linkages. Smith and Eisenschitz[22] studied stress relaxation of cellulosic fibres in 1931. Bone-dry viscose rayon filaments at room temperature (20°C) were loaded to 1, 2 or 3 g. corresponding to extensions up to 0.6%. After 10 minutes from the start of an experiment they found that the stress had decayed by about 16% of the stress at 10 seconds. The relative rate of relaxation of stress was roughly independent of applied load, and therefore of the cross-section. Their result agreed with Boltzmann's theory of after effect, which provides a useful approximation to the actual behaviour of rayon in stress relaxation. The relative rate of stress relaxation for rayon and silk between 50 and 1000 seconds at 38% r.h. and 22°C is about 1.3 times that of the dry filament. They expressed their stress decay results as a function of logarithmic time, as was first done by Kohlrausch (1863-1876) for torque relaxation of glass filaments. Smith and Eisenschitz concluded that: relaxation is largely independent of load; that the influence of variations in cross-sectio is of minor importance in relaxation experiments althoug it is important in creep experiments; that although th places of different cross-sections along the filament are under different absolute stress, they relax at abou same rate; and that the variation in the time interval from the beginning of the application of load to the first reading is the source of error whose influence is difficult to estimate. During this time, the filament flows at first under a small load, later under the full load.

In 1934 Steinberger[23] suggested that the relaxatic time, for simplest possible behaviour of the material, should be a function of the stress and strain. Bass and Kauppi[24] made stress relaxation studies of glass fibr In 1939, Frenzel and Bach[25] compared the stress relaxatior of two kinds of viscose rayon at 65% r.h. and 20°C. They used extensions from 1% to 15% and even up to 25% depending upon strength and extensibility of the rayon used. The specimen with the higher strength and lower breaking extension gave lower relative rate of relaxatio at any given extension, which was confirmed later by Meredith[17], in 1954, from his stress relaxation curves. The higher the rate of extension, the greater the streng and the smaller the extension. At 10% extension, after a long time of relaxation, there is standstill in tensio The initial tension at zero time is difficult to obtain practically, because it takes a certain time to put tension in operation during which time the tension relaxes. He also suggested that stress strain curves at any speed of extensometer can be plotted from the relaxation curves of the high speed relations.

In 1943, Tobolsky and Eyring[26], then in 1945, Hale White and Eyring[27], developed a reaction rate theory of viscoelasticity, which incorporated Eyring's[28, 29] non-linear hyperbolic sine law of viscous flow. This theory predicts the relation between time and stress to be a hyperbolic tangent one in stress relaxation. By measuring the stress plotted against log time curves, one can find values for the number of secondary bonds per unit area.

Tobolsky, Prettyman and Dillon[30] studied stress relaxation for many rubbers from 10 seconds to a few hours. Mooney and his co-workers[31], Pedderson and Nielson[32]; Bischoff, Catsiff & Tobolsky[33] and Berry[34] have made stress relaxation experiments to clarify the structure and properties of rubber and rubberlike materials.

In 1946-48 Tobolsky and his co-workers[35, 36] described stress relaxation behaviour of polysulphide rubbers, which obey the simple Maxwellian law of relaxation. This is of a chemical rather than a physical nature caused by intermolecular exchange reaction between disulphide linkage of one chain and a terminal group of an adjacent chain. During the same period, Green and Tobolsky[37] gave the molecular theory for the explanation of the "box" portion in the distribution of relaxation times, taking into consideration the rate of breaking and forming of crosslinks in a molecular network struct Later in 1953, Scott and Stein[38] confirmed this molecular theory.

Dart and Guth[39] studied the stress relaxation in cork.

Speakman and Saville[40] studied the stress relaxation of nylon 66 filaments, and concluded that th rate of tension decay is independent of pH value. The found that the relaxation curves change considerably at different temperatures in water, but the effect of temperature in general is to lower the absolute tension developed.

Burleigh and Wakeham[41] applied reaction rate theo to the analysis of their experimental results for stres relaxation of cotton and rayon at various humidities an at different temperatures. They used their results of stress relaxation to evaluate the molecular constants involved in this theory. They assumed the final stres to be zero at infinite time of relaxation.

Stress relaxation of wool at constant compressi strain between 30% and 50% of the proportional limits ha been studied by Kitazawa.[42] He was able to give the empirical equation governing the decay of stress.

Burte and Halsey[43] gave a two-phase theory of stre relaxation which was confirmed in 1948 by Peters and Speakman.[44]

During 1948-52, Tobolsky and his collaborators[45, 46, 47] showed a composite stress relaxation curve of poly-iso-butylene showing three regions: rubbery, transition and glassy. Also in 1948, Stein and Tobolsky[48] studied both the stress relaxation and birefringence to specify the nature of the molecular configurational changes associated with stress relaxatic For rubber-like materials, stress-birefringence ratio wa constant during relaxation; for other materials, e.g. elastic polyamides and plasticised poly-vinyl-chloride, the changes in the birefringence were very much smaller than the corresponding change in stress.

Zener,[49] and later in 1955, Anderson and Andereath[50] were able to give an appropriate discussion for the stre relaxation behaviour of metals. Before them Leaderman[51] has mentioned that the X-ray diffraction patterns of rayon and metals (e.g. mild steel wires) show that both contain oriented crystalline material.

Wegener[52] made a systematic study of stress relaxation behaviour in viscose rayon, cuprammonium rayon and cellulose acetate rayon yarns under a range of constant extensions at 65% r.h. and 20°C. Behaviour was studied from 1 second to 300 seconds from the time when the required extension was reached. A simple powe law involving two arbitrary constants was used to express the relation between stress and time. The same law holds good at varying humidities.[53] Dunell and Tobolsky[54] with practical evidence showed that the dynamic internal friction is proportional to the negative slope of stress relaxation curve plotted as stress/strain against log time under comparable scales of time.

In the following year, Mark and Tobolsky[55] (page 360) from the previous work[46, 56], suggested that the relaxation of stress of fibres at constant extensions i in fact caused by a completely different mechanism than is true in amorphous polymers. It often arises from a slow growth of new crystalline material or from the orientation of already existing crystallites. This i most readily shown by the fact that the birefringence will often increase at constant extension, whereas the stress decays.

Katz and Tobolsky[57] measured the temperature and extension dependence of stress relaxation of wool in water. They also gave a theory of relaxation for wool saying that the stress is partly supported by cross linkages like cystine linkages and salt linkages. This theory was not applicable to poly-iso-butylene[45, 46]. They concluded that the hyperbolic sine law of viscous flow is probably applicable to textile materials, while the relaxation spectrum function of linear viscosity is of greater use in the study of amorphous polymers. This theory was further modified in 1955 by Eyring and co-workers[58]. Andersen[59] contributed on the side of cellulosic fibres. He suggested that to sum up and describe the results of the relaxation tests is sometime only possible if they are fitted into a model system, th parameters of which can be calculated on the basis of tests. He applied his results of stress relaxation of viscose rayon filaments at different relative humidities and 20°C to evaluate the constants in the Tobolsky-Eyring theory. The rate of relaxation was found to decrease with increase in relative humidity.

Tobolsky, Dunell and Andrews[15] in 1951, have discussed the mechanical behaviour of an idealised polymer in terms of Maxwell relaxation theory. When a simple rectangular distribution of relaxation times i assumed, it is shown that dynamic properties can be related to those deduced from stress relaxation. They obtained better than order of magnitude agreement betwe observed and calculated values of internal friction for a number of textile fibres such as silk, viscose rayon, cellulose acetate rayon and nylon. Thus the relationsh deduced from the "box" distribution was extended to oth broad distributions of the relaxation times. Later on similar work has been reported,[16,17] but the results are conclusive.[18] Dunnell and Dillon[60] found in relaxation curves of viscose rayon, acetate rayon, silk, nylon 66 and polyethylene that 100 times increase in the extensi rate for 0.5% and 5% extensions caused a change in the curve shape from concave to convex to the log time axis The conditions of his experiments were 65% r.h. and 70°F and two speeds were 5% extension reached in 15 seconds (0.33% per second) and 25 minutes or 1500 secon (0.0033% per sec.) For slower speed there was no relaxation for the first 20 seconds after total elongation. The maximum stress developed was also higher when the speed of extension was increased, which shows that ther was a large amount of stress decaying during slow rate extension.

Andrews and Tobolsky [61,62] presented an idealised distribution function of relaxation times for linear amorphous polymers, which had the simple graphic aspect of "wedge" type [62] distribution in transition region, followed by a "box" type [61] in flow region (i.e. the very long time end). The "wedge" type distribution function is independent of molecular weight (for sufficiently high molecular weights), whereas the "box" type varies with the molecular weight of polymer. The distribution function, or relaxation spectrum, is mathematical representation which can conveniently describe the line viscoelastic behaviour of material. Different types of distribution functions may not be interpreted in terms of molecular contributions but then also Ferry et al.[63] in 1955 have been able to extend the molecular theories of Rouse[64] and Bueche [65] for possibility of molecular interpretation of "wedge" portion in distribution of relaxation times in terms of segmental motion. This proves the firm theoretical basis of Tobolsky and Ferry temperature-time superposition procedure.[11,61,62]

Miller, Ferry, Schremp and Eldridge[66] and later in 1955 Tobolsky [67] studied the stress relaxation behavio in gelatin and gels.

In 1952, Chen, Ree and Eyring[68] studied the stres relaxation of a crystalline polymer Saran, a vinylidene chloridevinylchloride copolymer. They found its behaviour to be linear on a log time scale over a range of times from one to 80 hours in air and from one to 80 minutes in water. The authors were able to describe the relaxation behaviour of Saran by a model containing only two relaxation times, since the time range in either condition of moisture was only two cycles of log time.

Gross[69] in his mathematical formulation of viscoelasticity in 1953, related stress relaxation and creep to one another through a function of "relaxation spectrum" i.e. a distribution of relaxation times, under given experimental conditions. The only provision is that "Boltzmann's superposition principle"[51,70] holds, i.e. viscoelastic behaviour must be linear.

Rance[71] has suggested that the stress relaxation of rapidly strained paper is worth noting. The effect of rate of extension on paper is similar to that observe for textile fibres.

Fujita and Kishimoto[72] also desired to verify the similar experimental investigations of Burleigh and Wakeham[41] with the similar assumptions of stress decay, being zero at infinite time. They obtained similar results. Hammerle and Montgomery[16] demonstrated that similar relationships exist between the shear modulus and energy loss per cycle and the relaxation of torque under constant twist. In torsional experiments for nylon 66 monofils, torque relaxed linearly with log time from 20 to 20,000 seconds after small twists on the basis of generalised Maxwell model, i.e. a distribution of relaxation times of the "box" type. The values of modulus and energy loss per cycle (or damping coefficient) predicted from relaxation experiments were tested by experiments with a torsion pendulum, whose period varied from 50 to 400 seconds, i.e. within the range of times at which torque was measured in the relaxation experime The observed dependence of the angular frequency upon the moment of inertia of the bob and length of filament agreed within 3% with predicted values.

Sorokin[73] has modified the formula for the stres relaxation curve of metals, given by Oding.[74] Rovinsku Lynthsau[75] have shown by X-ray analysis that the number interference spots for aluminium under pressure increas with stress relaxation. The curve of growth is similar to the curve of stress relaxation. This is due to the lower state of crystal perfection.

Meredith[76] has related mechanical properties and structure of fibres. Tenacity, extensibility, wet strength and elasticity of fibres are correlated to degree of crystallinity, molecular orientation, release of internal strain by swelling, and relaxation of secondary bonds within the fibre.

In 1954 Meredith[17] investigated stress relaxatio of cotton, flax, viscose and cellulose acetate rayons at 65% r.h. and 20°C over a time range from 1/50 second after start of relaxation to 24 hours, covering about 8 cycles of log time, which is the maximum time range studied up until now. He analysed his results both empirically according to the Nutting powerlaw[77] relating stress, strain and time. He has also demonstrated the application of the Tobolsky-Eyring reaction rate theory Meredith obtained very good agreement between values of internal friction of viscose rayon and cellulose acetat calculated from his stress relaxation data and directly observed values. Meredith[17] and later Armstrong[73] have recognised the desirability of obtaining stress relaxation measurements at very short times after initial stretching. They have described the apparatus for achieving this end.

Catsiff and Tobolsky,[79,80] by introducing a distribution of relaxation times, experimentally verified the mathematical relationship, in theory between stress relaxation and dynamic mechanical properties, for polyisobutylene in the rubbery and transition regions.

Wood[81] studied stress relaxation of human hair i water at 10% to 50% stretch from 0.1 second to 60 hours. His results showed two relaxation processes for wool fibre in water. The rapid and major contribution towar relaxation over a greater period of time was attributed to disulphide bond fission. It may be noted that in the case of very fast stretching, the shape of the early part of stress relaxation curve on log time scale is dependent upon the way in which the zero time is chosen. Wood took start of stretching as zero time. If the maximum stress developed time is taken as zero, the initial decay of stress would not appear so rapid as Wood's curves showed.

Akira Kishimoto[82] studied stress relaxation of Amilan (nylon 6) filaments of various draw ratios and of the order of different degree of heat pretreatment at 55% r.h. The data obtained over a range of elongation and temperature were shown to be represented empirically by a product of two functions: a function of strain and temperature only and a function involving four parameters, which are independent of elongation but dependent on the time and temperature.

In 1955, Watson, Kennedy and Armstrong,[78] after studying stress relaxation of several commercial plastic e.g. polystyrene, plasticised cellulose derivatives, polyethylene, nylon, etc., in short range of 0.1 to 2.5 seconds after application of load, found that the increasing strain, temperature or plasticiser content generally increased the relaxation rate. Feltham[83] found that the mode of stress relaxation in materials of vastl differing structures and chemical compositions e.g. meta gels, glass, synthetic resins, plastics and fibres, can accounted for on the basis of a log-normal distribution relaxation times, which can be derived on the assumption that the relaxing centres in the solid have almost the s heat of activation and that configurational relaxation centres are normally distributed.

Rigby[84] divided his stress relaxation curves of wool in water into fast relaxation occuring in the first 60 seconds (due to breakdown of weaker linkages) followe by a slower relaxation (due to breakdown of stronger linkages). He presented his results on a linear time scale. By converting his results to log time scale as usually adopted for stress relaxation studies, there appears only a single relaxation process in the range of time covered by his experiments. The fast relaxation according to him covers only about one cycle of log time and his data could be represented to a single Maxwell element.[85] He, in collaboration with Feughelman[86] tried to apply his above data to the two-phase theory of Burte and Halsey;[43] Peters and Speakman[44] by assuming that the unit in either state behaves according to a single Maxwell element. The assumption of a single relaxation time is arbitrary.

After the hyperbolic tangent law theories of relaxation of Tobolsky-Eyring and co-workers,[26,27] Ree, Hahn and Eyring[58] proposed a modified theory of stress relaxation by regarding stress relaxation as a molecular reaction with suitably defined rate constant. The drivi force acting on the reaction sites in a system is assume to be proportional to the number of such sites, which is again assumed to be proportional to the force which one measures. Unlike the original theory, the modified one is a generalised representation rather than a specific molecular theory. Relaxation in wool is explained as α and β transformation and that in polyisobutylene by slippage accompanying disentanglement.

Nakada[87] interpreted the "wedge" type of stress relaxation spectrum in polyisobutylene by a simple model. K.W. Scott[88] has given theoretical investigations of structural changes and stress relaxation phenomena in high polymers. Kuhn and Künzle[89] have determined experimentally the dynamic viscosity and elasticity and also relaxation time spectrum of rubber. Danas et al[90] explained magnetic relaxation in natural and synthetic rubbers.

In 1956, Matsuda[91] measured the stress relaxation in dry polyvinylalcohol filaments. For the insotropic sample the relaxation spectrum was found to be the "box" type, distributed uniformly over a time range from 100 to 10,000 seconds. The spectrum becomes narrower with increasing orientation of the sample.

Chatten, Scoville and Conant[92] gave stress relaxation behaviour of elastomers e.g. ebonite, etc. at constant elongation and at constant compression. Fast[93] has given molecular interpretation and a review of relaxation theory. He has also discussed dielectric relaxation, paramagnetic and internal friction of metals, whereas Böttcher[94] just gave molecular interpretation of dielectric relaxation phenomena. During the same year, Schwarzl[95] studied mechanical relaxation phenomena.

The mathematical linear viscoelastic theory of Gross[69] was successfully applied by Ninomiya and Fijita[13] in 1957 for correlation of stress relaxation and the dynamic compliance and internal friction of polyvinylacetate. They obtained a composite stress relaxation curve by using the time-temperature superposition principle. The above correlation was found in the transition region where experimental data of dynamic properties were available. Kishimoto and Fujita[96] studied the chemical stress relaxation in Amilan (nylon 6), and polyvinylalchohol, by the penetration of water vapours. The rates of water absorption were also studied. Relaxation theory based on breaking of internal bonds by the penetrant is proposed. Diffusion coefficient from sorption agrees with that calculated from chemical relaxation extrapolated to zero strain. The water diffusion rate for polyvinylalcohol depends on time and its concentration. Khutsishvili[97] gave magnetic relaxation the

Kästner and Schlosser[98] gave fundamental mathematical relations of linear scalar relaxation theory, which covers the entire range of viscoelastic behaviour of a substance.

Akira Miyaka[99] in 1958 gave a theory of mechanica relaxation spectra of crystalline polymers. By using the Rouse[64] model chain with anisotropic spring forces, the flat part in relaxation spectra of crystalline polymer is explained. The asymptotic shape for the large relaxation time of spectra thus obtained depends on the principal values of the spring force constants and variations of the directions of the principal axis along the chain.

Kenny and Chaikin[100] in 1959 illustrated that extremely complex effects can occur in the stress relaxation behaviour of non-uniform specimens. But during discussions over the same paper, Meredith suggeste that such complexities will arise, when the stress strai relations are non-linear. He further said that for many cases, the stress strain relation was linear, so that in practice, the effects of the non-uniformity might be quite small.

Thurn[101] in 1959 found that there is an influence of the mechanical and thermal history on the dielectric and mechanical relaxation behaviour of high polymers.

There is a change in mobility of chains due to the above pre-treatments. Tobolsky and Murakami[102] carried out stress relaxation of two polystyrene samples in thei rubbery flow regions. Haly and Feughelman[103] found the stress changes at constant strain and hydrogen bonding i keratin fibres. When keratin is extended in water, hel and dried, stress develops in the fibre.

Nakada[104] gave the theory of viscoelasticity of amorphous bulk polymers, dispersion of dynamic bulk modulus is also found. This theory explains volume relaxation phenomena and relation to shear and longitudinal relaxation. The origin of relaxation phenomena is attributed to the configurational relaxation of the three dimensional extension of the chain molecules. A diffusion equation of the chain configuration is compose of beads connected by Hookean springs. A dynamic relat between varying pressure and volume is derived by integration of the diffusion equation for sinusoidal pressur change. Thus the real and the imaginary parts of the b modulus are calculated. The dispersion of bulk modulus is specified by two time constants τ_β and τ_r the former relating to the rubber-like elasticity of energetic natu which comes from distortion of chemical bonds and the latter from the change of cohesive energy.

Ohira, Kitajima and Iino,[105] studied the stress relaxation of Terylene, cotton, wool, nylon, viscose, acetate and many other synthetic fibres. They found that the stress relaxation curves obtained as rate of relaxation against log time, were hyperbolic at the first stage (1 ~ 60 sec.). Logarithm of relaxation rate is plotted against logarithm of time. The straight line obtained is governed by

$$f/f_0 = A.\ t^{-k} \qquad \text{or} \qquad \ln (f/f_0) = A - K.\ \ln t$$

Where f_0 = initial stress, f = stress at time t,
t = time (sec.), A, K = constants.

2. Effect of moisture on stress relaxation

While studying stress relaxation of wool fibres in 1928, Speakman[21] showed the importance of relative humidity. In 1947, Burleigh and Wakeham[41] found the stress relaxation curves for cellulose fibres at several relative humidities of 37%, 70% and 100% at 25°C. Small changes in flow units (N_c/N) and activation energy were observed with increasing moisture content. At 100% r.h. the behaviour is different. Both cotton and rayon cord showed a sharp change of slope of the stress relaxation curve at approximately 0.5 minutes after extension. Thus two stress relaxation mechanisms occur under these conditions. This is later on confirmed by various workers.[106, 107]

Anderson[59] used the Tobolsky-Eyring reaction rate theory to calculate the constants of his relaxation experiments on viscose rayon filaments and cotton fibres, investigated at relative humidities of 0%, 37% 70% and 100% and in water at 20°C, with initial tensions up to about 2 x 10^9 dyn per cm^3. The technique used enabled the fibres to be stretched in 50 to 125 milliseconds and the tension to be observed from the time when the fibre length was constant. He claimed that the relaxation ceased after 15 seconds to 20 minutes and the time taken for the tension to fall to half its initial value was shown to decrease as the relative humidity was increased from 0% to 100% r.h.

Wegener and Luyken[59] were able to express their stress relaxation results at 45%, 65% and 85% and 100% r.h., by a powerlaw which involved two arbitrary constants.

In 1955 Roseveare and Poore,[108] from the thermodynamics of stretched cellulose fibres, found that the water content is more important than temperature in determination of the properties of regenerated cellulose.

Price, McIntyre, Pattison and Dunell[10] made stres relaxation measurements of single filaments of viscose rayon, acetate rayon, nylon 66 and polyethylene at severa humidities from 15% to nearly saturation, covering a tim range of six cycles of log scale from 0.02 seconds after elongation. For all specimen tested at 25°C and 2°C, th rate of relaxation appeared to decrease with increasing relative humidity. The maximum stress also became smaller with rise in humidity, or in temperature. Peters and Woods[109] measured the stress relaxation behaviour of wool at 25°C for several relative humidities below, satur ation. They condluded that the onset of slow relaxatio is deferred if not postponed indefinitely, and the slop of the fast relaxation curve remains almost constant at different humidities. The explanation given was that the effect of increasing humidity is to reduce the number of inter and intra-chain hydrogen bonds in the same proportion so that the rate of relaxation increase in such a way as to displace the curve along the log-time axis.

Newns[106] divided diffusion of water in fibre into two stages. First stage when the diffusion coefficient is a function of concentration of moisture alone, whereas at later and second stage, diffusion is dependent upon the relaxation of swelling stresses set up by the water molecules diffused into the fibre in the first stage. In other words, in the second stage water diffuses into cellulose at a rate determined by the breakin of hydrogen bonds due to swelling stresses.

Matsumoto and Ishikawa[110] in 1957 investigated the influence of relative humidity and temperature on the stress relaxation of nylon 6 under different elongation They used relative humidities of 8%, 33%, 55%, 75% and water at 25°C for one set of stress relaxation curves. Temperatures 25°C, 40°C and 55°C were used for the other set of experiments at 55% r.h. and in water. Their curves could be approximated by $(\log t - \log t_o) = 1.4 \left(\frac{1}{E-E_o}\right) - (E-E_o)$, where t = time, E = stress/strain, E_o and t_o are constants. Under small elongations (2%), the stress relaxation is much affected by humidity and temperature. At low humidity, a high rate of stress relaxation is obtained under 2% and 4% elongations.

In 1958 Yoshitomi, Nagamtsu and Kosiyama[19] reported stress relaxation in torsion of low crystallinity nylon 6 filaments at various temperatures from 20 to 80°C and 0%, 45% and 75% relative humidities. By using the master stress relaxation curves obtained from the curves at different temperatures, they were able to obtain a general master stress relaxation curve from the different relative humidity curves at 0% r.h. and 75% r.h.

Feughelman and Robinson[111] studied the stress relaxation of keratin fibre and the effect of moisture diffusion on the stress relaxation. When they studied the stress relaxation in a changing atmosphere between dry and wet, they found that diffusion of water affects the rate of relaxation. The tension increases when the humidity is decreased thus causing the fluctuations in tension due to fluctuations in humidity. Mackay and Downes[112] also found similar effect of fluctuating humidity between 0% and 94% r.h. on wool.

Feughelman[113] also found that when wet wool fibre is strained to a fixed extension and allowed to remain at this extension for a time and then dried, the stress in the fibre rises. This rise of stress is independent of the time as long as it is greater than about one minute and also independent of number of chemical and physical modifications to various fibres. The rise in stress is between 30% and 50% strain and no further increase was recorded. From the evidence present, it is suggested that drying the fibre in a strained state introduces strained hydrogen bonds, which are responsible for the stress rise in drying.

Algie[114] concluded from his experiments on stres relaxation of hair and effect of cycling relative humidity, that the change in relative humidity causes reversible change in tension, indicating that in this experiment the function of the absorbed water is to weaken bonds according to the scission process propose by Fujita and Kishimoto[115] for nylon-water.

Recently, Shaw and his collaborators[116] studied the sorption of water in wool, silk and nylon fibres, and in wool, cortical cells, by nuclear magnetic resonance. Proton resonance line shapes and relaxation times were determined as a function of moisture content The results of this study suggest that the water is bound in clusters to the sorbant and the surface migration is the dominant mode of magnetic relaxation.

3. Effect of strain on stress relaxation

Shorter[117] found that the higher the rate of extension the lower the breaking extension, because the impeded elements in the representing dynamical three element model do not have time to extend much before rupture occurs. Speakman[118] also found that for wool in water, the breaking extension decreases and breaking load increases up to certain increased rate of loading and after that both remain approximately constant. The extension of previously extended and recovered fibre increases with further same megnitude of loading.

Leaderman[51] found that on stretching or cooling rubber becomes more crystalline, so amorphous halo of X-ray diagram gradually disappears with increase in magnitude of stretching or lowering of temperature. Th original pattern is obtained by releasing stretch or b heating to same temperature. In explaining Kinetic theory of high elasticity, he mentioned that atoms in long molecular chain are connected by homopolar bonds, so application of load should cause straightening of the chain due to elastic extension and bending of primary valence bonds and consequently increase in internal energy. On removal of load, reverse is the process. For very flexible chains, e.g. rubber and nylon, depending upon flexibility and temperature, chains will be i various degrees of contraction and agitation. Applicatio of load will straighten them, i.e. entropy of the syste will be decreased. Removal of load will cause contraction of such chains to original, more probable and more kinked form. This theory is the Kinetic theory of rubber elasticity.

By application of reaction rate theory of Eyring,[28,29] Tobolsky and Eyring[26] in 1943 concluded that the number of relaxing mechanisms per unit area increase with increasing initial deformation (or stress), and the free energy of activation for flow decreases linearly. This shows that when initial deformation is increased, the units of flow become smaller.

Andrews, Tobolsky and Hanson[119] from their experimental evidence have found that the stress relaxation is a function of the amount of extension and also the time of stress relaxation. They further added that the permanent set also increases with increase in extension and/or increase of time.

Burleigh and Wakeham[41] were able to establish that the rate of elongation or flow in the cellulose fibres is greatly increased as applied stress or strain increases. This phenomenon is probably due to both the increase in the number of shifts the flow units make per unit time interval and to an increase in the number of flow units shifting. The limiting condition will be reached when the number of flow units are all under sufficient stress to move rapidly (or frequently) with respect to each other. The total stress on the fibre at this condition will then be the maximum, which one might expect the fibre to bear without rupture. By studying the dry fibre, it has been shown that the experimental tensile strength is much lower than the maximum calculated values, which could be obtained with rapid test. This observed reduction in strength shows that fibre breakage occurs by a mechanism involving slipping of the cellulose chains in the fibre rather than by rupture of those chains.

Meredith[120] studied the stress relaxation in cotton yarns at small constant extensions of 2%, 4% and 6%. The relaxation curves were approximately of the same shape with difference of scale factor, which was proportional to the extension. In other words, cotton fibre exhibits linearity at small extensions. He was able to outline Eyring[28] theory and could successfully apply it for the molecular interpretations of his stress relaxation results.

Wegener[52] also gave relaxation behaviour of rayons at different magnitudes of extension, 2% to 18%.

Katz and Tobolsky[57] from their experimental observations concluded that stress relaxation of wet wool depends upon the magnitude of strain and temperatur

Andersen[59] suggested that the magnitude of the tension has a direct influence on degree of orientation of wet viscose rayon: on the other hand, stretching of dried cellulose fibre will not generally increase its degree of orientation. He found it very difficult to study stress relaxation of bone dry rayon and cotton at low extensions, because relaxation here is small. At increasing degree of stretching (near break), the relaxation proceeds more slowly. There is no jerky change from conditions of wet fibres to those at 100% and 0% r.h. fibres. The slow relaxation at high degree of stretching is assumed to take place when the fibre is stretched, the resulting greater binding energy corresponds to a lower rate of relaxation.

Treloar[121] and Barkas[122] observed that at constant relative humidity the moisture regain of horse hair and viscose rayon was dependent upon the applied stres The higher the stress (or strain), the greater the moisture absorption, which is in agreement with prediction of thermodynamic theory. The extra amount of moisture absorbed by horse hair due to applied stress was different at various relative humidities. It increases with increasing relative humidity up to about 65% r.h. beyond which any further increase in relative humidity only reduces the extra amount of the moisture absorbed. Barkas also found that the time for relaxation depends on the dimensions of the test piece, whereas the time for moisture diffusion through it increases rapidly with dimensions, we may, in principle achieve this condition by making test piece sufficientl small.

Barkas,[122] in dealing with swelling of wood, showed that the moisture absorption of wood under stres is related to the magnitude of stress. In simple terms one may imagine that when the material is stressed and deformed, there will be more accessible space in the material available for accommodation of water molecules so resulting in increased moisture absorption.

Kubu[123] investigated the stress relaxation behaviour of wool, silk and nylon. He concluded that within range of 20% extension, wool behaviour is independent of the degree of extension. Similar results were observed for nylon up to 15% extension and silk up to 10% extension.

Roseveare and Poore[108] in 1955, stated that the thermodynamic treatment of the stretching of cellulose fibres shows that moisture and temperature control the bonding between chains in the amorphous regions. Increase in the moisture content due to stretching is more important than temperature effect.

During their study of stress relaxation of viscose rayon in water, Clark, Preston and Shroff[124] were able to conclude that the change of stress with time as a function of maximum stress was independent of the amount of extension in the range 1% to 20%. Meredith[125] has shown in the same year (1956), that if the stress relaxation data at given temperature and relative humidity, for viscose rayon and cellulose acetate, at different extensions be plotted as stress/strain, agains log time, each curve appears to be part of a common sigmoidal curve, which is called a "composite relaxation curve", shifted to lower values of log time as the constant extension is increased. Similar analysis is applied to nylon and Terylene by Hsu[107]. He could approximately find a composite relaxation curve for Terylene, with certain deviations between two yield points at 4% and 10% extensions. Nylon did not give any composite curve at 65% r.h. and dry state. The composite stress relaxation curves obtained by Meredith[125] were up to time range of 10^{16} seconds for rayon at 65% r.h. and 20°C.

In 1957, Nissan[126] studied the stress relaxation behaviour of paper at very small extensions. He was able to discuss the theory concerning the moisture absorption during small strains. He found no need of use of mechanical models.

Passaglia and Koppehele[127] studied the stress relaxation behaviour of isotropic and oriented cellulose monofilaments at 25°C and 50°C, at 50% r.h. and strains between 0.5% and 5%. Log modulus v/s log time plots were different at different strains, but superposable by simple translation along log time axis.

During 1959 Tsujimoto and Motoji[128], while studying stress-temperature behaviour of nylon 6 filaments, at constant extension, found that the amorphous regions dominate stress relaxation at low extensions, whereas crystalline regions dominate at high extensions.

4. Effect of temperature on stress relaxation

During 1944-45, Tobolsky[10,30] and co-workers, by using the time-temperature superposition procedure of Tobolsky-Eyring, through translation of time axis, have plotted composite stress relaxation curves and hav proved that in hydrocarbon rubbers there are the three regions of stress-temperature-time relations. At intermediate temperatures there exists a region of relative stability in which the statistical thermodynamical theory of rubber elasticity is valid. At low temperature, the stress relaxation is due to slippage of secondary interchain bonds, which are continuously breaking and reforming, whereas at high temperature, the process is due to the oxidative scission of the primary valence bonds, making up three dimensional net work. This type of chemical reaction in the visco-elastic[31] behaviour is also confirmed by Mooney and co-workers. This can be termed "thermo-rheology".

Speakman and Saville[40] were first to study the effect of temperature on the stress relaxation of nylon 66 in water (1946). They found that, in general, the effect of high temperature is to lower the absolute tension developed. Between 25°C and 55°C, the relaxation curve is linear and the rate of decay of tension remains approximately unchanged with temperatur for a time range of from 30 seconds to 30 minutes. Above 55°C, the slope of the relaxation curve is somewhat similar to that for wool in water. In the following year, 1947, Burleigh and Wakeham,[41] from their experiments on dry cotton and viscose rayon cords, concluded that there is increase in the rate of relaxation, with increase in temperature with a given initial stress. This increase in temperature increases the frequency of shifts of flow units, since the number of chains per flow unit remains about the same, free activation energy ΔF increases with temperature, as would be expected. Tobolsky and his collaborators[45,46,47] used Tobolsky time-temperature superposition principle or Ferry's reduced variable method to obtain the composite stress relaxation curve of polyisobutylene. They were able to give three regions, e.g. rubbery, transition and glassy

Stein, Krimm and Tobolsky[129] found that polyethylene shows little or no relaxation of birefringence with time, at various temperatures between 40°C and 100°C, although initial value progressively decreased with increasing temperature. Thus the molecular structure and deformation mechanisms in crystalline polymers is dependent on the temperature. This has been proved later by Tobolsky[14] in 1956. Crystallinity and orientation tend to change with temperature[130], so a master curve cannot be obtained to correlate static and dynamic functions (for crystalline materials, and with amorphous material at high degree of strains). Possibility only at low strains, but not conclusive, according to Price and his co-workers[10]. They have suggested that the correlations between static and dynamic experiments were not conclusive because the strain in stress relaxation experiments (2% to 4.5%) were probably too large for linearity of behaviour of filaments.

In 1950, Ferry[11] published a very useful, reduced variable, method for obtaining master relaxation curve for amorphous polymers (solutions), from the individual relaxation curves at different temperatures and differen concentrations. He has proved that the relaxation time depend identically on temperature and concentration of the amorphous polymer. Katz and Tobolsky[57] found that the rates of relaxation for wool depend on the temperature (30°C - 80°C). Their theory says that the stress is partly supported by cross linkages like cystin linkages and salt linkages. This was not a successful theory for stress relaxation of polyisobutylene above 30°C. Therefore it can be concluded that the hyperbolic sine law of viscous flow is probably applicable to textile materials, while the relaxation spectrum function of linear viscosity is of greater importance in the study of amorphous polymers.

Mark and Tobolsky[55] suggested that if crystalline material is stretched, the force resisting stretching arises mainly from the decrease of configurational entropy in the amorphous region. The crystallit retard molecular diffusion almost as effectively as chemical cross links, so the relaxation of stress at constant extension is relatively slow, on the other hand, as the temperature is raised, some of the crystallites will melt out completely so that the concentration of "cross links" becomes smaller with increasing temperature and the modulus of the material is therefore lowered as the temperature is raised.

Andersen[59] carried out relaxation experiments at high temperatures. To avoid complication about maintaining constant relative humidity at different temperatures, he used dry conditions, where of course relaxation is very small and the relaxation time is great. His experiments proved, however, that an increase in temperature brings about a more rapid tension drop because the relaxation time is diminished.

In 1951, Tobolsky, Dunell and Andrews[15] and previously in 1946, Stern and Tobolsky,[35] found that at high temperatures the elasto-viscous behaviour is controlled by chemical reaction. In relaxation curves obeying this, the decay of stress occurs almost completely within less cycles of logarithmic time. When this relaxation function is plotted against log time as abscissa, a change in the value of the relaxation time τ merely shifts, the relaxation curve horizontally along the logarithmic time axis. For vulcanised rubber at room temperature, the stress relaxation curve is fairly linear. At high temperatures the initial portion of relaxation curve plotted against log time is still linear, but the log time end of the curve approaches the form of a Maxwell decay curve.

The stress relaxation data of polyisobutylene at 30°C have been extended back for several decades of logarithmic time by superposition of data at lower temperatures.[10] On the same graph are plotted the dynamic modulus data obtained at 30°C. The agreement between extrapolated stress relaxation data and dynamic modulus data is rather good.

According to Schwarel and Staverman,[131] in the materials obeying the time-temperature superposition principle,[10] the same sequence of molecular events follow in similar deformations at different temperatures, whereas in the materials other than this type, not only the speed but also the sequence of molecular processes changes when the temperature of the experiment changes.

This shows that the materials of the former type do not change in structure with heat treatment, whereas in other materials heat treatment modifies the structu Thus the expectation is that the materials which obey the temperature-time superposition principle would be found only among the polymers containing no crystallites, and no pronounced polar groups. Thus they have been able to give theoretical interpretations between stress relaxation and dynamic complex or compliance of amorphous polymers, which can be studied by using Tobolsky time-temperature superposition principle or Ferry's reduction method. This has been confirmed later by Tobolsky[10] in 1956 for polyisobutylene and by Ninomiya et al.[11] in 1957 for vinylacetate, above the glass transition temperature, where the nature of the rate proces is independent of temperature. McLoughlin and Tobolsky[1] obtained a composite stress relaxation curve for polymethylmethacylate (a linear amorphous polymer), explaining its states at all temperatures from rubbery to glassy.

In 1953, Lasater, Mimer and Eyring[153] investigate the stress relaxation behaviour of dry and wet cotton fibres at various temperatures between 0°C and 60°C. They correlated their results up to one hour approximately with a mechanical model consisting of two Maxwell elements in parallel. Provided the time interval is sufficient for completion of fast relaxation process, constants were reproducible and were independent of initial load from 1g to 3g, but were markedly influenced by temperature. They concluded that the relaxations occurred through segmental motion of the chains rather than the whole chain moving at one time. In the following year Kubu, Frei and Montgomery[134] showed that the early period of stress relaxation of wool in water is not much affected by temperature rise from 30°C to 70°C, but later period is affected much by temperature. Kishimoto[82] found that stress relaxation in Amilan at 55% r.h. is a function of strain and temperature. Seidman and Mason[135] analysed his stress relaxation results of paper cellulose, at different temperatures and relative humidities by using reaction rate theory.

In 1955 Ferry, Landel and Williams[69] found that the distribution function or relaxation spectrum is a mathematical representation which can conveniently describe the linear viscoelastic behaviour of the material. Different types of distribution functions may not be directly interpreted in terms of molecular theories of Rouse[64] and Bueche[65] for possibility of molecula interpretations of "wedge" portion in distribution of relaxation times in terms of segmental motion. This proves the firm theoretical basis of Tobolsky and Ferry temperature-time superposition procedure. Tobolsky and McLoughlin[136] presented stress relaxation of crystalline polymers, e.g. polytrifluoroethylene, and polyethylene behaviour was studied later in the following year by Catsiff, Offenbach and Tobolsky[137]. They found that at various temperatures, the change in stress was very gradual for both crystalline polymers. The transition between the rubbery and the glassy state is spread over a wider temperature range than from an amorphous polymer and throughout the region, the relaxation rate is slower. The simple time-temperature superposition which holds for amorphous polymers in the transition region, was found to be not valid for crystalline polymers. There is horizontal displacement along the logarithmic time axis due to changing crystallinity and orientation with temperature.

Watson et al.[78] from their stress relaxation stud of several commercial plastics, e.g. polystyrene, plasticised cellulose derivations, polyethylene and nylon, etc., in short range of 0.01 second to 2.5 secon after application of load, found that increasing strain temperature or plasticiser content generally increased the relaxation rate. During his stress relaxation studies on wet wool up to yield point extensions, Rigby[81] found that an increase in temperature from 10°C to 50°C reduced the amount of stress which decayed.

Forry[138] has given the temperature dependence of stress relaxation controlled by Brownian motion. For change of temperature T_o to T, there will be shift of relaxation curve by an amount log a_T. Tobolsky[14] in 1956 reviewed many aspects of chemical stress relaxation, stress relaxation in amorphous polymers, in crystalline polymers and certain natural polymers and polyelectrolytes. He found that the molecular structure and deformation mechanism in crystalline polymers is dependent on temperature. It has already been proved by Tobolsky and co-workers[46,129] that crystallinity and orientation tend to change with temperature, so a maste curve cannot be obtained to correlate static and dynamic functions. Price and others[18] could not get conclusive correlation of static and dynamic properties of single filaments of viscose rayon, acetate rayon, nylon and polyethylene even at low strains, but in this case the strains (2% to 4.5%) were probably too large for linearity of behaviour of filaments. Peters and Woods[109] found that at high temperature the relaxation curves for hair in water assumed the simple shape characteristic of a single rate process, this may be due to the fast relaxation being too rapid to be observed.

Clark, Preston and Shroff[124] while studying the effect of extension and temperature on stress relaxatio of wet viscose rayon, found that the ratio of stress after 90 minutes to original stress was increasing slightly with temperature, from 20°C to 55°C, and decreasing beyond that temperature range. They also found change in several other properties, e.g. a minimu swelling, a maximum breaking extension and a sudden dro in breaking load. They concluded that above 50°C ther is a rapid rise in the rate of dissociation of cellulos cellulose bonds.

Ferry and Landel[139] have explained the dependence of viscoelastic and dielectric relaxation processes, an also of molecular internal friction coefficients on temperature for polyisobutylene, polymethacrylate and polyvinylacetate.

In the case of crystalline polymers, the character of junctions and the chain mobility are certain functions of the degree of crystallinity. Takemuraa[140] obtained master curve from crystallinity relationship, of water non-absorbing polymers, e.g. polyethylene.

Matsumoto and Ishikawa[110] carried out stress relaxation experiments on nylon 6 at different elongations, several relative humidities and various temperatures e.g. 25°C, 40°C and 55°C at 55% r.h. They found that stress relaxation was much affected by humidity and temperature. Yoshitomi, Nagamatsu and Kosiyama[19] reported the stress relaxation in torsion of low crystallinity nylon 6 filaments at various temperatures from 20°C to 80°C, and humidities 0%, 45% and 75%, putting small enough torsional strain within Boltzmann's superposition test for the linear behaviour of the material. At 0% r.h. and 75% r.h. that data for different temperatures could be reduced to a respective master relaxation curve by a horizontal as well as a small vertical shift. The relaxation time spectrum calculated then, covered a wide time range and showed too weak but distinct maximum corresponding to the "wedge" and "box" type of relaxation spectrum of the amorphous polymers. The maximum on the shorter time scale was thought to be on vibration of the segments. Comparing the spectra of the amorphous polymers and nylon 6, on the log time scale, they suggested that there should exist in nylon, some sort of clusters, probably due to joining of the short chain molecules in the crystalline region, effective in its mechanical behaviour.

Kovacs[141] found that the isothermal volume contraction of amorphous polymers (e.g. Polystyrene, polyvinylacetate, polyacrylicpeperdide and polyacrylic-morpholide etc.) below transition temperature, is the function of time; as in stress relaxation. Illers and Jenckel[142] studied the mechanical relaxation phenomena in polytetra-fluoroethylene (Teflon) a crystallising polymer, between temperature ranges -150°C and +150°C, at varying degree of crystallinity.

Feughelman and Mitchel[143] in 1959, studied the stress relaxation and permanent set in keratin fibres at 10% and 40% extensions in water, at temperatures between 20°C and 100°C. At 100°C and 40% extension, the force after one hour (the remanent force) was mainly elastomeric and between 60°C and 70°C a second transition occurs for the stretched wool in water. Chemical treatments, which accelerate or retard the ability of the fibre to permanent set also reduce or increase the value of the remanent force in the fibre. Rigby[144] has given stress relaxation and transition temperature of wool. Independent of physical or chemical modification of wool, its stress decay in one hour is 33% and 73% of its initial stress below and abo transition temperature, respectively.

Faucher[145] made an attempt to apply the theory of reduced variables to the stress relaxation behaviour of the crystalline polymers polyethylene and polypropylene He concluded that the theory could be applied if suitab restrictions were made in temperature range and amount strain in the stress relaxation experiments. Curves a different temperatures could be superposed to give a single master curve, and the shift factor so obtained fell on a straight line in an Arrhenius plot. He was able to calculate the distributions of relaxation times for both polymers and were found to be very similar. I could compare the behaviour of two crystalline polymers with amorphous polypropylene whose behaviour is much lik polyisobutylene.

Tsujimoto and Motoji[128] have given stress-temperat behaviour of nylon 6 at various extensions. The tensil stress relaxes with rise in temperature and relaxation decreases with fall in temperature. Tsujimoto et al.[146] have studied viscoelastic behaviour of nylon 6 yarns during heating. Mechanical properties in the region of comparatively small strains at various temperatures can be represented by a dynamic model. They show abnormali at 60°C and 140°C-160°C.

Tobolsky and Murakami[147] found that the master stress relaxation curves of amorphous polymers, e.g. polystyrene, could only be resolved by approximation method into a continuous distribution of relaxation time They have described that this is obviously not entirely satisfactory in all cases, e.g. for Maxwellian stress decay or if the Rouse distribution for the rubbery flow region were truly applicable. They have proposed a new Procedure X, where, in favourable cases the master relaxation modulus in rubbery flow region can be resolve into a discrete distribution of relaxation times, inclu a well defined maximum relaxation time. This procedur was applied to monodisperse and polyisodisperse polysty the latter disperse of heterogeneity index 1.5. It appears that the Procedure X gives reasonably well defi values for at least the two highest relaxation times in those two cases. Later they further explained this through equations in their editorial letter.[148]

Takemura[149] has given theoretical consideration to the effect of crystallinity and draw ratio, to the visco elastic properties of polyethylene, which is much more complicated than the amorphous polymers. He thought that it is impossible to use Ferry's reduction method to obtain master stress relaxation curves of polyethylene (crystalline polymer), but considerations of crystallin and draw ratio could help in this direction.

Last year, Dunell, Joanes and Rye[20] have been abl to obtain master stress relaxation curves for nylon 66 monofilaments by superimposing the various stress relax curves between -100°C and $+ 10^{\circ}$C. Their results could be approximated by Ferry's reduced variable method, whic can be seen from his straight line plot of shift factor log a_T against reciprocal of absolute temperature. He was also able to correlate his stress relaxation results with his results obtained from forced longitudinal vibration studies.

Malinin[150] gave a general mathematical theory of stress relaxation and creep, for high polymers, as funct of time and temperature. Begen and Walstenholme[151] studi the effect of temperature, 25°C, 50°C, 70°C and 100°C, on long term properties of common plastics, e.g. acrylonitrile, butadiene and styrene polymers of varying monomer ratios. Analytical expressions are given for prediction of long term room temperature stress relaxation from short term high temperature ones. It was possible to convert stress-relaxation-data by any simpl treatment.

Very recently Fijino, Senshu and Kawai[152] studied the stress relaxation behaviour of methylmethyacrylate and methylacrylate copolmyers at various temperatures. They could obtain master stress relaxation curves very conveniently and the relationship between "shift factor a_T and temperature, agreed well with W.L.F. equation[63] within the temperature range of ± 50°K, about glass transition temperature, a distinctive temperature.

5. Stress relaxation and accessibility

In about the last ten years some of the workers have used stress relaxation as a tool of measuring accessibility of the textile fibres. They tried to investigate the effect of various reagents, e.g. reduci and oxidising agents, neutral salt solutions and alkali solutions, on the stress relaxation behaviour of fibres By studying the diversion from the usual relaxation behaviour, they have been able to find the accessibilit and also more confirmation about the structural behavio

In 1950 Katz and Tobolsky[57] while studying the stress relaxation of wool in water, studied such behaviour by replacing water with sodium bisulphite a reducing agent or with a neutral salt solution. They concluded that the stress which relaxes is partly supported by cross linkages like cystine linkages and salt linkages.

Mooney et al.[31] and Tobolsky and Co-workers[30] studied the effect of oxygen on stress relaxation and creep. Mark and Tobolsky[55] suggested that the accessibility of cellulose to various reagents can help us in determination of crystallinity percent.

Reese and Eyring[153] studied the effect of acids, bases, oxidising agents and reducing agents, on the stress relaxation behaviour of hair, under constant elongation, with a view of studying the amount of mechanical strength contributed by various bonds.

Kubu[123] in 1952 found that the early period of stress relaxation of wool, silk and nylon is controlled by hydrogen bond, but the latter period of relaxation i case of wool is controlled by the scission of disulphid crosslinks. He investigated this by using different reagents e.g. urea, hydrochloric acid, cysteine, thioglycolic acid and sodium bisulphite in the specimen already relaxing in water. Sodium bisulphite does not have any effect on relaxation behaviour of silk and nylon, but it gives drastic change in the relaxation behaviour of wool. This is presumably because of its action on the disulphide bonds. During the same year the author in collaboration with Montgomery[154] studied the stress relaxation to study the kinetics of the reaction of cysteine solutions with wool keratin.

In the following year Lasater, Nimer and Eyring[155] investigated the stress relaxation behaviour of cotton in mineral acids (e.g. HCl, HNO_3 and H_2SO_4) and alkali hydroxides of sodium, potassium and lithium. They fou that the stress relaxation of specimen already relaxing in water, was due to breakdown of secondary bonds (most probably hydrogen bonds), between the cellulose chains. They represented their results, in acids and alkalis up to two log. time cycles, by their mechanical model. There was no effect of temperature between 0°C and 60°C on the relaxation in the above reagents. Potassium hydroxide causes more relative rate of force reduction than sodium and lithium hydroxides, at particular molality or alkali concentration. Increase in alkali concentration increases breakage of bonds.

By comparing the results,[133] the same authors[155] noted that the relaxation constants obtained from subsequent curves were the same as those obtained from the initial force-relaxation curves (at constant elongati for single cotton fibres. This provides the basis for a method of measuring quantitatively the effect of chemicals on cotton fibres. Using this characteristic behaviour, a study of the reaction of the strong acids (HCl, HNO_3 and H_2SO_4) with fibre was conducted. These reactions are of interest, since it is well known that β -glucosidic linkages of cellulose are hyrdrolysed by even dilute acid solutions. They proposed that the relaxation element participating in the fast relaxation process is easily hydrolysable material. Acid has a more pronounced effect on slow relaxation constant than on the fast relaxation constant.

In 1954 Kubu, Frei and Montgomery[194] showed that dilute salt solutions of NaCl, KCl, NH_4Cl, KBr, KF, KI, LiCl, Na_2SO_4, $FeCl_3$ and $MgCl_2$, produce a varying rate of relaxation behaviour of wool in water. Specially FeCl showed much difference, probably due to its oxidising effect. When salt solutions were replaced by 0.1N HCl, there was further 20% more relaxation, hence the salt sensitive cross links are distinct from the acid sensitive ones. Similarly, by replacing salt solution by cysteine solution, more relaxation resulted, which shows that the salt sensitive linkages are different from cysteine sensitive ones. Thus it can be said tha the water sensitive linkages are hydrogen bonds, acid sensitive ones are salt bridges and the cysteine sensit ones seem to be distinct from all of these. The possible explanation is given that there exists hydroge bonded regions of higher order, which are accessible to the salt solutions, though not to water alone. Such regions would be characterised by high entropy change and would thus require a strong reagent to affect them, but they would be associated with a small energy and hence the reaction rate would not be affected much by temperature change. This behaviour of wool fibre accords this hypothesis, but they did not have any conclusive evidence for it.

Werner, Schefer[157] studied the stress relaxation of polyamide synthetic fibres at 10% constant elongatio in swelling agents like, benzene, water and alcohol, to study their chemical behaviour.

In 1955 Watson, Kennedy and Armstrong[78] during their investigations of stress relaxation of several common plastics, also found that the increase in plasticiser content generally increased the relaxation rate. During the same year, Lemiszka and Whitwell[158] found that there was no apparent change in stress relaxation rate of viscose rayon in water after 24 hours, when water was replaced by hydrogen bond breakin reagents like lithium and fluoride salt solutions. Thus, it was concluded that after 24 hours the relaxati rate is not controlled by secondary bonds or hydrogen bonds. That was why acid was attacking primary bonds, in which cellulose molecules react with acid, which can be interpreted in terms of accessibility. Nylon 66 with larger draw ratio showed smaller rate of relaxatio in water, and the absolute stress supported by the fibr is greater. At the diminished draw ratio, there was more drastic increase in the rate of relaxation, when water was replaced by HCl after 24 hours relaxation.

This effect of draw ratio on stress relaxation behavio was interpreted as due to difference in availability of primary and secondary linkages in the molecular network of the fibres. Drawing generally, results in a more ordered fibre structure, in which bonds become less accessible to the action of solvents and reagents.

Normally oriented specimens of various material including wool, silk, cellulose, rayon and many synthet fibres with hydrogen bonds, show similar stress relaxat behaviour in distilled water at normal temperature. A addition of acids to Dacron, Dynel, Teflon, Orlon and polyethylene (which do not contain hydrogen bonds), und going stress relaxation in water, did not show any effe on the relaxation rate. Thus Lemiszka suggested that the relaxation of stress in water is caused by scission of weaker secondary linkages, peculiar and common to all the materials investigated.

Jass and Fosdick[159] have shown that there is influence of electrode potential, by reducing agents, on the reduction of cysteine in hair fibres. The available reducibility is not due to the screening of the cysteine bonds by hydrogen bonds or salt bonds, because the equilibrium stress levels are apparently independent of pH or ionic strength. The correlation of stress reduction with cysteine reduction makes it quite evident that the stress in hair fibre is due solely to cystine linkages.

Steele and Giddings[160] in 1956, correlated the stress relaxation of fabric, treated with hydroxymethyl and bishydroxymethyl ureas, with the molecular structur of the fibre.

In the subsequent year, Valentine[161] used stress relaxation method of determining the accessibility of fibres to HCl. This method ranks cellulose in the same order of accessibility as other methods, but due t uncertainties of interpretation of results it makes it doubtful value without confirmation.

Tokita and Kanamaru[162] in 1958 found that the strongly polar polymers like viscose rayon and cellulos acetate, both can be crosslinked to various extents, with tetra-methylene-bis-ethylene urea (TBU) and tetra-methylene-dis-isocyanate urea (TDU). They were able t measure apparent activation energy for relaxation in relation to the degree of cross linking.

CHAPTER III

EXPERIMENTAL METHODS:

1. Introduction

The fact, that even very little work on the stress relaxation study of the textile fibres and filaments have contributed much towards the studies of the fibre structure, has inspired many enthusiasts to use different types of device for its accurate study. They all have considered certain factors of much importa in the normal stress relaxation study. Meredith[17] and Armstrong[78] have recognised the desirability of obtaining stress relaxation measurements at very short times after stretching. They have described apparatus for obtaining such measurements. During the complete tests it should not be forgotton that the extension should remain constant throughout the stress relaxation investigations, so a device should be provided to achiev that. The proper study of stress relaxation takes a lo of time, so some workers have used apparatus in which more than one specimen can be studied at a time.

Speakman[21] used a helical spring as a device for measuring the stress relaxation in the wool fibre. Later on in 1931 Smith[163] modified the Polanyi tester for the stress relaxation study of viscose rayon.[22] He fixed a specimen on one end of a beam balance and a dead weight float on the other. This float was controlled fo its weight by the level of liquid in a container. Thus he could put small strains in a specimen by removing some liquid and the constant length of the specimen was maintained by putting in some liquid according to requirements to compensate for the stress decay.

Steinberger[23] used a lever device for study of stress-strain measurements and he suggested that this apparatus can also be used for stress relaxation study. He measured stress by an optical method by using telescope and scale. Dead weight dropping method as stretching device was used by Treloar[164] in 1940. He used a flat spring method for tension measurement. Wegener[52] also used a similar device.

Sookne and Rutherford[165] indicated a balance system where the stretching speed is controlled by photo electric current. Later on, Gross[69] also used a beam balance system for tension measurement in stress relaxation study. Ninomiya, Kishimoto and Fujita[166] have described an autographic beam balance relaxometer for stress relaxation study in textile fibres. Tobolsky, Prettyman and Dillon[30] used a similar method of tension measurement, but with a screw type of stretching mechanism which can be operated manually or driven by motor. A similar method of stretching was used by Lasater, Nimar and Eyring.[133]

In 1947 Burleigh and Wakeham[41] used a bonded wire resistance strain gauge for tension measurement in their stress relaxation study of cellulosic fibres and filaments. A wire resistance strain gauge was also used by Thorsen[167] in his multi-unit instrument for stress decay measurement in single fibres. In his instrument the forces were automatically recorded with precision and accuracy. This instrument is stable over long periods.

Armstrong and his co-workers [78] also used an electronic strain gauge for measurement of tension, but spring expansion method was used for stretching. Price et al.[18] in 1956 modified the apparatus of Armstrong to obtain a reliable stress relaxation measurement at 0.02 sec. after stretching of the fibre. Chatten, Scoville and Conant [92] utilised a load cell incorporating a strain gauge for measuring the stress in an elastomeric specimen held under constant elongation or at constant compression. Stein and Schaevitz [168] devised an autographic stress relaxometer, utilising a linear variable differential transformer.

Wood and Chamberlain [169] used a spring expansion method of stretching, but a condenser device was used for tension measurement. They were able to take a continuous record of tension in wool during its very early relaxation. Osawa,[170] used an electric relay as tension measuring device.

In 1960 Begen and Walstenholme [151] developed a flexural stress relaxometer that records the stress loadings and stress decay for studying the effect of temperature and other variables on the longterm properties of common plastics.

From this short literature survey, it is clear that the main devices for stretching have been used until now are:- dead weight dropping method, which gives trouble in getting correct extension due to creeping of the specimen. Hand pulling method can give fairly rapid but uncertain extension. Screw device of stretching can give fairly constant rate but slow rate of extension. The spring expansion method has maximum advantages over others for providing very rapid stretching for study of early stress relaxation behaviour although it suffers from the disadvantage of a variable rate of extension.

Meredith[17] in 1954 constructed a stress relaxometer in which he used a helical spring contraction device for obtaining rapid extensions. He studied stres decay in cellulosic fibres and filaments at constant extensions, by an optical lever arrangement. He was able to extend the specimen within 0.01 sec., and could recor photographically the first reading at less than 0.05 sec after the start of extension. Hsu[107] modified Meredith's apparatus by introducing a dash-pot containing liquid, in parallel with the helical spring. Thus he increased the period of stretching from 0.01 sec. to 0.02 to 0.10 sec. depending upon the extension imposed, but he could get an improved record of readings due to less vibration in the tension measuring system.

Considering all the advantages and disadvantages of Hsu's modification in Meredith's stress relaxometer, it was decided to adopt the same modified apparatus for some of the investigations in the present work, where th early period study of stress relaxation carries some importance. With some changes in the technique, it was possible to obtain a continuous record of tension decay readings at 0.01 to 0.02 sec. onwards, irrespective of the extent of the extension. This type of stress relaxometer in which one studies the stress relaxation behaviour of one specimen at a time can be called a single unit stress relaxometer. In these investigations the main interest was the comparison of the behaviour of a number of different types of fibre under the same conditions. To achieve this end it was decided to build up a six unit stress relaxometer, which has the similar optical lever device for tension measurement as in the single unit relaxometer and a screw type of stretching arrangement. This instrument is based on Meredith's[71] apparatus used for rate of extension measurements.

(2) Description of apparatus

(A) Single unit stress relaxometer

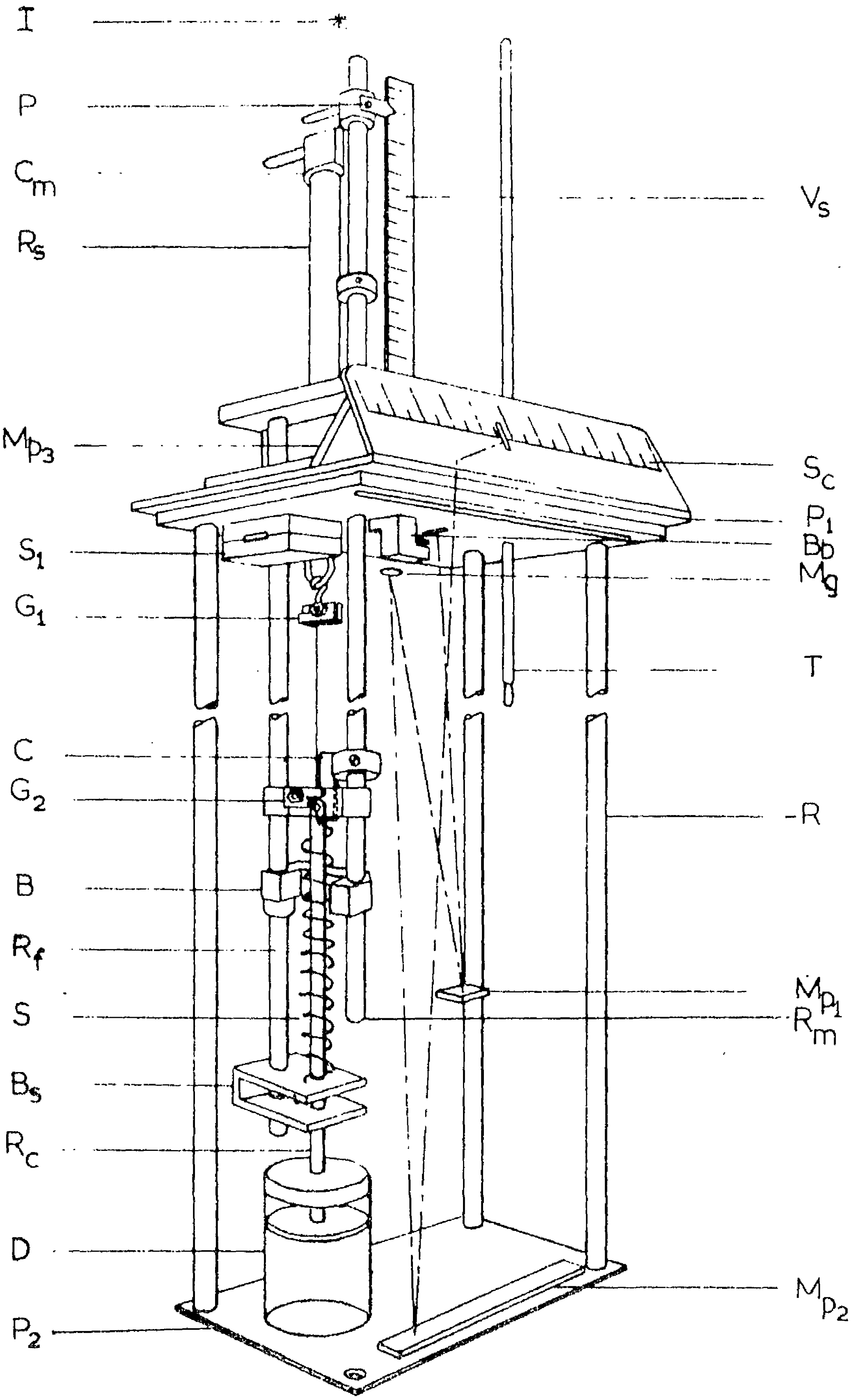
(i) General

The general arrangement of the essential parts of the apparatus is shown in Fig. 1. They are all mounted on a rigid framework, consisting of four brass rods (R) 17" long and diameter ¼", with two end plates (P_1, P_2). This whole framework can be accommodated in a copper tank 18" x 5½" x 3¼". The top plate (P_1) forms a good fit with the opening of the copper tank.

(ii) Stretching mechanism

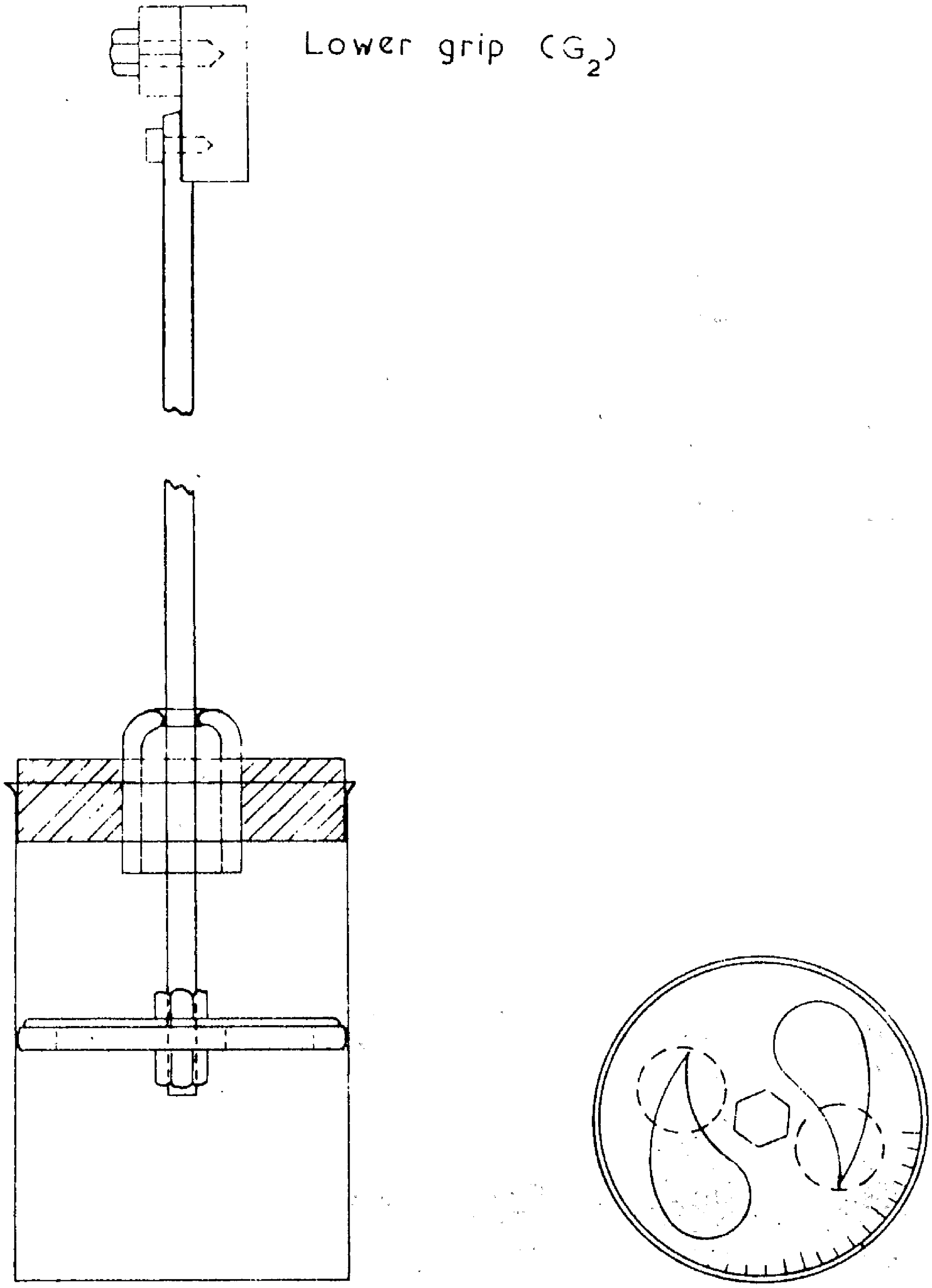
Two grips (G_1, G_2) made of Duralumin are provide the lower grip (G_2) being very light, gives rapid acceleration during extension. The specimen is held between

Fig 1



Single unit stress relaxometer

Fig 2



Dashpot

Piston

Fig 3

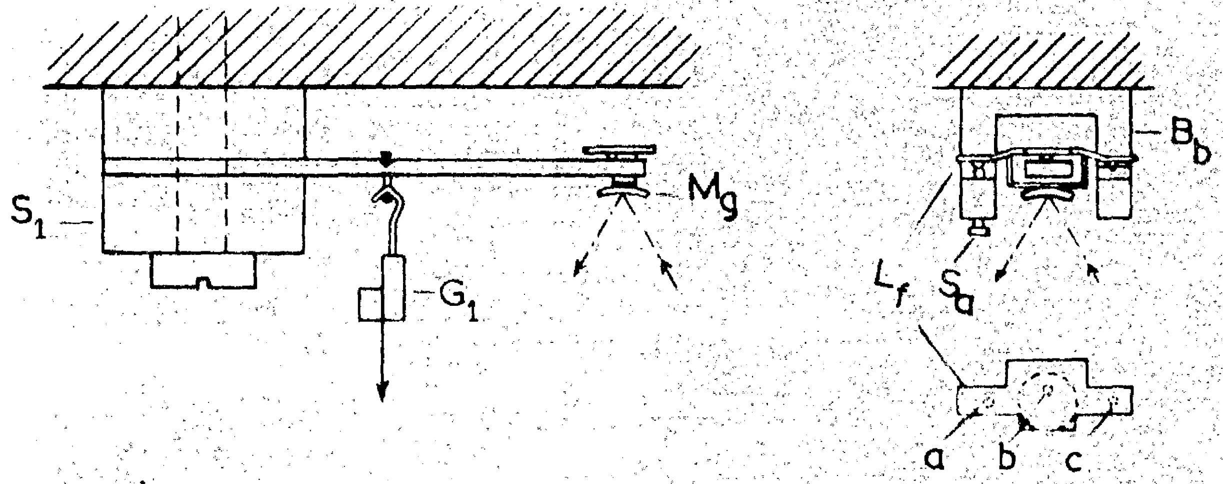
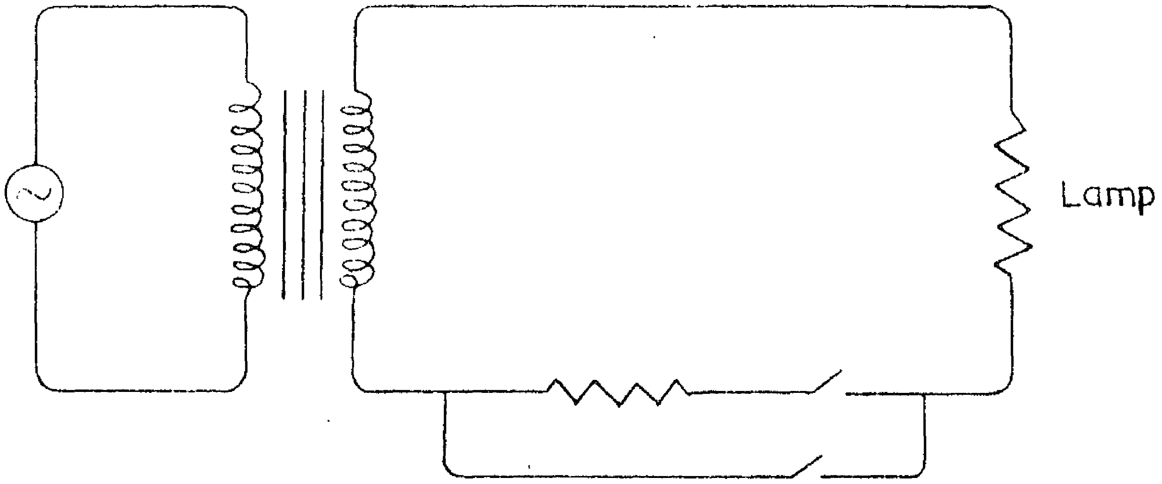


Fig 4



Circuit diagram of light source

them at some fixed distance (here 20 cm.). Because of the slipperiness of synthetic fibres, the two inside surfaces of the grips are lined with paper or thin adhesive plaster to provide a firm grip without unduly damaging the fibres, especially at large extensions of 10%. The fibres become embedded in the lining, and cannot slip past one another. The lower grip (G_2) slide on two brass rods, one (R_f) being fixed to the frame and another (R_m) capable of being moved up or down and carrying a release catch (C) which holds the lower grip against the pull of the helical spring (S), until the start of the experiment. Rotation of this rod (R_m) releases the catch. A brass block (B) clamped to the fixed brass rod (R_f) and capable of sliding on it and the free ended rod (R_m). On this block (B) the lower grip (G_2) stops when the required extension has been reached. Its position can be adjusted to give a predetermined amount of extension. The upper grip (G_1) is hooked into a stirrup on the tension measuring head.

The distance between grips at their initial position determines the test length of the specimen. The upper grip is fixed in position, but the initial positio of the lower grip can be adjusted, if necessary, by changing the position of the release catch (C) along the brass rod (R_m). Throughout the present work, the initia distance between grips is maintained at 20 cm.

The helical spring (S) extends the specimen rapidly and holds the lower grip (G_2) against the stop (B) for the duration of an experiment. One end of the spring is hooked on to a small screw on the lower grip, and the other end attached to a brass support (B_s) which is in turn clamped to the fixed brass rod (R_f). The position of this support can be adjusted along the brass rod, thus giving the required amount of initial spring extension. Two springs of constants, 230 and 510 gm.-wt/cm. are kept available to cover the range of tensions required.

The dash-pot (D) is connected to the lower grip (G_2) by means of a connecting rod (R_c) passing through the helical spring (S) screwed to the lower grip, the other end of the connecting rod being attached to a bras piston immersed in some liquid medium (here water) containedgin a glass cylinder 2" long and 1.1" in diameter. The piston thus moves at the same pace as the lower grip The top of the connecting rod where it touches the lower grip is made semi-cylindrical in shape with the flat sid inward, so as to ensure a smooth transmission of force from the grip to the piston. The piston (3 cm. in diameter) actually consists of two discs tightened together by nuts (Fig. 2). The bottom thick disc having two diametrically opposite holes of 0.8 cm. diameter, is usually fixed to a connecting rod, while the top thinner disc, which has two curved holes as shown in Fig. 2 can be rotated in relation to the bottom one, as desirable, then fixed in place. By this arrangement the effective area of the holes through which the liquid medium flows, can be easily adjusted. In other words, the dash-pot constant can be easily altered over a fairly wide range without changing the medium. In the present investigations water was quite a satisfactory medium. A reference mark is engraved on the edge of the bottom disc and the top disc is marked with a circular scale. The dash-pot constant is noted nominally in terms of the number on the scale opposite the reference mark.

The glass cylinder of the dash-pot is covered with a rubber stopper having a collar at the centre (Fig. 2). The glass collar is made up of such a shape that its top inside diameter is about the same size as that of the connecting rod (R_c), but the remaining part is considerably larger. The collar together with the rubber stopper serves two purposes; to keep the frictior to the movement of the connecting rod as small as possible and to prevent the liquid from splashing out at the rapid downwards movement of the piston, while providing an escape for the air at sudden change of air pressure inside the cylinder. The piston movement is limited to just over 3 cm. For the present work, in the case of dry viscose rayon experiments, the extension of maximum 10% is put so that when the specimen length is 20 cm. the piston movement for it will be 2 cm. only. The abov limit, of maximum extension, is taken because at higher extensions, due to sudden extension, some of the filaments of viscose rayon break.

(iii) Tension measuring mechanism

The optical lever system enables the tension to be measured accurately while maintaining the length of the specimen constant during the test period. The constant length is maintained due to very small movement of the tension measuring head.

A cast spring steel strip 0.63 cm. wide is clamped between two steel blocks (S_1) screwed to the frame (see Fig. 3) so that it forms a cantilever with a free length of 4.1 cm. Different thicknesses of such strips could be used for wide range of stress with reasonable sensitivity. A concave surface-aluminised galvanometer mirror (radius of curvature about 65 cm.), is attached t a light frame (L_f) carrying small polished steel balls arranged in the form of an isosceles triangle (abc) (see Fig. 3). One of the two balls at the base of the triangle rests in a V-groove, cut in a brass block (B_b) attached to the frame of the instrument, while the other rests in a conical hole in the end of an adjusting screw (S_a), passing through the brass block (B_b). The third ball "b" rests on the polished top surface near the end of the cantilever. Bending of the cantilever causes the ball "b" and therefore the galvanometer mirror, to rotate about an axis passing through the two steel balls (a, c) at the base of the isosceles triangle. The adjusting screw (S_a) permits the adjustment of the equilibriu position of the galvanometer mirror, which in turn determines the zero reading. The distance from the apex to the base of the triangle is 0.174 cm. and the optical path from the galvanometer mirror to the transluscent scale (S_c) is 87 cm. For a deflection of 10 cm. on the scale, the angular displacement of the reflected light from the galvanometer mirror is $^{10}/87$. Since the incident light to the galvanometer mirror is fixed, the corresponding angular displacement of the mirror is $\frac{1}{2} \cdot \frac{10}{87}$. Hence the movement of the cantilever where it touches the steel ball "b" is

$$\frac{10 \times 0.174}{2 \times 87} = 0.010 \text{ cm.}$$

The stirrup which carries the upper grip (G_1) has a knife edge bearing in a shallow V-groove on the cantilever at a distance of 1 cm. from the clamping blocks (S_1). The distance from the steel ball "b" to the clamping blocks is 3.4 cm. Consequently, the movement of the end of the specimen for a full scale deflection o 10 cm. is only 0.01 (1.0) / 3.4 = 0.0029cm (a magnificatio of 3400 X), and this is negligible when compared with th test length of 20 cm.

The source of light from the optical system is a 36-watt head lamp car bulb (I) (with filament parallel t the slit), of 12 volts situated at top of plate (P_1). A lens in the top plate of the frame focuses this source via a surface-aluminised plane mirror (Mp_1) on to the galvarometer mirror (M_g). An image of a slit placed immediately beneath the lens, is focused by the galvanometer mirror via the surface-aluminised plane mirror (Mp_2) and the mirror (Mp_3) on the transluscent scale (S_c The plane mirror (Mp_1) is fixed on a brass plate which i clamped to the brass rod of the framework. Its position on the brass rod can be adjusted to allow focusing of a sharp image of the slit, on the scale. All mirrors are attached to the supports by Durofix cement, which gives a satisfactory adhesion not affected by temperature.

Part of the light, forming an image of the brigh filament in the form of a slit, passes through the Perspex support for the transluscent scale (S_c) and on to a sheet of fast bromide recording paper (Kodak RP 30) wound inside a drum camera placed with its slit aperture parallel and opposite to the scale (S_c). The drum insid the camera is driven through a spur and worm wheel by a synchronous motor at 1.00 rev./sec., and enables the decay of tension during the first two seconds or so to be recorded. The lamp is switched on for the minimum possible time according to the requirements of readings; if left on continuously, the heat from it is sufficient to raise the temperature of the apparatus. To get a clear record on the photographic paper, the lamp during recording is controlled by a push button switch (operate by the foot), which overruns the light source by increasing the voltage from 12 to 15. This is achieved (as shown in Fig. 4) through a transformer.

For the present investigations, A, B, C and D cantilevers with conversion factors 42, 52, 112 and 150 g/cm. deflection of light on the scale covered the various tension ranges of all samples at the required conditions of humidity, temperature and extension. Depending upon the initial tension developed in the specime for a particular fibre extension, the appropriate cantilever is chosen and fixed in the apparatus. The calibration is effected by hanging slender weights at the ends of an iron rod, which is, in turn suspended at its middl from the stirrup and then observing the corresponding deflection on the scale (S_c). The relation between the load and deflection is linear with a conversion factor as mentioned above. Since the recording bromide paper i farther than the scale from the galvanometer mirror by about 1.12 times, the conversion factor for the deflections recorded on it are

$$\frac{42}{1.12}, \frac{52}{1.12}, \frac{112}{1.12} \text{ and } \frac{150}{1.12} \quad \text{g/cm.,}$$

depending on the cantilever in use.

Because of some static friction between the stee balls and their resting surfaces, the observed load usually tends to lag behind the actual load by about 0.03 cm. on the scale. To eliminate this extremely small friction, a small buzzer, which vibrates at 180 cycles per second and draws power from an accumulator of 2 volts, is attached to the top frame. During any observation of the load it is switched on to overcome the small static friction.

(iv) Mechanism for adjustment of specimen during test

After mounting the specimen, the frame-work is placed inside a copper tank for the purpose of obtaining constant temperature and humidity conditions. Some mechanism capable of controlling the specimen from outside is, therefore, necessary in carrying out the experiment.

The cam (C_m) on a supporting rod (R_s) serves to prevent the brass rod (R_m) and therefore, lower grip, from dropping. Rotation of the cam allows the brass rod (R_m) and the catch (C) to be lowered to pick up the lowe grip at the end of the run, so that a second test can be made on the same specimen, without removing the whole framework.

The rod (R_s) is screwed into the top plates of the frame by this means the cam which it carries, can be lowered or lifted over a maximum distance of 0.5 cm. By this method the initial longitudinal position of the brass rod (R_m) can be precisely altered, thus facilitating the fine adjustment from outside of the initial height of lower grip (G_2) during an experiment.

A vertical scale (V_s) mounted on the top plate of the frame and a pointer (P) on the brass rod (R_m)

allow the amount of temporary or permanent set to be measured, by observing how much the rod (R_m) has to be lowered to develop an arbitrary small tension in the specimen.

(v) Temperature and humidity control

During an experiment the main framework shown i Fig. 1 rests inside a copper tank such that the top end plate (P_1) becomes the cover of the tank. A rubber gasket around the edge of the plate (P_1) provides an effective seal, when the plate is firmly clamped. The tank is held inside a water thermostat, on a piece of thick sponge rubber, which absorbs any vibrations from the bench. Temperature is maintained constant at 25°C ± 0.1°C by a mercury-toluene regulator and 200 watt immersion heater via a mercury-toluene valve relay. The humidity inside the copper tank is controlled at 65% r.h by circulating the air from a small air circulating pump through three Dreschel bottles placed in the thermostat, then through the copper tank and back to the pump. The first bottle contains air and serves to bring the circulating air to the temperature of the thermostat, second bottle (with sintered glass air bubbler) contains about 100 c.c. of a saturated salt solution of sodium nitrite to give 65% r.h. at 25°C. A piece of glass fabric is fixed on the inside of the bottle, dipping into the salt solution, thus the surface area of the salt solution is increased much, due to its capillary rise in the fabric. The third bottle contains cotton wool to act as a filter for any spray carried over from the conditioning solutio The saturated salt solution is prepared by dissolving sodium nitrite crystals in water at 35°C to an excessive amount and is then allowed to cool to 25°C. A dial hair hygrometer is connected at the outlet of th copper tank to measure the relative humidity. This hygrometer measures relative humidity as 66% for 65% at 25°C because it is calibrated at 20°C. The hair hygrometer is actually capable of measuring relative humidity from 0% to 100%. For the experiments at dry conditions the above system of air circulation is replaced by one containing drying agents. Air is pumped through a tube containing phosphorus pentoxide and via three empty Dreschel bottles in the thermostat into the copper tank of the apparatus. From the tank the same air passes through the same hair hygrometer, through the tube of phosphorus pentoxide before returnin to the electric pump. Immediately before and after eac tube of phosphorus pentoxide, glass wool filters prevent the powder from being carried over. The Dreschel bottles in the thermostat have the function of bringing the circulating air to the temperature of the thermostat before entering the tank. The first Dreschel bottle may be used as a filter with glass wool filling. To prevent vapour from diffusing into the system it is necessary to seal every junction with high vacuum wax. Those parts which cannot be permanently sealed have to be covered with silicone grease.

Inside temperature near the specimen can be measured by inserting from the top a thermometer (T) whose bulb is situated near the middle of the specimen. A 50°C thermometer with 0.1°C divisions is used. Owing to the heat loss through the top of the tank, the temperature inside the tank is lower than that of the thermostat. This difference is negligible at the temperature 25°C in the present investigation because the room temperature was maintained just over 20°C.

(vi) Device for mounting the specimen at dry condition

An air-tight wooden box 9" x 9" x 22" was made for this purpose. This box is thickly painted with white rubber paint for perfect seal. Front has a thin Perspex sheet (12" x 6") through which inside of the box can be seen. The frame-work of the relaxometer can be inserted from the top opening 2½" x 4". The upper plate (P_1) makes a perfect seal with the surface of the box; it is also clamped for its stability. A very small hole (which is generally corked) of a size so that a screw driver can just pass through is made in the Perspex. This box has inlets from the top for a thermometer, toluene regulator and heater. The arrangement for air circulation by small pump is provided such that the air enters from the top, reaches the bott through a narrow glass tubing up to the phosphorus pentoxide kept in the bottom of this box, in the Petri dishes. The outlet for air is also from the top. Thu at the required temperature of 25°C, viscose rayon coul be conditioned at 0% r.h. (Dial hair hygrometer capable of reading 0% relative humidity is connected at outlet) and clamped at the lower grip. This device was introduced to avoid the inaccuracy that is possible due to the difference in the length of specimen at room humidity and temperature and the test conditions.

(B) Six unit stress relaxometer

(i) General

In this apparatus stress relaxation behaviour of six specimens can be studied at a time. The Fig. 5 shows a diametral section of the main part of the instrument with the rigid frame-work omitted for clarit Actually it consists of a heavy rigid mild steel framework structure of three solid rods (R) each 22" long an $\frac{5}{8}$" in diameter. Each rod (R) is fixed at the bottom with the three corners of the heavy platform (H_p). Th overall length of the instrument is 25" including three bottom levelling screws (L_s). The maximum triangular distance of the plates is 8" and that between levelling screws (L_s) is about 12" (to ensure stability of the instrument). The following short description of the apparatus should be read after having a complete pictur of the single unit apparatus.

(ii) Stretching mechanism

For the experiments to be carried out on this apparatus, the main object was to get many reliable stress relaxation observations from 10 seconds after the start of stretching. For the study of the earlier part of stress relaxation, the single unit apparatus was used, wherever required. Thus to avoid the complications of stretching device, a screw type of arrangement, with hand driving mechanism, was used.

Fig. 5

Front view

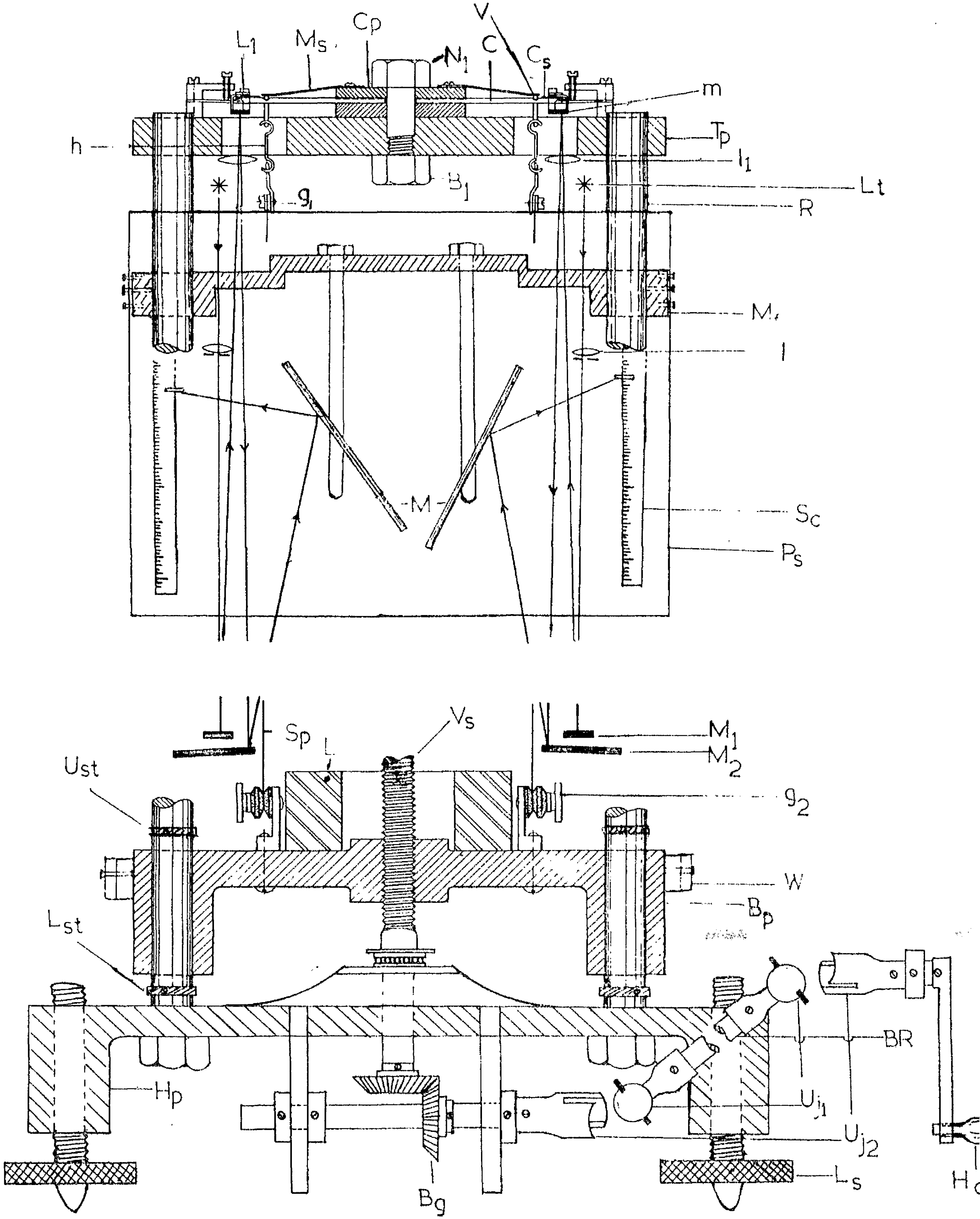
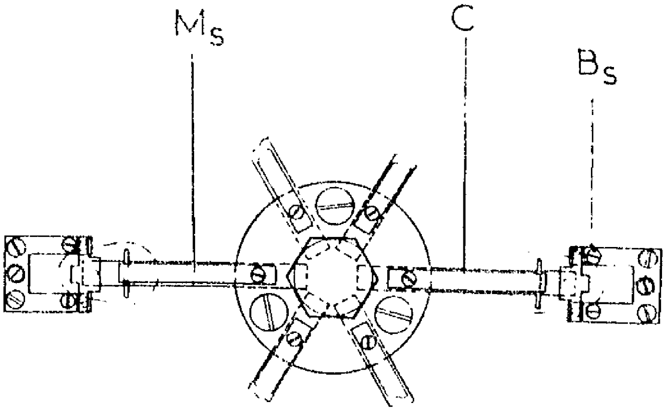
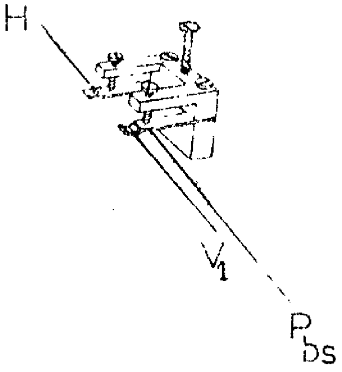


Fig. 6

Plan View

Six unit stress relaxometer





Light brass frame

The specimen (S_p) is held between upper and lower grips (g_1 and g_2). They are made of brass, with fibre washers, for avoiding slippage and/or damage of the filamentous material. The upper grip (g_1) is hung via about 2" long steel hook (h) on to the stirrup in the tension measuring cantilever system. Lower grip (g_2) is fixed, exactly below the upper grip, on the bottom plate (B_p) which in turn can slide up or down on the rods (R). On this plate is kept a heavy cylindrical lead block (L) to increase acceleration during stretching. The acceleration is also improved by fixing 500 gm. weights (W) on each sliding corner of (B_p). Through the exact centre of this plate (B_p) and (H_p) passes a vertical screw (V_s) about 8" long and ½" in diameter, which is connected through bevel gears (B_g) below (H_p), to the horizontal hand driving mechanisms of either a simple long shafted handle or to the universal joint device. Thus by turning the handle, we can transfer that effect at right angles, for driving the screw, which in turn moves the bottom plate (B_p) along with the six lower grips (g_2). With the help of the adjustable upper and lower stops (U_{st}) and (L_{st}), which slide or fix on the rods (R), the preadjusted exact extension can be put in the specimen. The required distance to be moved for any extension is fixed with the help of a cathetometer using telescopic lens. The distance between two grips (g_1 and g_2) can be increased or decreased by either moving the bottom plate (B_p) or by varying the length of the hook (h).

Throughout the present investigations on this apparatus, the test-length of the specimen was maintained at 40 cm. and the magnitude of strain did not exceed 4% (1.6 cm.), although this apparatus can be used for much higher extensions.

The ordinary driving arrangement consists of a smooth steel rod about 8" long and $\frac{1}{4}$" in diameter, provided with the arrangement of handle. This rod ha a temporary device of connection with the gearing system (B_g).

The universal joint driving mechanism consists of two pairs of steel joints (U_{ji} and U_{j2}). U_{ji} screwed on to the two ends of an 18" long $\frac{1}{4}$" diameter brass rod (BR) whereas U_{j2} are screwed on to the gearing device (B_g) and on to the driving handle devic (H_a). This arrangement for stretching was needed when the Gallenkamp humidity oven (No. 7900) was used for th control of humidity and temperature.

(iii) Tension measuring mechanism

The optical lever tension measuring mechanism in the six unit apparatus, with slight variations, is similar in principle as used in the single unit apparatus. While describing this mechanism, only one of the six specimens is given, which represents the other five also.

The cantilever strip (C) is made of cast spring steel 0.63 cm. wide and 5.1 cm. long. Different thicknesses of such strips were used to cover the different specimen strengths at different extensions. The cantilever is fixed between two circular plates (C_p), on the centre of the top plate (T_p) with the nut and the bol (N_1 and B_1) at the proper grooved place. The V-groove (V at a distance of 3.9 cm. from the fixed end is made for housing the fine blade edge of the stirrup which carries the upper grip (g_1). A thin brass strip (M_s) fixed on the plates (C_p) serves to protect the stirrup carrying the upper grip (g_1) from slipping out of the V-groove (V) due to some external disturbances. The distance between the V groove (V) and the free end is 1.1 cm.

A small plane mirror (m) about 1 cm. square is used instead of a small galvanometer mirror in the single unit relaxometer (described previously). A small light brass frame carrying this small plane mirror (m) also has three small polished steel balls (a,b,c), which form an isoscel triangle, (see Fig.3). The central ball rests on the free end of the cantilever (C) on the small piece of cover sli (C_s), which minimises the frictional effects, for the fre rotation of the ball. On the roof of this light brass frame is stuck with Durofix, a small weight of lead (L_1) which promotes the stabilisation to the frame from any jerks. The distance between the central ball and the V-groove (V) is 1.0 cm. The extreme balls are seated, one o the V-groove made by two very thin needle size glass rods, which are fixed with Durofix on the free end of a flexibl thin phosphor-bronze strip (P_{bs}) (about 0.3 cm. wide and 2.5 cm. long). A similar strip carries another steel ball on the groove (see Fig. 6) made by three glass hemispheres (H). These strips (P_{bs}) being fixed at one end by a small solid frame, can be moved up or down with the help of brass screws (B_s) about 2.5 cm. long. These screws hel in arranging the initial angle of the plane mirror (m) fo obtaining initial zero reading of the slit image on the transluscent scale (S_c). These screws are made longer for convenience of operating them by hand.

Source of light consists of a transformer giving 12 volts and an arrangement for increasing voltage to 15 volts, and a 6-watt car bulb (L_t) with a focussing lens (l) and slit arrangement in the sliding brass tubes (not shown in fig.) The narrow slit of light thus focused falls on a plane mirror (M_1) 1 x 2.5 cm., gets reflected back to the small plane mirror (m) 1 x 1 cm. through a lens (l_1) situated in front of it. From mirror (m) the slit of light traces back its way to plane mirror (M_2) 1 x 4 cm., reflects to the mirror (M) 1 x 7.5 cm. and thus we get a very thin slit image of light on the transluscent scale (S_c) fixed on to the transparent cylindrical Perspex screen (P_s), about 15 cm. high and 25 cm. in diameter. All the scales are numbered for identification. This Perspex screen (P_s) is fixed outside the small middle frame (M_f), thus it can be fixed at any height by sliding and fixing (M_f). This Perspex screen is very close to the outside surface of the three rods (R). Six vertical transluscent scales (S_c) 2 x 12 cm. can be conveniently fixed on the perspex at convenient positions. The image of the slit is managed to be obtained in horizontal way for convenience and accuracy in reading. All the plane mirrors are carefully surface-aluminised to avoid double images and are fixed by Durofix to their proper positions. Durofix can stand high temperatures. They have arrangements of ball and socket to provide the facility for obtaining three degrees of translation. The mirrors (M) are fixed on the small rods, which are fixed in the central part of the middle small plate (M_2). Mirrors (M_1 and M_2) are situated on a steel ring which can slide or fix (with screws) on the three rods (R). In the Gallenkamp humidity oven, due to only one glass opening, just two scales could be seen. Thus the reflected images of the two side scale were seen in 4" x 3" plane mirrors and the two scales on the other side of the apparatus were seen, enlarged, in the two 6" diameter concave mirrors.

When the tension develops in the specimen, the cantilever (C) bends and the mirror (m) gets tilted so that the narrow slit of light moves vertically upwards on the transluscent scale (S_c), on the Perspex screen (P_s). Since the distance from the steel ball at the apex of the isosceles triangle to the base is only about 0.15 cm., a small displacement of the end of the cantilever produces a relatively large rotation of the plane mirror (m). Thus the resulting linear magnification is about 1330X. This means that for the full scale deflection of about 5 cm. used in the present experiments, the upper grip (g_1) moves by less than $\frac{1}{25}$ mm. (0.004 cm.) This movement of the upper grip produces absolutely negligible change in length of the specimen, when it is 40 cm.

The cantilever from range 49 to 108 g/cm. deflection were used according to the initial tensio developed in the specimen (from the stress strain st on Instron M/C, (Figs. 9 and 10). Calibration of cantilevers is necessary after every disturbance of the cantilever or optical system. The calibration is carried out in a similar way as in single unit relaxometer (see Page 62). The load-light slit deflection behaviour is linear.

(iv) Mechanism for change in magnitude of strain during test.

During the change in magnitude of strain, three smooth ebonite blocks were made to the slide fit in the three rods (R). They were tied with a strong thick nylon yarn and the other end of the yar taken out of the conditioning chamber through a fine hole. The height of the three blocks was same according to the later extension requirements. In the present experiments the blocks were made 0.8 cm. in height. The arrangement was made in such a way that after 2% extension of the specimen, the stretchi system stops with these temporary stops of ebonite blocks, and they could be pulled from their position by outside nylon leads when 2% more extension is to be introduced.

(v) Temperature and humidity control

There are two devices used for controlling th temperature and humidity during the investigations of the present work on the six unit stress relaxometer:- a Perspex box arrangement and a Gallenkamp humidity oven.

The Perspex box arrangement for temperature and humidity control was built up in the laboratory for the experiments, where the humidities could be controlled, at constant temperature 25°C, with the help of saturated salt solutions. This is a long cubical box 12" x 12" x 30" made from four Perspex walls. The top and the botto lids, made of aluminium sheet, could give quite a good seal and could be removed when needed. For the effectiv seal, black Plasterseine is also packed at the joints of the lids. The bottom aluminium lid is screwed down to a wider (15" x 15" x 1") wooden platform for the proper stability requirements. Through this base the connectio are introduced for the lamp heaters which are again connected through outside to the mercury-toluene regulat fixed in from the top lid. Arrangement for connections for the six head-lamps of the main apparatus is also mad A transformer provides 12 volts and 16 volts for the head bulbs. In the top lid, two small holes are made to fit in the mercury-toluene regulator for temperature control and a long stemmed dial hair hygrometer already calibrated for the conditions to be used. Three thermometers are fixed on each rod (R) of the main apparatus itself for the proper check on the temperature control. Above arrangements are made in such a way that the main relaxometer can be placed in the approximate middle of the bottom lid.

For the air circulation, two holes in the diagonal position of the cubical box are made and air flows from lower hole to the upper hole in the box. According to the proper position of the main apparatus, a small hole in the box is made for introduction of the shaft of the ordinary driving mechanism through a Perspex bearing. This gives no leakage during air circulation.

For circulating air of the required conditions, a water bath thermostatic control arrangement is made with a toluene regulator, immersion heater, thermometer and an efficient stirrer, as in the case with the single unit apparatus. In this case due to about 70 litre capacity of the Perspex box, and quick humidity change requirements, a special type of device is made and a higher capacity pump is used. The special type of device is a thick wooden box with a long shaft passing through the three independently sealed compartments. Each compartment is provided with a dish containing different saturated salt solutions of magnesium chloride sodium nitrite and potassium nitrate to obtain relative humidities of 33%, 65% and 92%, but in experiments 35%, 65% and 90% were obtained due to slow air circulation, at 25°C. The shaft carried a wooden pulley in each compartment which carried a thick cotton strip (both ends stitched together). This cotton strip dipped well into the saturated salt solution and revolved due to the revolution of the wooden pulley which was driven by a slow driving motor through a gear and chain arrangement.

The shaft has an air-tight bearing arrangement at each compartment wall. Each compartment has two face to face holes in the middle of the outside walls through which the air is circulated by a pump, which enters this box from a large bottle kept in the thermostat at 20°C. The wide wooden box is well lagged with thick woollen flannel so that the temperature inside remains 25°C due to air circulation through the bottle in thermostat. The oil vapours coming from the rotary pump are trapped in a bottle containing glass wool. This device gave quite good control of humidity in the large Perspex box. The relative humidities of 35%, 65% and 90% with variation of ± 1% could be obtained for the experimental purposes. The rubber or glass tubings in the air circulating system were provided with wide internal diameters of about ½" to minimise an resistance to the air flow.

The Gallenkamp humidity oven is needed when a constant relative humidity of 65% is required at variou temperatures up to 50°C. In this oven salt solutions, which generally give varying relative humidities at different temperatures, are not required for the present experimental conditions.

This oven consists of an insulated copper humidi chamber, heavily tinned inside, with a separate control compartment, mounted in an all welded steel case. It i designed to be entirely self-contained except for electrical and water main connections and provision of drainage for condensation water.

The working space of the humidity oven is 2' 4" x 2' 8" x 2' 3". Access to the chamber is by a single door sealed by a rubber gasket and having an opening of 2' 4" x 2' 4". Thus the six unit relaxometer with 25" height and maximum base distance of 12" can be easily accommodated in this oven. A universal joint arrangement is used for inserting stretch in the specime and this is operated through an outside handle (Ha).

The details about the working precautions, etc. can be obtained from the instruction pamphlet of Gallenkamp humidity oven No. 7900.

For the present investigation the conditions required included 65% r.h. at 20°C. To obtain such conditions with much accuracy, a cooling coil made of copper was fitted in the boiler of the above humidity oven through which the cold tap water with temperature about 10°C was circulated. The rate of water flow depends upon the cooling requirements. The cooling coil was able to draw out the excess of heat given by the heater, thus proper vapour pressure could be maintained for the proper requirements of humidity at any temperature. This modification also improved the accuracy and speed of the humidity control system even at high temperatures.

Measurements of the conditions in the oven were made as follows:-

Although the contact thermometers are of the best quality, it must be remembered that they are primarily controllers and that as they are mounted near to the heater and the boiler out-let, they tend to register temperatures a little higher than those prevailing in the working space. There is such a difference, even though an efficient air circulating fan is very near to the heater and the boiler out-let. Thus to ensure the proper temperatures and humidity conditions around the test specimens, it was thought advisable to fix (temporarily) three similar centrigrade thermometers capable of reading from 0°C to 100°C onto the three rods (R) of the main relaxometer. For humidity, a Negretti and Zambra recording electrical hygrometer with Gregory type element is used. The details about the construction of this hygrometer and its use etc., can be obtained from their catalogue Nos. H/1311-H/1314 The recorder is fitted outside the oven and a wire lead carrying a small Gregory element sensitive to humidity, is kept near the centre of the six unit relaxometer in the oven. To avoid damage to the element it should no be exposed to temperatures exceeding 50°C.

(3) Experimental Procedure

(a) Preliminary information about the materials

Before starting with the proper stress relaxati study the following information about the nine filament materials: nylon 66, nylon 610, Perlon, Grilon, Terylen Courlene X3, Courlene PP, viscose rayon and silk, was obtained at 65% r.h. and 20°C, which is given in Table

Stress-strain behaviour of the samples was foun on an Instron tester by taking a mean of 5 to 10 specimen observations. The crosshead speed and the chart speed were respectively selected as 5"/min and 10"/min to obtain satisfactory curves at 2.08% per seco constant rate of extension, specimen length being 4 inc

From the stress strain curves thus obtained, the maximum tension developed at any extension can be found. Thus by taking into the consideration of the effect of rate of extension[174] on the tension behaviour of different fibres the selection of the cantilevers was made. In order to obtain better and clear information about the tension at various extension used, a separate plot of load-extension (up to 5% extension) was made and the information derived from such plot is given in Table 8 (see Chapter IV), up to 4% extension. This gave better information about the selection of the cantilevers, as given in Tables 2 and 3.

(b) Preparations for experiments.

When all the above information is obtained, a sufficient number of specimens are preconditioned to approximately 65% r.h. and 20°C. This approximate conditioning is made to keep the specimen straight and it should be kept at least 10 cm. longer than the required test length, to make an allowance for the convenience in fixing the specimen between two grips. This preconditioning is done by winding loosely but straight the specimen on a frame and keeping it in a jar over magnesium acetate saturated salt solution (for 65% r.h. at 20°C) in a room at 20°C. According to the requirements of the experiments, the different samples are taken out from the frame.

TABLE 1

Filamentous Material	Symbol	Type	Form	Diameter mm.	Density* g/cm.^{3}	Denier	Tex g/km.	Moisture regain*
1. Nylon 66	66	Nylon 66	Monofil	0.20	1.14	325	36.1	4.2
2 Nylon 610	610	Nylon 610	Monofil	0.31	1.09	740	82.2	2.6
3. Perlon	P	Nylon 6	Monofil	0.20	1.14	350	39.0	4.0
4. Grilon	G	Nylon 6	Monofil	0.20	1.14	330	36.7	4.0
5. Terylene[172] 16.7/72 S0.5	T	Polyester	Multifil	–	1.38	150	16.7	0.4
6. Courlene X3	X3	Polyethylene	Monofil	0.19	0.95	270	30.0	0.0
7. Courlene PP	PP	Polypropylene	Monofil	0.19	0.90	225	25.0	0.0
8. Silk[172] 30.1/4 S11.1: 7.4/3 S14.4: 2.44/14 Z10 c.f.	S	Protein	Multifil	–	1.35	280	31.1	10.0
9. Viscose Rayon[172] 33.3/50 S2.9c.f. bright.	V	Cellulose	Multifil	–	1.52	300	33.3	13.0

*Values obtained from references: 173, 174, 175, 176.

TABLE 2

Cantilever for	Single-unit stress relaxometer				Six-unit stress relaxometer					
Cantilever identification	A	B	C	D	E	F	G	H	I	J
Conversion factor g/cm.	42	52	112	150	49	49	67	78	108	85

T A B L E 3

Helical spring H_1 = 230 g/cm. deflection of light on scale, in single unit relaxometer.

Helical spring H_2 = 510 g/cm. deflection of light on scale, in single unit relaxometer.

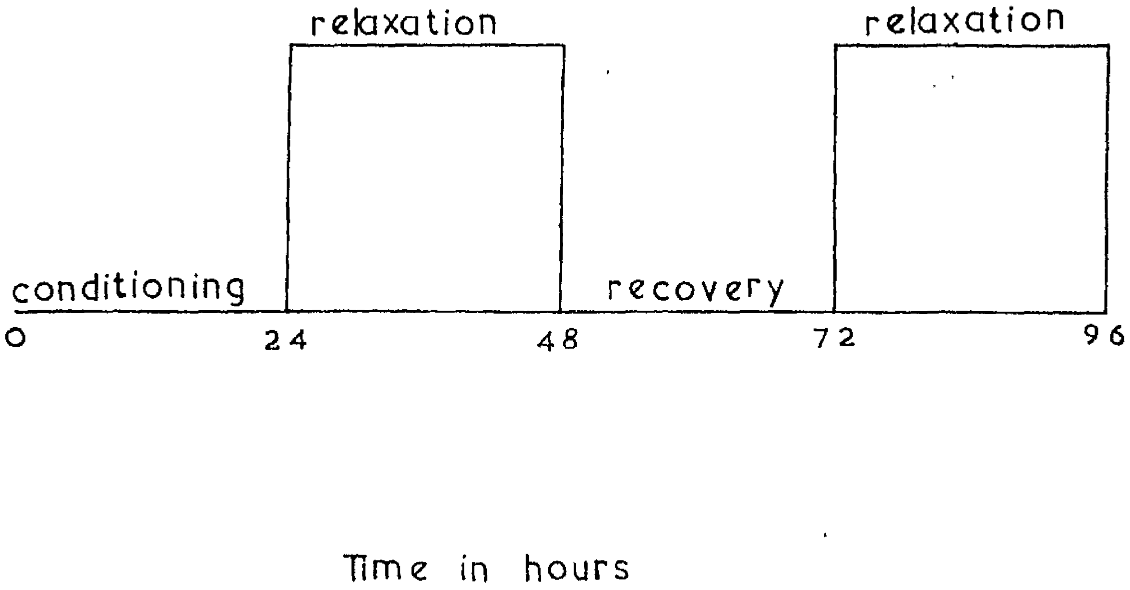
Material	Nylon 66	Nylon 610	Perlon	Grilon	Terylene	Courlene X3	Courlene PP	Silk	Dry Viscose Rayon
* Cantilever No.	B	C	B	B	B	-	-	C	A,B,D
Spring No.	H_1	H_1	H_1	H_1	H_1	-	-	H_1	H_1 H_2
+ Cantilever No.	E	I	G	F	H	I	F	J	-

* For single unit stress relaxometer according to Table 2.

\+ For six unit stress relaxometer according to Table 2.

Fig. 7

Sequence of relaxation tests with single unit apparatus



(A) Experimental procedure with single unit stress relaxometer

(i) General

On this single unit stress relaxometer the experiments were carried out at following conditions:-

(a) Nylon 66, nylon 610, Perlon, Grilon, Terylene and silk were studied at 2% extension, 65% r.h. and 25°C The cantilevers which covered all these tests were with respective conversion factors 52 and 112 g/cm. deflection of the slit image on the scale (S_c). Sodium nitrite gives required humidity.
Helical spring (H_1), with factor 230 g/cm. was successfully used.

(b) Viscose rayon at strains of 1%, 2%, 5% and 10% was studied for its relaxation behaviour at 0% r.h. and 25°C. Phosphorous pentoxide is carefully used for obtaining 0% r.h.

Cantilevers A, B, D with conversion factors 42 gms, 52 gms, 150 g/cm. deflection and helical springs H_1 and H_2 with factors 230 and 510 gms were used.

The cantilevers in all the experiments were calibrated before and after every experiment. The experimental sequence is shown in Fig. 7. First the specimen is mounted carefully and then conditioned for at least 24 hours. The experimental observations taken for 24 hours. The recovery period was made 24 hours for proper recovery of the specimen. Then the permanen set was measured wherever required. Again the same procedure was adopted for the run on the mechanically conditioned samples.

In the present set of experiments on the single unit apparatus, it was decided to obtain the relaxation behaviour in the earlier period also. Thus by the trial and error method of arrangement of the holes in the dash pot piston and by fixing the maximum length of the helical springs, it was possible to obtain a first reliable reading at less than 0.02 sec. from stretching, along with the continuous record of readings from 0.02 sec. from beginning of extension.

A cathetometer was used for measuring the extensions to be put in the specimen (e.g. 1 cm for 5% extension when specimen length was 20 cm.) The specime distance between two grips was fixed with the help of a ruler. These distances were fixed when the catch (C) was holding the lower grip. The block (B) was fixed at a required distance, to stop the lower grip after the required extension. The brass rod (R_m) carrying the catch was held against the cam(Cm), which on rotation releases a catch and thus specimen extends.

(ii) Mounting of specimen

The specimen is mounted in a conditioned room at 65% r.h. and 20°C and then sealed into the experimental copper tank for the experiments to be carried out at 65% r.h. and 25°C. Before clamping the specimen to the lower grip it is checked that there is no unwanted twist in it. To remove any crimp a small weight of 0.1 g/Tex (Tex = Denier/9 = Linear density in gms/km number of grammes per thousand meters of yarn). After sealing the mounted frame in the copper tank, conditione air is circulated over-night for the proper conditioning of the specimen.

For the experiments ~~at~~ under dry conditions, the arrangement described previously is used for mounting. The dry specimen is fixed at 20 cm length in the mountin box (as described before). After mounting, the frame is taken out and the mounting box is well sealed again for use with other specimens. As soon as this dry mounted specimen comes in the room atmosphere, it absorbs moisture and increases in length and slackens. After fixing the required extension the mounted frame is transferred to the copper tank for the usual conditionin for 24 hours at 0% r.h. and 25°C. Thus the specimen again becomes dry at 0% r.h. which can be checked by the reading on the scale which should be somewhat more (equivalent to load attached to the specimen) than when it was slackened. Thus we are ready ~~for the~~ to start ~~of putting on~~ exten~~sion~~ding the ~~to an exactly~~ 20 cm long specimen at 0% r.h. and 25°C.

(iii) Measurement of tension

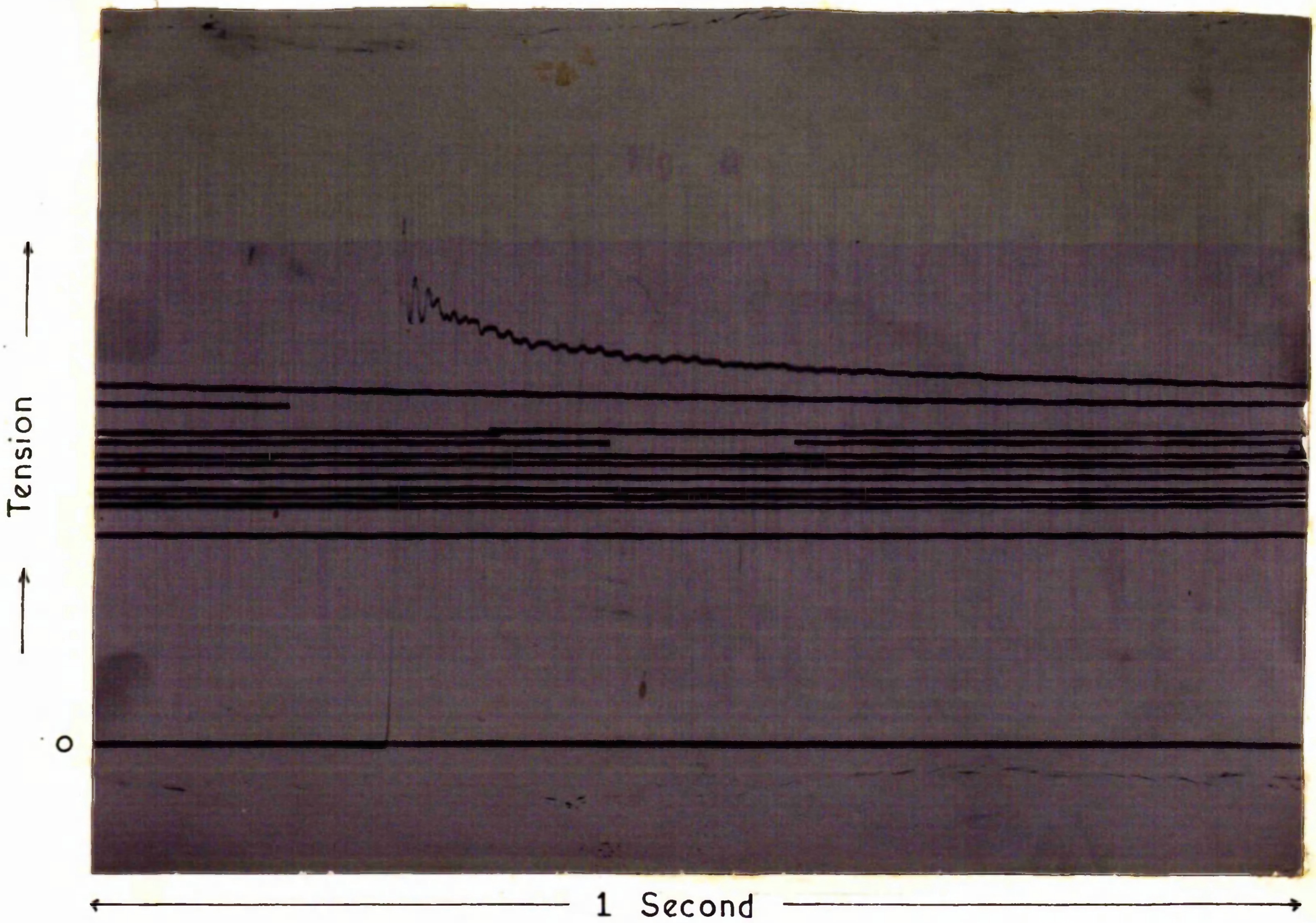
A metronome calibrated for a tick per second is left ticking, camera drum started for its rotations (1 revolution per second), small buzzer connected to the battery, initial reading noted. A well trained second person is ready to start the stop-clock and for calling the numbers along with each tick of the metronome. The second person also records the observations.

The sequence of operations is as follows in Table 4.

TABLE 4

Person A	Time in Seconds	Person B
	-5	
Light on		
Extra light on, open shutter		
Start - Release catch	0	Start counting seconds, along with starting of stopclock.
Extra light off, close shutter		
Extra light on		
Open shutter		
Close shutter, extra light off	5	
Light off		
Light on		
Extra light on, open shutter		
Read scale, close shutter	10	Note A's reading, while counting.
Extra light off		
Light off		
Light on		
Extra light on, open shutter		
Read scale, close shutter	20	Note A's reading, while counting.
Same repeated		
Photo taken	30	Note A's reading, stop counting.
Photo taken, read scale and note	60	
	120	
	180	
	240	
Photo taken, read scale and note	300	

Fig. 8



The readings below 10 seconds after start of stretching have been recorded photographically because of the rapid decay in the tension. From 10 seconds the stress decay is quite slow enough to permit the visual observation. A typical photographic record of the initial tension decay is given in Fig. 8 showing the sequence of tension right from the start of rapid extension. Camera records are made up to 30 seconds and then at 300 seconds according to the Table 4, along with visual observations of the scale, which helps in obtaining the correlation between the recorded and observed deflections of the spot of the light.

After the first run for 24 hours, the lower grip is lifted up to the original specimen length (marked on the vertical scale V_s), and allowed to recover for 24 hours under same conditions of temperature and humidity. The specimen after the recovery is called "mechanically conditioned". The permanent set is measured on the vertical scale for large values or with a cathetometer for small values. Now the experimental procedure for a mechanically conditioned specimen is exactly the same as described previously in Table 4.

The photographic records are developed in the bath made up according to Kodak formula D-171 made as follows:-

Sodium Sulphite (anhydrous)	25.0 g
Sodium Carbonate (anhydrous)	60.0 g
Potassium bromide	0.5 g
"Elon" or "Metal"	14.0 g
Hydroquinone	3.0 g
Water to make	1000 c.c.

The fixing of the developed photograph was carried out in an acid hypo solution.

(iv) Experimental accuracy

1. The temperature was constant at $25^{\circ}C \pm 0.1^{\circ}C$, so there is negligible error in the experimental results due to temperature variation.

2. The Negretti and Zambra dial hair hygrometer is not considered to be very accurate at extreme humidities. Thus, efforts were made to use maximum possible drying and it was seen that the pointer was steady at zero reading even when the circulation had been stopped overnight. Thus it was considered as a reliable reading The hygrometer was already checked in a conditioned room at 65% r.h. and $20^{\circ}C$. Due to the high experiment temperature ($25^{\circ}C$), the same hygrometer read 66 ± 1% r.h. for 65% r.h. Thus slight error due to humidity recorder is tolerable.

3. The extension distance was fixed with the help of a cathetometer with telescopic lens which could be read to third place of decimal in cm. Thus the maximum possible error can be ± 0.01% of extension.

4. Despite the linearity between the applied load and the deflection of the spot on the scale, the linearity may divert to about ± 1%. Thus the error in the conversion factor of the cantilever can be possibly not more than 0.8%.

5. By introducing a device for mounting the specimen at dry experimental conditions the error due to change in

length due to different mounting humidities was removed and straight away experiment was carried out.

6. Although the spot of light is very sharp, the accuracy of reading cannot be more than 0.1 mm. The smaller the deflections of the spot, the more will be the percentage error in reading. Thus it was decided to use convenient cantilevers to give maximum possible deflection of the spot. The greatest possible error for deflection of 2 cm can be about 0.5% of tension.

7. Due to some vibrations in the tension measuring system in the early stage of relaxation, a waviness of photographic recordings might be obtained. This can be up to 0.2 second after completion of extension; the average values are then taken. Thus, there is the possibility of an error of less than 1% for tensions before 0.05 sec and 0.5% for those after 0.05 sec.

Thus the over all accuracy of the apparatus is quite satisfactory for our purpose.

(B) Experimental procedure with six unit stress relaxometer.

(i) General

For the present investigations, this six unit apparatus was found to be useful in obtaining the stress relaxation behaviour of six specimens at a time. All the experiments were repeated at least once or twice or even more times according to the requirements. Nylon 66 nylon 610, Perlon, Grilon, Terylene, silk, Courlene X3 and Courlene PP were tested for the study at various conditions of relative humidity, temperature and extension. There were two devices used for control of humidity and temperature (described in the description of the six unit apparatus). The Perspex box device was used for the following experiments:-

(a) Experiments for study of stress relaxation behaviour of nylon 66, nylon 610, Perlon, Grilon, Terylene and silk for 48 hours made to get the fit of the similar curves obtained on the single unit stress relaxometer. This was done for only 2% extension. This gave the reliability of the new apparatus.

(b) Experiments to study the effect of humidity on the stress relaxation at 1%, 2%, 3% and 4% extension with relative humidities varied between 35 and 90%, taking 65% as an intermediate relative humidity.

The Gallenkamp humidity oven was used for the following experiments:-

(a) Study of stress relaxation behaviour of nylon 66, Perlon, Terylene, silk, Courlene X3 and Courlene PP at various temperatures as 20°C, 30°C, 40°C and 50°C at extensions of 1%, 2% and 3%, the relative humidity being constant at 65%.

(b) Study of the effect of magnitude of strain on the stress relaxation behaviour of nylon 66, nylon 610, Perlon, Grilon, Terylene and silk. The experiments were carried out at 2% extension for 2 days and again further sudden extension by 2% and again study of stress relaxati for two more days, temperature and humidity being constant at 25°C and 65% r.h., respectively.

(c) Long duration stress relaxation curves were obtained up to a more than 4 weeks duration, for nylon 66, nylon 610, Perlon, Grilon, Terylene and silk at 2% constant extension at 25°C and 65% r.h.

(ii) Mounting of specimen

The specimen was mounted on the upper grip (G_1) and its lower end was attached to a small weight (0.1 gm/Tex). The specimen was fixed in the lower grip when the mounting was done in the conditioning room. When conditioning room could not be used, the specimen was left unclamped at lower grip for 24 hours for conditioning at the required conditions especially when the conditioning was to be made at 90% r.h. After 24 hours conditioning the specimens were clamped in the lower grips taking care that minimum time is used for clamping. Then again conditioning for 24 hours was made. All the precautions were taken not to disturb the optical system because this system is very sensitive.

(iii) Measurement of tension

The tension measurement was made directly from the scales on the Perspex screen (P_s) through the optical lever system.

Due to the six scale readings, the first reading on the first scale was obtained at 10 seconds after the start of extension and the first reading on the sixth scale could be obtained at 60 seconds (every reading being taken at 10 second intervals). Concave mirrors and plane mirrors (when Gallenkamp oven was used) helped in the reading of back and side scales.

The metronome was started, the specimens were stretched, and the readings were taken as in Table 5.

TABLE 5

Left hand	*Time in seconds*	*Right hand*
	-10	*Start counting*
	-5	
Start clock	*0*	*Start extension*
Bright light on *Light off*	*10*	*Take reading on scale I*
Bright light on *Light off*	*20*	*Take reading on scale II*
"	*30*	*Take reading on scale III*
"	*40*	*Take reading on scale IV*
"	*50*	*Take reading on scale V*
"	*60*	*Take reading on scale VI*
"	*2 minutes*	

After taking first readings at 10 second intervals, the second reading on the scale No.1 was taken at 2nd minute and second reading on sixth scale at the 7th minute. Every reading at an interval of one minute. Then at the 10th minute quickly all the six scale readings were noted, and so on. The experimental observations ended after 48 hours. In the case of the experiments where the humidity is changed after 48 hours, and so on, the readings are noted every hour, for six hours and then at 24 hours and 48 hours. This gives the complete behaviour of the specimen during humidity change and allows time for substantial moisture equilibrium to be reached. In some cases it was found that 24 hours exposure to the changed humidity was not sufficient for proper equilibriu between moisture and fibre.

In the case of the experiments for the study of the effect of magnitude of strain, the experiments were carried out as usual at 2% extension at 65% r.h. and 25°C for 48 hours. Then sudden rise of 2% more extensio was put and the readings again recorded as for a fresh experiment, e.g. from 10 seconds onwards.

Precautions during the use of Gallenkamp humidity oven:-

1. The temperature recorded by the contact thermometers was a little higher than in the centre of the oven, because the heaters are near them. So, on the body of the main apparatus three centigrade thermometers of similar type are fastened to determine the accuracy of the temperature around the specimen.

2. As in (1) the humidity also can be fixed roughly by contact dry and wet bulb thermometers, thus Negretti and Zambra automatic chart along with a sensitive Gregory type element is used. At different temperatures the chart records different reading for the same humidity, because the calibration of the element is made at 20°C. Thus Negretti and Zambra Drawing No.1752 - C2, provides the correction for temperature and they were as follows for present experiments:

TABLE 6

Temperature Correction for recording of humidity on Negretti & Zambra automatic chart device.
% relative humidity needed is 65%.

Temperature °C	*Temperature °F*	*Chart Reading for 65% r.h.*
20	68	65
25	77	68
30	86	71.2
40	104	77.4
50	122	82.8

(iv) Experimental accuracy

1. Humidity of the conditioning air at 35%, 65% and 90% relative humidities and at 25°C, could be measured up to the accuracy of ± 1% on the long stem Negretti and Zambra dial hair hygrometer, with necessary temperature corrections. Gallenkamp humidity recorder is more accurate even at different temperatures. It could record up to accuracy of ± 0.5% r.h. with little careful adjustments of the controlling device. Thus negligible chances of the error due to humidity control.

2. Temperature control could be achieved up to ± 0.1°C in both devices. In oven at high temperatures, e.g. 40°C and 50°C the accuracy was ± 0.2°C. So it can be assumed that the experimental results did not suffer any variations due to improper temperature control.

3. Although the extension imposed was fixed with the help of an accurate cathetometer, then also it can be said that there might have been an error of about 0.05% of the extension, which is not very much in comparison to the 40 cm. test length.

4. The sharp reflection spot has an accuracy of 0.1 mm reading and it can give an error of about 1%, depending upon the distance of vision and the deflection of the spot.

5. The calibration of the optical system can also produce an error of about 1%, because of very small deflection range of the spot (5 to 6 cm.).

6. The error due to the little friction between the steel balls (B) and glass V-grooves made by glass hemispheres and by glass rods, in the optical system, can be minimised by little vibrations due to the air circulating pump or the fan of the oven itself.

Considering all the errors due to the tension measuring systems, it was thought advantageous to use the six unit stress relaxometer at slow rate of extension. By using this we have greatest advantage of obtaining six results at a time. Moreover, the accuracy of results could be increased by taking an average of more than one result in the present investigations.

CHAPTER IV

RESULTS

(1) Introduction

For the effective comparison of various mono- and multifilamentous materials, most of the experiments were carried out under the same conditions of temperature and humidity. Initially the specimens were conditioned for several days at 65% r.h. and 20°C, and then put to the required conditions of the experiment for at least 24 hours. Table 7 gives the various sets of experiments carried out during the present investigations. The main object was to study the stress relaxation behaviour of various synthetic fibres in comparison with silk under varying atmospheric conditions and various tension conditions. A subsidiary set of experiments was made on dry viscose rayon at strains from 1% to 10% extension to provide data for evaluating the number of secondary bonds simultaneously involved in the relaxation process.

Two or more specimens were tested at each set of conditions and the results averaged after discarding the extreme nonreliable values. This variability in the experimental results had negligible effect on the average stress relaxation behaviour of the materials at various conditions. Most of its effect was in the very early stages of stress relaxation, say up to 2-5 seconds, depending upon material and the magnitude of strain.

However, in most of the experiments we were interested in the relaxation from 10 seconds, after start of extension, and the variation between duplicate specimens was very small for times greater than 10 seconds.

The load-extension curves for all fibres Terylene, Perlon, Grilon, nylon 66, nylon 610, silk, Courlene X3, Courlene PP and viscose rayon, were determined on the Instron tester at constant rate of extension 2.08%/sec., as cross head speed was fixed at 5"/min. and chart speed at 10"/min. and the specimen length being 4". The results are shown in the form of graphs on Fig. 9.

These curves are plotted as stress (g/den.) versus strain (% extension) to study the general behaviour of the various materials used. The breaking stress and the breaking strain are tabulated in Table 8, along with the calculated tenacity as shown in Fig. 9.

Fig. 10 shows a separate plot of tension (g) versus % extension up to 5%. This was plotted with a view to estimating the tensions likely to be developed at 1%, 2%, 3% and 4% extension in the relaxation tests an thus enabling an appropriate selection of the cantilever to be made (see Table 8).

(2) Stress relaxation curves under standard conditions.

Prior to a comparison of the behaviour at various conditions, a study of stress relaxation at 65% r.h. and 25°C was considered to be essential.

The intervals between readings were the same throughout the experiments and are as shown on typical curves in Figs. 11 to 14. The general shape of each stress relaxation curve is slightly convex towards log time axis at very early stages of relaxation up to 1-2 seconds and then it becomes almost linear. The thick monofilament of nylon 610 and the twisted multifilamento yarn of silk show further concave nature up to about 10-20 seconds.

Stress relaxation curves as tension (g) v/s log time (seconds) obtained on the single unit stress relaxometer are given in Figs. 11 to 14. Figs. 11 and 12 show the stress relaxation behaviour of Terylene, Perlon, Grilon, nylon 66, nylon 610 and silk at 65% r.h. and 25°C, the extension being constant at 2%. Similar curves for the same materials, but mechanically conditio are also given in Figs. 13 and 14. These experiments were carried out to study the early behaviour of stress relaxation from 0.02 sec. up to 24 hours, covering nearl seven decades on logarithmic time scale. These results also helped to check the reliability of the newly constructed six unit stress relaxometer. The whole curve represents the stress relaxation with time measure from the start of extension and the dotted line represent the behaviour if the time is measured from the completion of extension. Average percent change in tension per decade of time for these fibres, over a time range from log t = -1 to log t = 5 is given in Table 9. This table contains such results for first run and mechanicall conditioned specimen.

All the eight fibres e.g. Terylene, Perlon, Grilon, nylon 66, nylon 610, silk, Courlene X3, and Courlene PP were studied for their stress relaxation behaviour at 65% r.h. and 25°C, at 2% extension for 48 hours. These results are not separately given, because they nearly coincided with the general stress relaxation behaviour of the fibres given in the section (of this chapter. Such curves can be represented by the curves in Figs. 16 and 17, only up to the end of 48 hour i.e. 5. 24 on the log time scale.

To study the long term stress relaxation behavio at 65% r.h. and 25°C for one month, the curves for Terylene, Perlon, Grilon, nylon 66, nylon 610 and silk are given on Fig. 23. These results are also of simil nature as in Fig. 16.

The average percent change in tension per decade of time, at 65% r.h. and 25°C, is given in the last column of Table 9, and data for 1%, 2%, 3% and 4% extensions are given in Table 10.

(3) Effect of fluctuating humidity on stress relaxation

The experimental results for this set are given the Figs. 15 to 22 in the form of tension (g) versus logarithm of time in seconds. The fibres used, being according to Table 7.

Read the following according to the footnote under Table 7:-

Initially the curves were obtained at 25°C and

2% constant extension for series (a_1) for 6 days only, and then for series (b) for 6 days (see Fig. 18). Seri (a_1) was chosen for the rest of the experiments because both series showed similar results, with very little variations. Fig. 17 shows the curves according to series (a_1), which are plotted for Courlene X3 and Courlene PP. As the duration of experiment was not enough to give reliable conclusions for the sensitivity of tension to fluctuating humidity, so the duration of test was increased by one more cycle of humidity change than in series (a_1).

In expectation of better results, series (c) was tried, under the same conditions of series (a), except that the time of exposure after every change of humidity was increased to 48 hours from 24 hours, as shown in Fig. 19. Then an experiment was carried out according to series (d) for four days and the stress relaxation curves are shown in Fig. 20.

Among all the above experiments, series (a) was selected to be the best, especially from the considerati of economy of time and reliability of results. Thus after obtaining such results at 2% extension (see Fig. 1 further experiments were carried out at 1%, 3% and 4% extensions according to series (a) and the curves from the stress relaxation are respectively given in Figs. 15, 21 and 22.

Table II contains the data for the sensitivity of tension to humidity, giving the average difference of tension in grammes during one humidity cycle in the last column. In the third and the fourth columns is given the tension in grammes read from the Figs. 21 and 22 after one day ($\log_{10} t = 5$ approx) at each humidity. The second figure in each row refers to the second time the specimen was conditioned at 35 and 90% r.h. At 2% extension the relative humidity was 40% instead of 35% and in the last column the average differences in tension between 35 and 90% r.h. have been corrected as in following example:-

> Consider Grilon at 2% extension. Average difference in tension $g_{40} - g_{90} = 48g$. Therefore average difference in tension $g_{35} - g_{90} = 48\ (90-35)/(90-40) = 53g$. ($g_{35}$, g_{40} & g_{90} are tensions in grammes at 35%, 40% and 90% relative humidity respectively)

Table 12 gives the sensitivity of tension to humidity for Terylene, Perlon, Grilon, nylon 66, nylon 610 and silk for series (a) and series (b).

4. Effect of temperature on stress relaxation

For this set of experiments, the specimens selected were Terylene, Perlon, nylon 66, silk, Courlene X3 and Courlene PP. The humidity was maintained at 65% r.h. Figs. 24 to 29 in sequence represent the stress relaxation behaviour of Terylene, Perlon, nylon 66, silk, Courlene X3 and Courlene PP. Each figure gives curves at 20°C, 30°C, 40°C and 50°C at each constant extension of 1%, 2% and 3%.

Table 13 shows the percent change in tension per decade of time, from 10 seconds to 10^5 seconds, at 20°C, 30°C, 40°C and 50°C and also at each extension of 1%, 2% and 3%.

5. Effect of changing the strain during stress relaxation

Graphs shown on Figs. 37 and 38 are the plots, where it is shown that left hand side curves are the stress relaxation curves represented in group A and right hand side curves (group B) are for the stress relaxation of the same specimen at 4% extension which is due to a sudden rise of tension after two days relaxation study at 2% extension at 65% r.h. and 25°C. This sudden rise in tension for each material is shown by a pointed line connecting the end of relaxation curve at 2% extensions and beginning of relaxation curve at 4%. The dotted line curves in group B are also plot to show the stress relaxation behaviour of the same specimen which is directly put to 4% constant extension. These results of curves at 4% constant extension are sam as given in Fig. 22 at 65% r.h. and 25°C, and for 48 hours. This dotted curve can be well used for comparis of effect of magnitude of strain (4% extension) on the rate of decay. The materials used in this set of experiments are Terylene, Perlon, Grilon, nylon 66, nylon 610 and silk.

It can be seen from the experimental curves in Figs. 37 and 38, that there is no appreciable effect on the rate of decay at 4% extension (from its normal behaviour) due to previous relaxing period at 2% extension, provided this period at 2% extension is enough for completion of rapid relaxation. This period in present investigations was fixed for 48 hours to assure proper equilibrium of the relaxing system. In connection with the effect of magnitude of strain, from the results of Table 10, it is clear that there is no appreciable effect of magnitude of strain for low strains up to 2% extension on the per cent change in tension but there is little effect at high extension where per cent change in tension values decrease.

6. Master stress relaxation curves

(a) from results at different temperatures

The superimposed master stress relaxation curves at 20°C are obtained by shift of the stress relaxation curves at higher temperatures i.e. 30°C, 40°C and 50°C. The curves at higher temperature are actually moved horizontally along the log time axis to superimpose with the curve at 20°C and 65% r.h. for Terylene, Perlon nylon 66, silk, Courlene X3 and Courlene PP, at 1% constant extension. Such curves are shown in the Fig.3 The approximate fit of the superimposed curves is shown by different signs plotted and the dotted line shows the amount of shift up to 50°C. Similar curves at 2%

and 3% constant extensions could not be obtained for Terylene, Courlene X3 and Courlene PP, but Figs. 31 and 32 show the master curves for Perlon, nylon 66 and silk, which were obtained not as neatly as obtained at 1% extension. But they can be relied on for their average behaviour.

Table 14 gives the amount of shift log a_T along log time scale for the proper superposition of the curves at higher temperatures to that at 20°C. Three columns for each temperature, show shifts for 1%, 2% and 3% extension curves.

Fig. 39 show the plots of log a_T versus reciprocal of absolute temperature (1/T). The graphs represent the plots for 1%, 2% and 3% extension respectively, as given in Table 14. At 1% extension, this relation gives straight lines, but at 2% and 3% extensions there is little diversion from straight line. Higher the extension, larger is the diversion from straight line in such plots.

(b) <u>from results at different extensions</u>

An attempt has been made to obtain master stress relaxation curves by shifting the stress/strain v/s log time curves at higher extensions to superimpose the similar curves at 1% extension. Fig. 33 gives such master curves for Terylene at 20°C, 25°C, 30°C, 40°C and 50°C. Fig. 34 gives same type of curves for nylon 66 at 20°C, 25°C, 30°C and 40°C. Figs. 35 and 36 represent the master curves for Courlene X3 and Courlene PP ~~reply~~ respectively and at temperatures of 20°C, 30°C and 40°C.

The superimposition of the curves can be seen from the representative different kinds of circles plotted for different curves. The whole line curve is the average superimposed curve through some scattered points.

7. Tension at 10 seconds from the start of relaxation

Tension at any time, divided by tension at any arbitrarily chosen time from the start of relaxation, gives the relative rates of relaxation.

Table 15 gives the maximum tension (g) at an arbitrarily chosen time 10 seconds from the start of relaxation. Table 16 again gives the complete list of maximum tension at 10 seconds, at all temperatures and all strains for the experiments carried out on a six unit stress relaxometer at 65% r.h.

With the help of Tables 15 and 16 and the stress relaxation readings at any time (up to two days), the relative rates of relaxation curves at 65% r.h. can be plotted. Such relative rates of relaxation curves can help in comparing the different fibres at various conditions of temperature and strain.

8. Dry viscose rayon

Table 17 gives the tension observed in dry viscose rayon for extensions of 1%, 2%, 5% and 10%

over a time range of 10^{-1} to 10^{5} seconds at 25°C. The calculated values of stress/strain for each extension are also given in the same table.

TABLE 7

Scheme of experiments

Apparatus	Experiment	r.h.%	Temp. °C	Extension %	Materials tested	Figure Nos.
Single-unit stress relaxometer	Comparison of rates of relaxation	65	25	2	Terylene, Perlon, Grilon, nylon 66, nylon 610 & silk	11,12,13, 14
	Relaxation in the dry state	0	25	1,2,5,10	Viscose rayon	-
Six-unit stress relaxometer	Rate of decay of tension at different extensions	65	25	1,2,3,4	Terylene, Perlon, Grilon, nylon 66, nylon 610 & silk	16
		65	25	2	- do -	23 (for one month duration)
		65	25	2	Courlene X3 and Courlene PP	17
	Effect of fluctuating humidity at constant temperature	*series (a)	25	1,2,3,4	Terylene, Perlon, Grilon, nylon 66, nylon 610 & silk	15,16,19, 22
		*series (a_1)	25	2	Courlene X3 and Courlene PP	17
		*series (b)	25	2	Terylene, Perlon, Grilon, nylon 66, nylon 610 & silk	18
		series (c)	25	2	- do -	19
		*series (d)	25	2	- do -	20

TABLE 7 (Contd.)

Apparatus	Experiment	r.h.%	Temp. °C	Extension %	Materials tested	Figure Nos.
	Effect of temperature at constant humidity	65	20,30, 40 & 50	1,2,3	Terylene, Perlon, nylon 66, silk, Courlene X3 & Courlene PP	24,25,26, 27,28,29
	Effect of changing the strain during relaxation	65	25	+series (e)	Terylene, Perlon, Grilon, nylon 66, nylon 610 & silk	37,38

* Experiments started at 65% r.h. stress relaxation studied for 48 hours and then :

Series (a):- Change humidity to 90% and then after every 24 hours change humidity to 65%, 35%, 65%, 90%, 65%, 35% and 65% (total 10 days),

Series(a1):- Same as series (a), for only 6 days

Series (b):- Change humidity to 35%, then after every 24 hours change humidity to 90% and 65% (total 6 days)

Series (c):- Change humidity after every 48 hours according to order of humidity change of series (a) (total 18 days)

* Series (d):- Condition and start experiments at 90% r.h., study stress relaxation for 48 hours, then change the humidity to 65% and study further stress relaxation for 48 hours (total 4 days)

+ Series (e):- Study stress relaxation for 48 hours at 2% extension, then raise extension to 4% and further study the stress relaxation at 4% for 48 hours at same conditions.

TABLE 8.

Tensile properties at 65% r.h. and 25° C.

Instron Instrument
Rate of extension = 2.08% sec.

Cross head speed = 5"/min.
Chart speed = 10"/min.
Test length = 4"

Material	No. of Tests.	Breaking Extn. %	Breaking Load (g)	Denier	Tenacity g/den.	Tension (g) at Extn. (%)			
						1	2	3	4
1. Nylon 66	5	35	1120	325	3.45	70	150	195	225
2. Nylon 610	5	25	4100	740	5.54	270	510	670	770
3. Perlon	5	36	1900	350	5.53	65	125	190	270
4. Grilon	5	32	2010	330	6.09	60	115	160	205
5. Terylene	5	18	700	150	4.67	115	220	290	375
6. Courlene X3	5	14	870	270	3.22	120	220	300	400
7. Courlene PP	5	24	945	225	4.20	105	180	245	360
8. Silk	5	24	1040	280	3.90	120	260	390	460
9. Viscose Rayon	5	24	580	300	1.93	165	252	262	272

Table 9

Average % change in tension per decade of time, at 65% r.h., 25°C and 2% extension, based on the tension at 10 seconds after start of relaxation.

Fibre	A* Average slope over a time range from log t = -1 to log t = 5		B* Average slope over a time range from log t = 1 to log t =5.
	First run	Mech cond.	Average from Series (a) (b) (c)
Terylene	8.0	7.3	6.3
Perlon	8.3	8.2	6.8
Grilon	12.0	11.8	10.8
Nylon 66	15.3	14.5	10.8
Nylon 610	12.2	11.8	12.3
Silk	12.0	11.2	13.6

A* - Results from single unit stress relaxometer

B* - Results from six unit stress relaxometer

Table 10

Average % change in tension per decade of time at 65% r.h. and 25°C. (Av. values between log t = 1 and log t = 5.24), based on tension at 10 seconds after start of relaxation.

Specimen	Extension (%)			
	1	2	3	4
Terylene	6.3	6.3	3.3	4.8
Perlon	6.8	6.8	5.5	4.5
Grilon	10.8	10.8	9.3	7.5
Nylon 66	10.8	10.8	9.8	8.1
Nylon 610	12.1	12.3	10.5	9.2
Silk	14.0	13.6	13.6	10.8

TABLE 11

Sensitivity of tension to humidity

Material	Constant extension (%)	Tension (g) at r.h. of 35%	Tension (g) at r.h. of 90%	Average difference g35 - g90	Tension (g) at 65% r.h.
1. Terylene	1	92	91	1.5	88
		95	93		84
	2	154*	154	0.5	150
		148*	147		148
	3	232	229	2.5	229
		231	228		228
	4	280	276	4.5	279
		284	279		279
2. Perlon	1	74	23	51	32
		75	24		32
	2	97*	50	54	72
		96*	44		71
	3	144	98	51	120
		146	91		120
	4	208	154	55	182
		207	152		181
3. Grilon	1	57	7	51	29
		56	4		28
	2	84*	32	53	50
		82*	38		46
	3	114	61	57	86
		114	54		83
	4	159	91	68	123
		154	86		120

TABLE 11 (contd.)

Sensitivity of tension to humidity

Material	Constant extension (%)	Tension (g) at r.h. of		Average difference g35 - g90	Tension (g) at 65% r.h.
		35%	90%		
4. Nylon 66	1	56	10	47	29
		54	6		27
	2	81*	37	46	56
		72*	31		52
	3	102	61	46	78
		101	51		74
	4	124	76	48	99
		120	71		96
5. Nylon 610	1	140	89	52	110
		131	78		99
	2	210*	156	55	175
		178*	133		152
	3	297	236	65	260
		279	210		240
	4	382	301	77	343
		372	300		330
6. Silk	1	27	15	11	16
		25	15		14
	2	58*	40	16.5	42
		54*	42		40
	3	62	50	14	48
		59	44		42
	4	85	65	18	67
		79	63		62

* At 40% r.h. not 35% r.h.

Table 12

Sensitivity of tension to humidity.

Material	* % change in tension	
	Series (a)	Series (b)
	90% to 35% r.h.	35 to 90% r.h.
Terylene	2.6	5.0
Perlon	47.0	52.5
Grilon	53.0	59.0
Nylon 66	46.0	48.0
Nylon 610	13.0	19.5
Silk	8.0	37.0

* Based on tension at 10 seconds after start of relaxation.

TABLE 13

Average % change in tension per decade of time (from 10 sec. to 10^5 sec.) at 65% r.h., based on tension at 10 seconds after start of relaxation.

Temperature	20°C			30°C			40°C			50°C		
	Extension (%)			Extension (%)			Extension (%)			Extension (%)		
Material	1	2	3	1	2	3	1	2	3	1	2	3
Terylene	7.6	5.4	3.3	7.8	5.3	3.6	8.3	5.5	2.8	8.0	4.4	2.3
Perlon	8.3	6.5	4.8	9.1	6.3	5.4	9.1	5.9	5.0	7.8	4.7	4.9
Nylon 66	9.0	11.0	9.1	9.0	9.7	9.4	10.6	11.2	8.9	11.5	10.5	10.5
Silk	14.1	14.1	12.3	15.0	14.6	12.6	15.1	14.1	12.6	13.2	12.7	12.9
Courlene X3	9.5	8.0	4.8	9.3	7.5	9.5	9.4	9.8	10.5	9.8	7.5	8.1
Courlene PP	16.0	16.0	16.0	16.0	15.8	17.3	18.0	15.6	16.4	16.4	16.5	15.8

TABLE 14

Amount of shift log a_T at different temperatures and extensions.

Material	log a_T at temperatures of								
	30°C			40°C			50°C		
	Extension (%)			Extension (%)			Extension (%)		
	1	2	3	1	2	3	1	2	3
Terylene	1.00	-	-	2.72	-	-	4.30	-	-
Perlon	1.30	1.14	2.60	2.96	2.66	5.21	5.44	5.51	7.8
Nylon 66	0.46	1.55	2.16	3.13	2.24	2.57	4.38	3.63	3.7
Silk	0.52	1.00	1.48	2.22	1.84	1.66	2.91	4.98	4.6
Courlene X3	1.87	-	-	3.50	-	-	4.76	-	-
Courlene PP	0.92	-	-	1.96	-	-	2.88	-	-

Table 15

Tension (g) at 10 seconds from start of the test, at 65% r.h. and 25°C and extension = 2%, on single unit stress relaxometer.

Material	Tension (g)	
	1st run	Mech. Cond.
Terylene	202	196
Perlon	108	108
Grilon	108	105
Nylon 66	114	112
Nylon 610	431	416
Silk	292	212

TABLE 16

Tension (g) at 10 seconds from the start of the test at 65% r.h. at different extensions and different temperatures – on six unit stress relaxometer.

Temperature	20°C			25°C				30°C			40°C			50°C		
	Extn. (%)			Extn. (%)				Extn. (%)			Extn. (%)			Extn. (%)		
Material	1	2	3	1	2	3	4	1	2	3	1	2	3	1	2	3
Terylene	168	221	234	133	217	274	356	154	200	238	136	188	245	116	167	221
Perlon	57	101	173	54	112	164	232	52	92	150	45	85	130	35	70	114
Grilon	–	–	–	66	111	156	194	–	–	–	–	–	–	–	–	–
Nylon 66	67	114	143	66	105	150	178	61	88	115	47	85	107	39	74	100
Nylon 610	–	–	–	345	440	550	638	–	–	–	–	–	–	–	–	–
Silk	111	243	263	114	229	284	321	103	209	211	78	161	205	63	83	125
Courtene X3	195	332	373	–	–	–	–	154	259	332	128	216	268	110	190	203
Courtene pp	101	153	200	–	–	–	–	73	135	159	53	93	139	41	73	100

TABLE 17

Relaxation of stress in dry viscose rayon at 25°C.

Time Sec. Extension.		10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}
1%	A	294	291	281	267	244	216	187
	B	12.80	12.70	12.30	11.70	10.70	9.40	8.20
2%	A	493	443	390	332	276	234	207
	B	10.80	9.70	8.50	7.25	6.02	5.10	4.53
5%	A	567	524	478	427	378	335	301
	B	4.94	4.58	4.18	3.73	3.30	2.92	2.62
10%	A	690	643	592	544	501	462	437
	B	3.01	2.81	2.58	2.37	2.18	2.02	1.91

A = tension (g): B = stress/strain (10^{10} dyn/cm^2)

Note:- To convert tension to stress/strain, multiply tension by $\frac{9 \times 981 \times 10^{5} \times \text{density} \times 100}{\text{denier} \times \%\ \text{extension}}$

$$= 4.37 \times 10^{8} \times \frac{\text{tension}}{\%\ \text{extension.}}$$

Since density of dry viscose = 1.49 g/cc. and denier = 300.

Fig.9

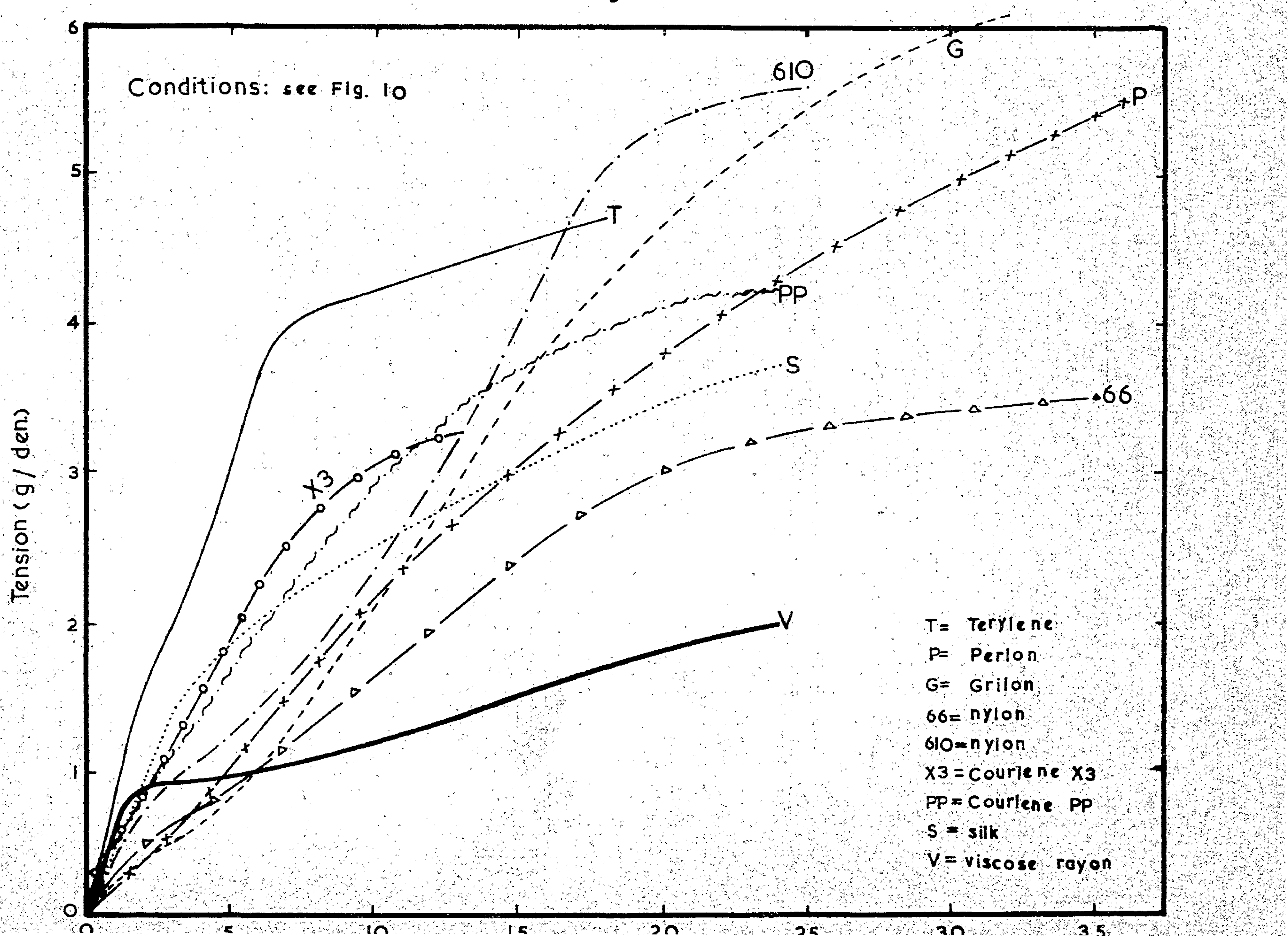

Conditions: see Fig. 10
Tension (g / den.)
0
1
2
3
4
5
6
0
5
10
15
20
25
30
35
T
610
G
P
PP
S
66
X3
V
T= Terylene
P= Perlon
G= Grilon
66= nylon
610=nylon
X3 = Courlene X3
PP = Courlene PP
S = silk
V = viscose rayon

Fig. 10

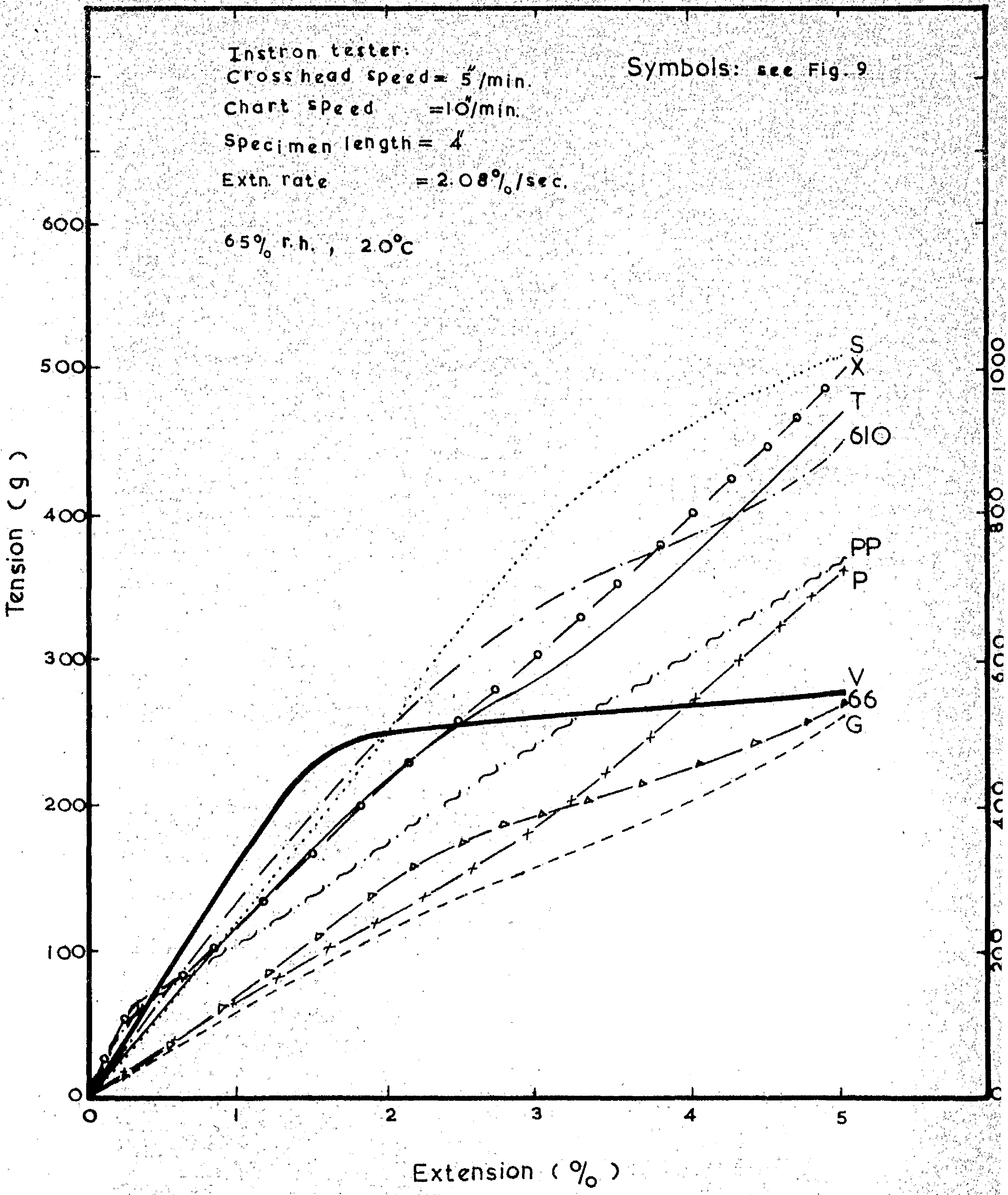

Instron tester:
Cross head speed = 5"/min.
Chart speed = 10"/min.
Specimen length = 4"
Extn. rate = 2.08%/sec.
65% r.h., 20°C
Symbols: see Fig. 9
S
X
T
610
PP
P
V
66
G
Tension (g)
0
100
200
300
400
500
600
200
400
600
800
1000
0
1
2
3
4
5
Extension (%)

Fig. 11

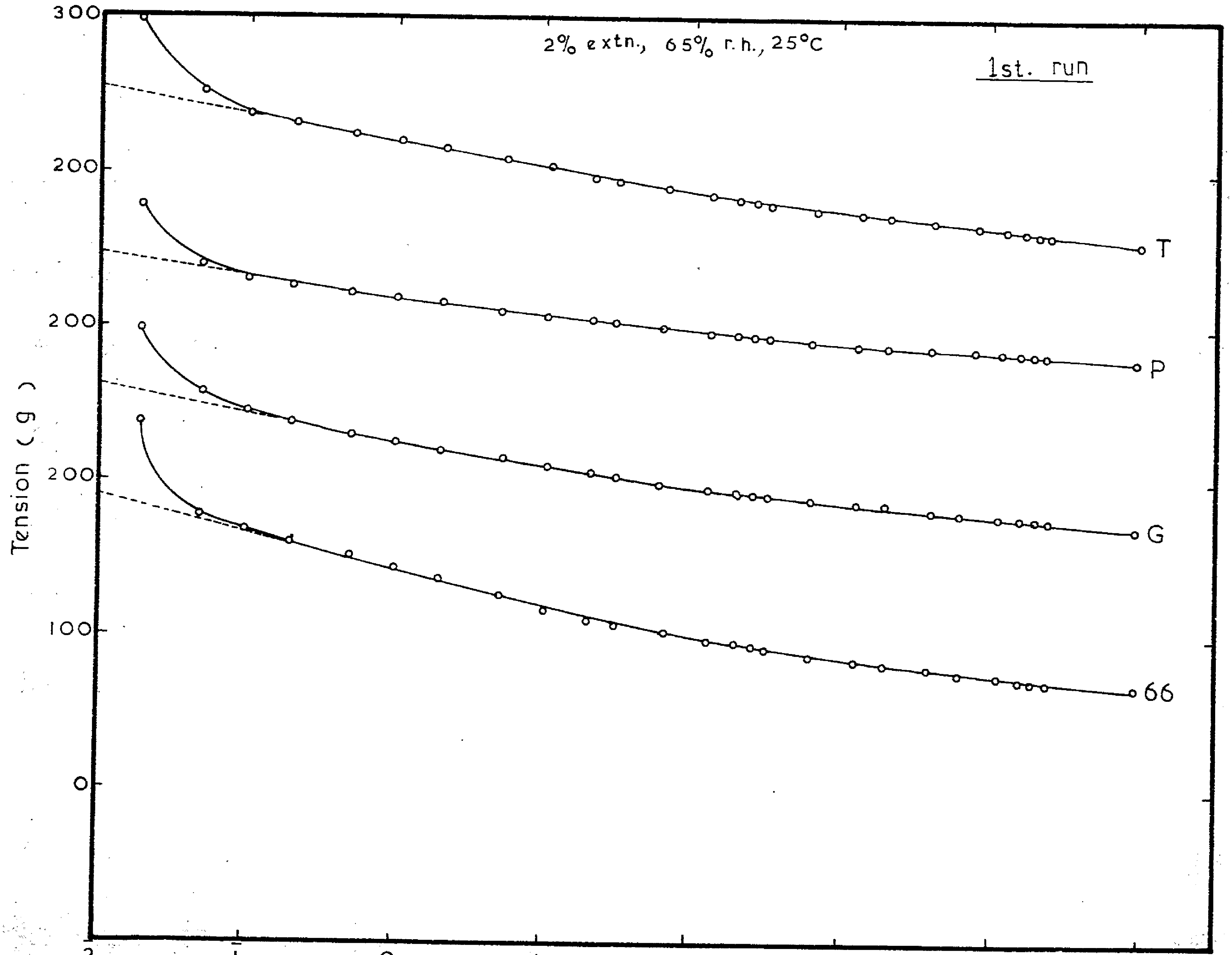


Fig. 12

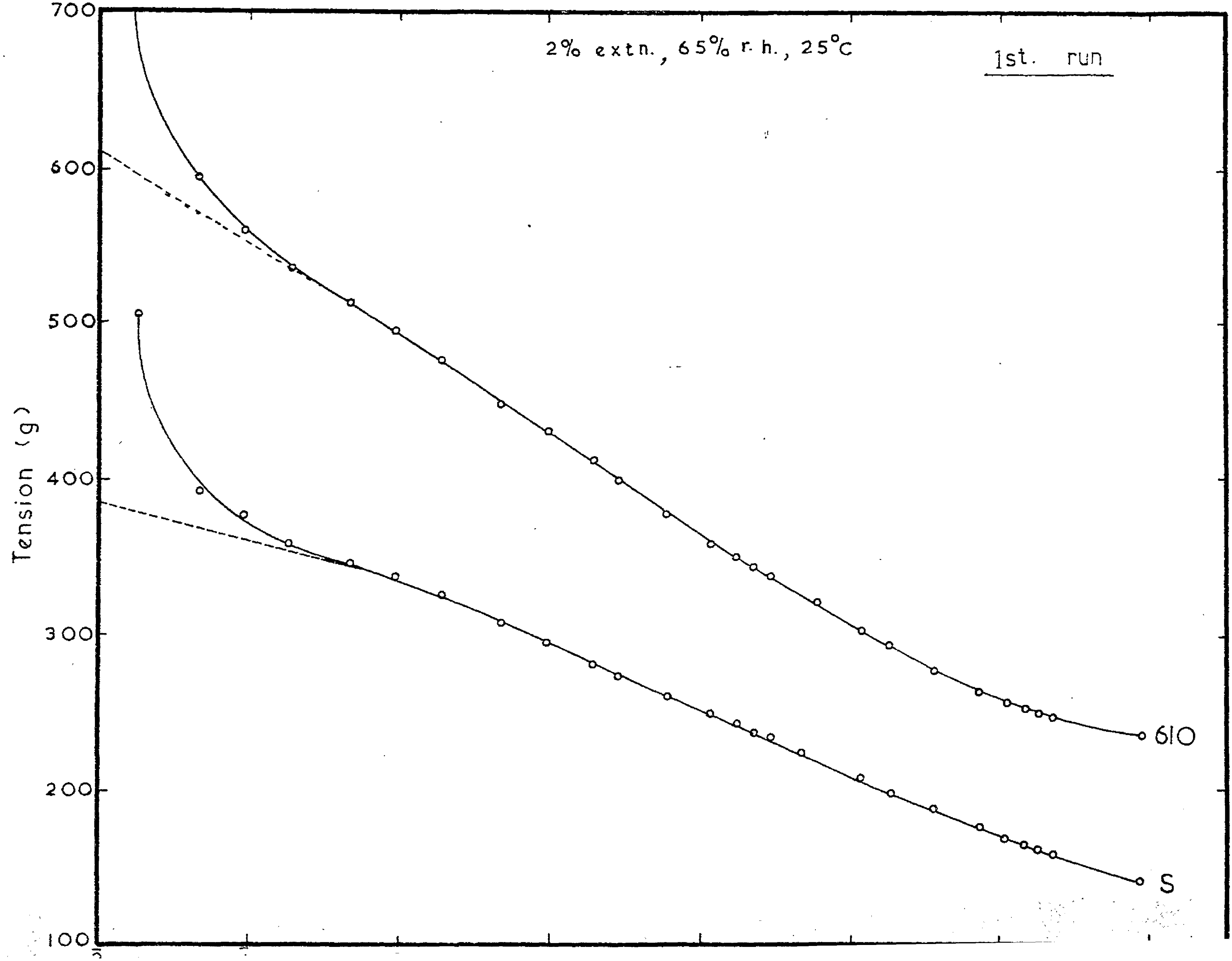

2% extn., 65% r.h., 25°C
1st. run
Tension (g)
700
600
500
400
300
200
100
610
S

Fig 13

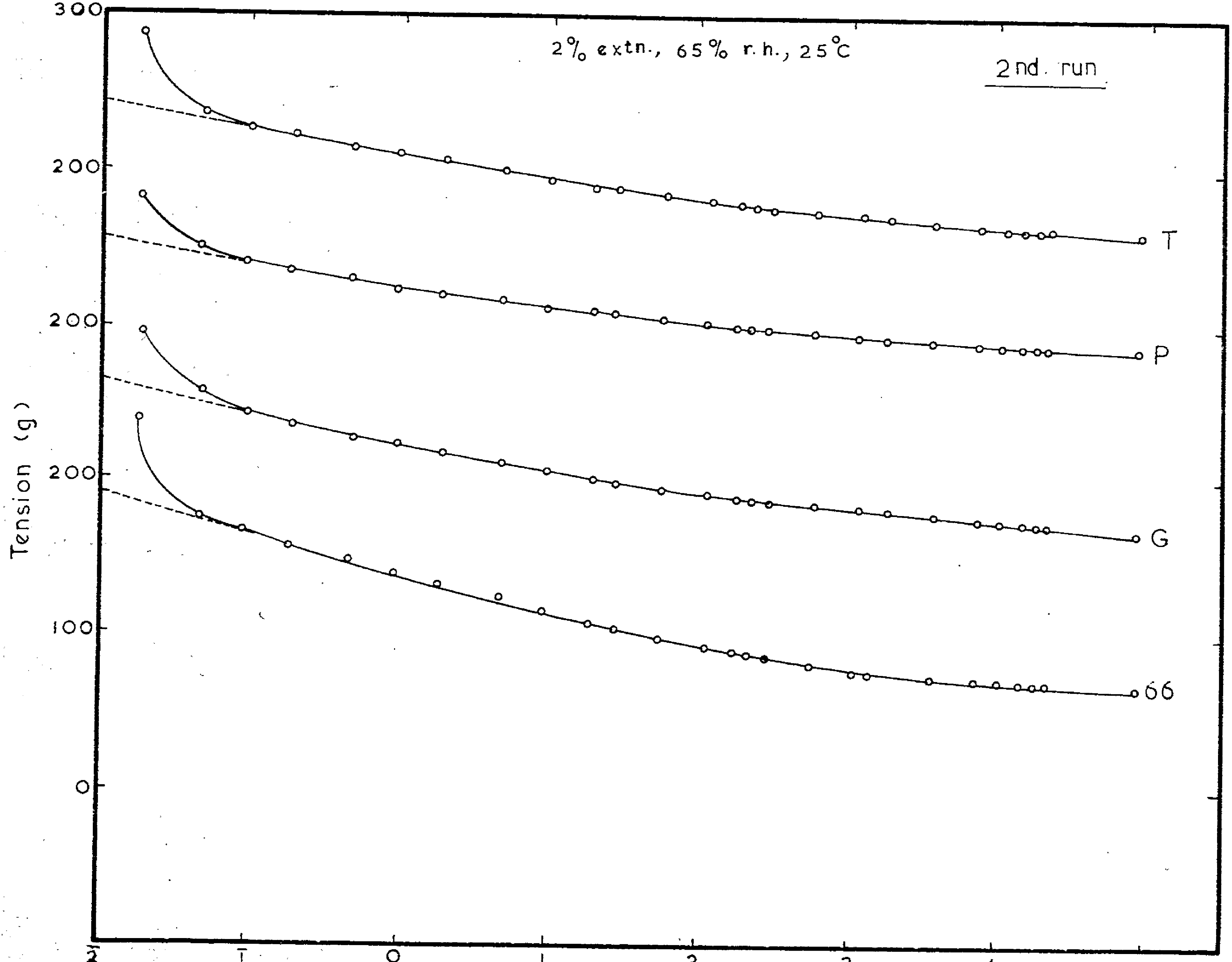

2% extn., 65% r.h., 25°C
2nd. run
300
200
200
200
100
0
Tension (g)
T
P
G
66
$\bar{2}$
$\bar{1}$
0
1
2
3
4

Fig. 14

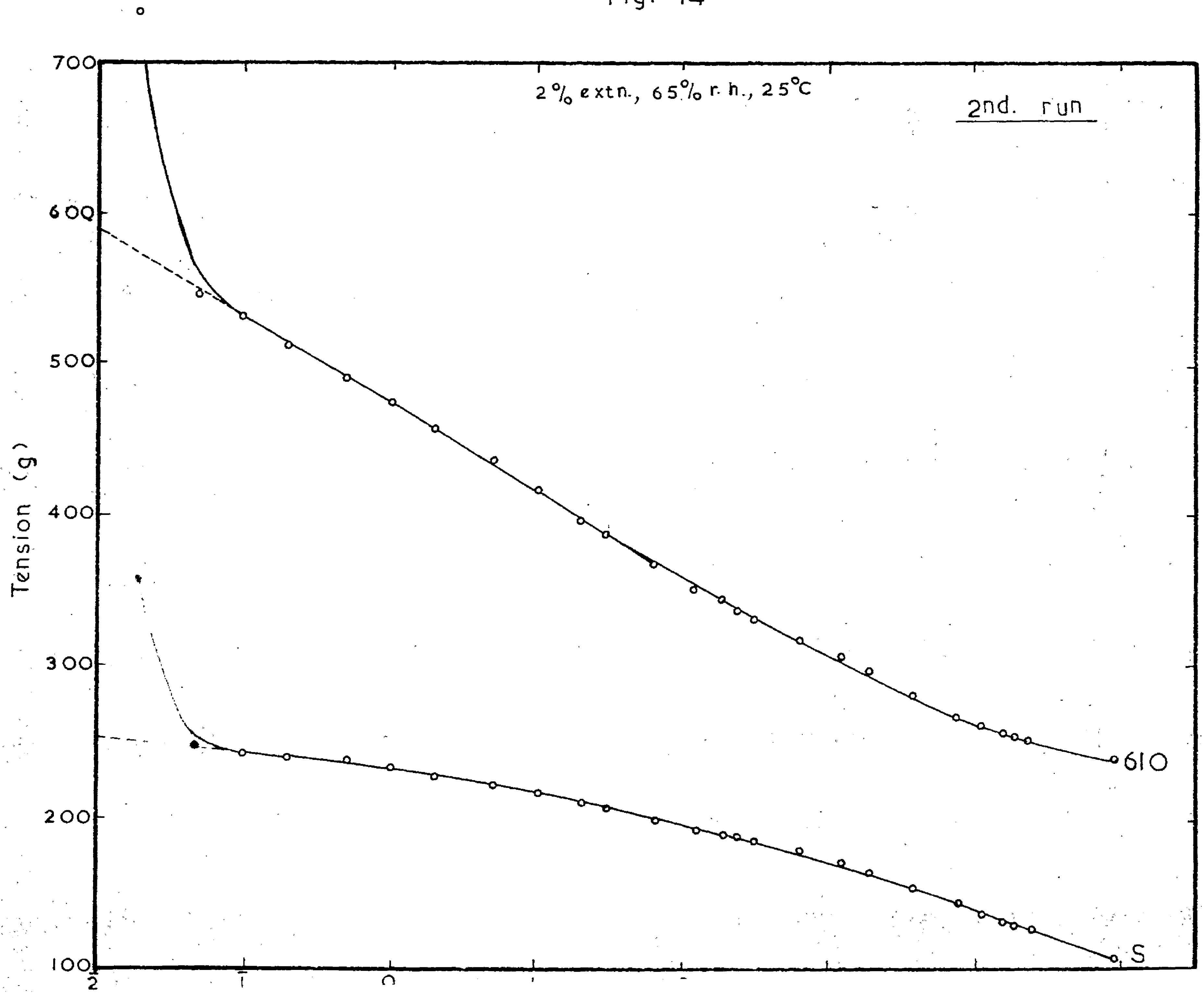

2% extn., 65% r.h., 25°C
2nd. run
Tension (g)
700
600
500
400
300
200
100
610
S
2
1
0

Fig. 15

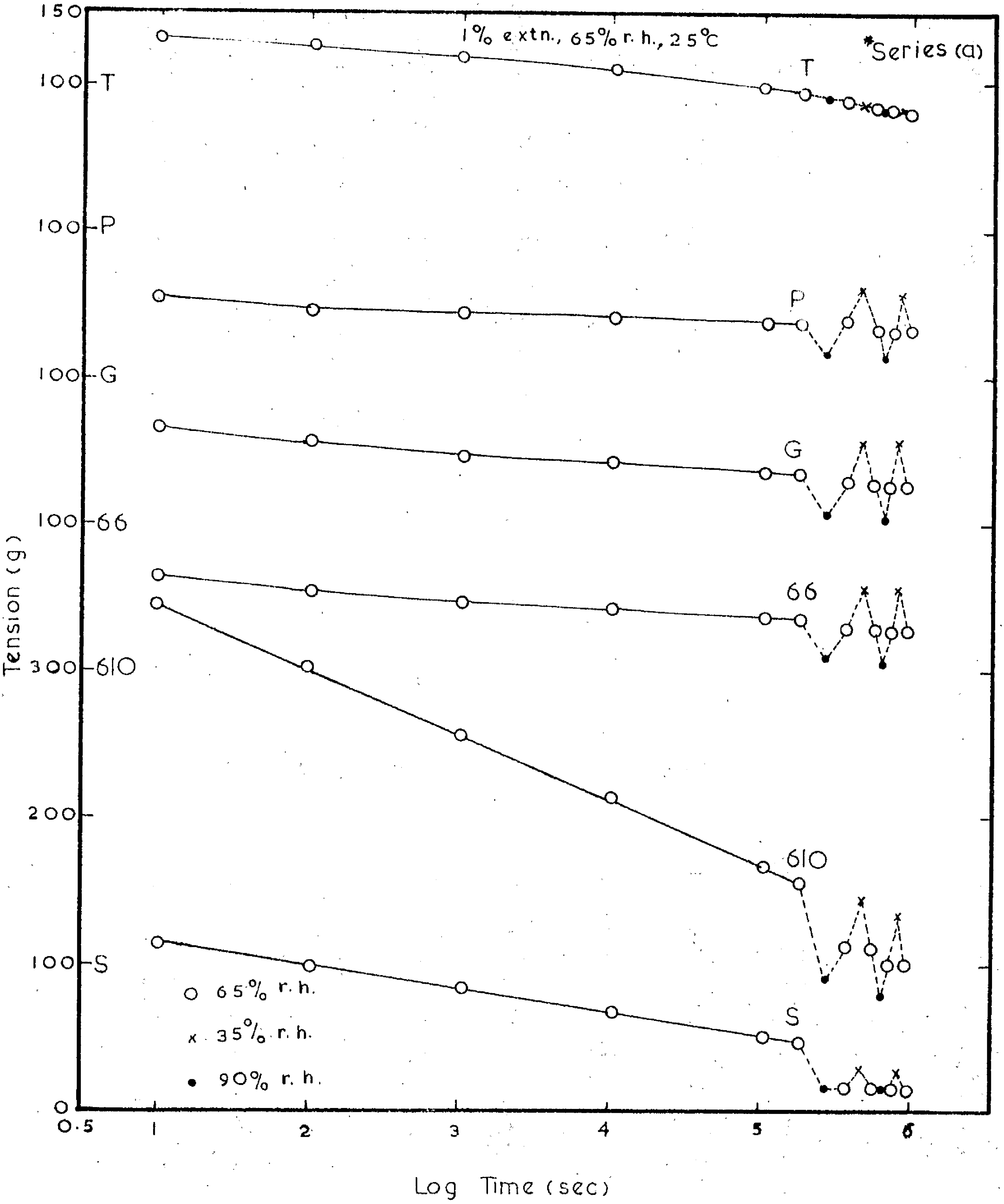
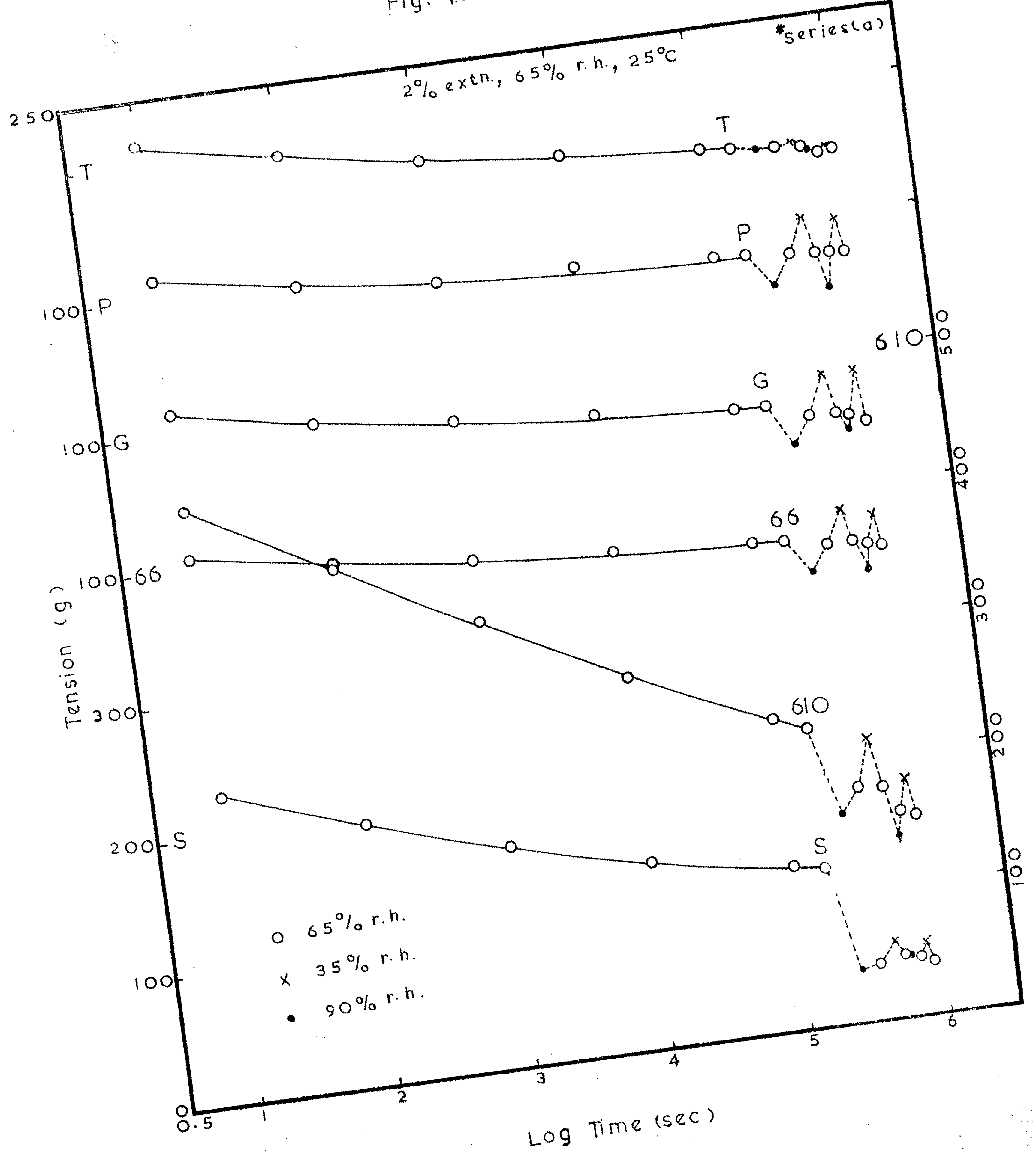

1% extn., 65% r.h., 25°C
*Series (a)
Tension (g)
Log Time (sec)
150
100-T
100-P
100-G
100-66
300-610
200
100-S
0
0.5
1
2
3
4
5
6
T
P
G
66
610
S
○ 65% r.h.
x 35% r.h.
• 90% r.h.

Fig. 16



*Series (a)
2% extn., 65% r.h., 25°C
T
P
G
66
610
S
250
T
100 P
100 G
100 66
300
200 S
100
0
Tension (g)
500
400
300
200
100
610
0.5
1
2
3
4
5
6
Log Time (sec)
○ 65% r.h.
x 35% r.h.
• 90% r.h.

Fig. 17

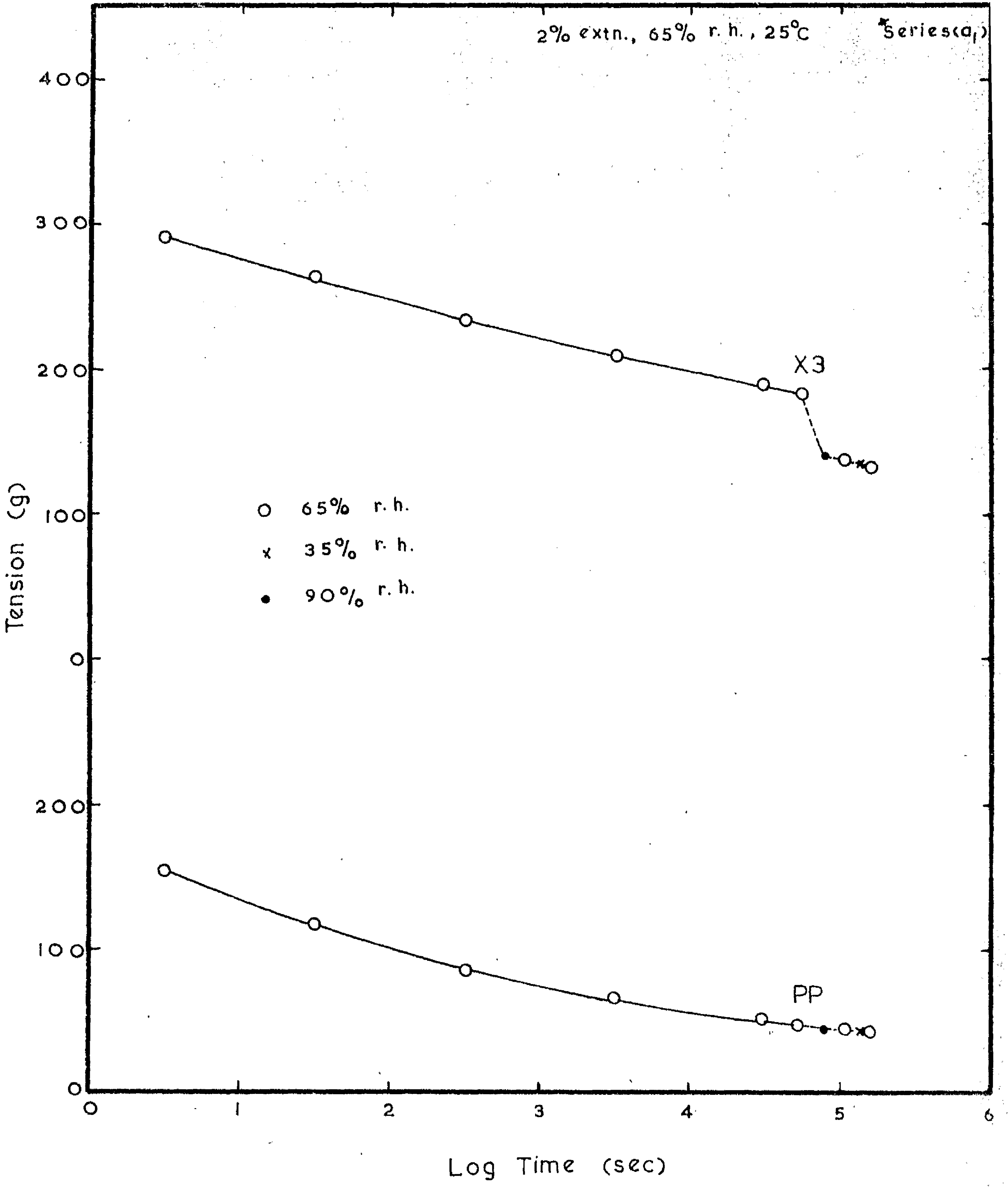

2% extn., 65% r.h., 25°C
*Series(a_1)
X3
PP
○ 65% r.h.
x 35% r.h.
● 90% r.h.
Tension (g)
400
300
200
100
0
200
100
0
0
1
2
3
4
5
6
Log Time (sec)

Fig. 18

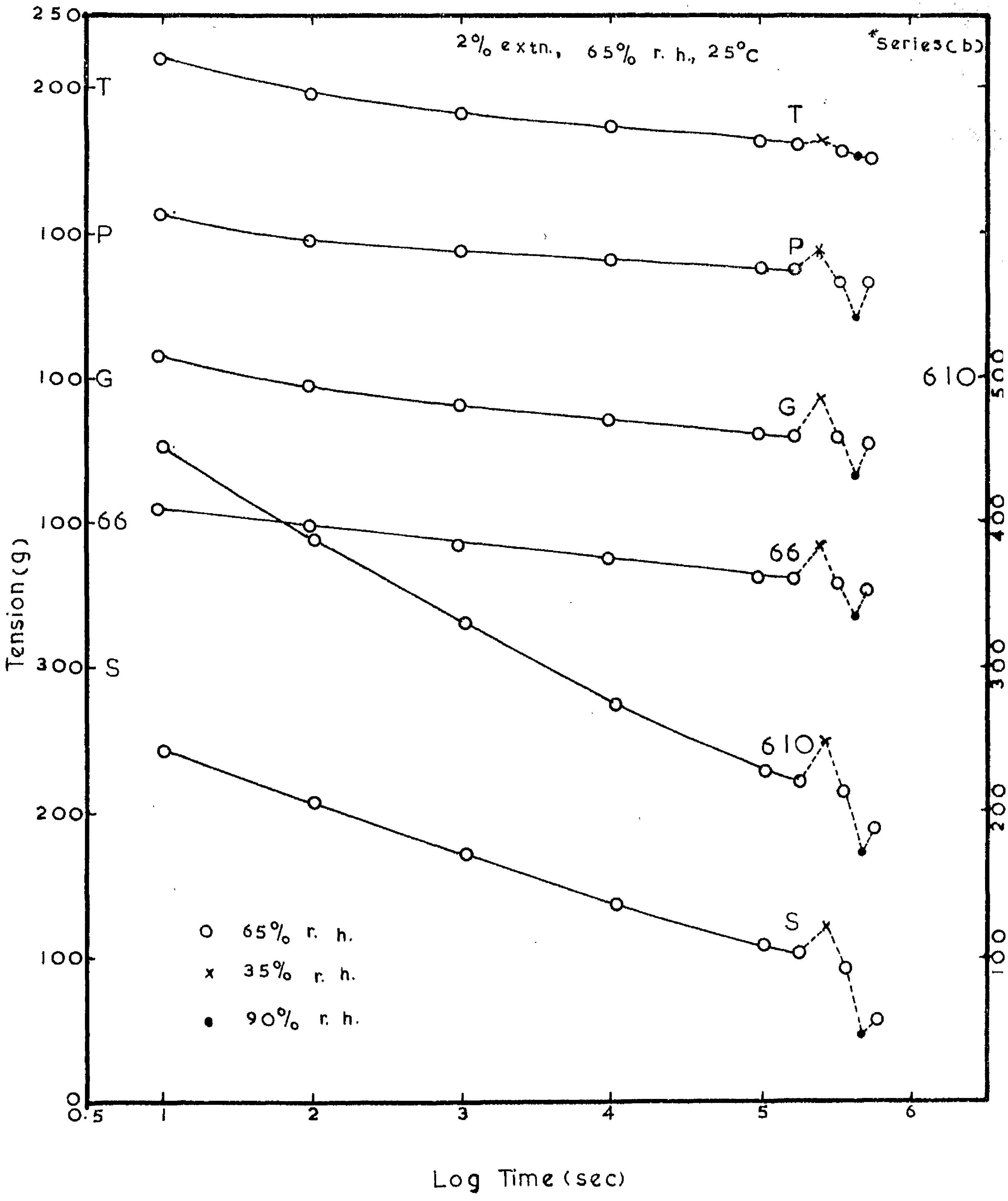
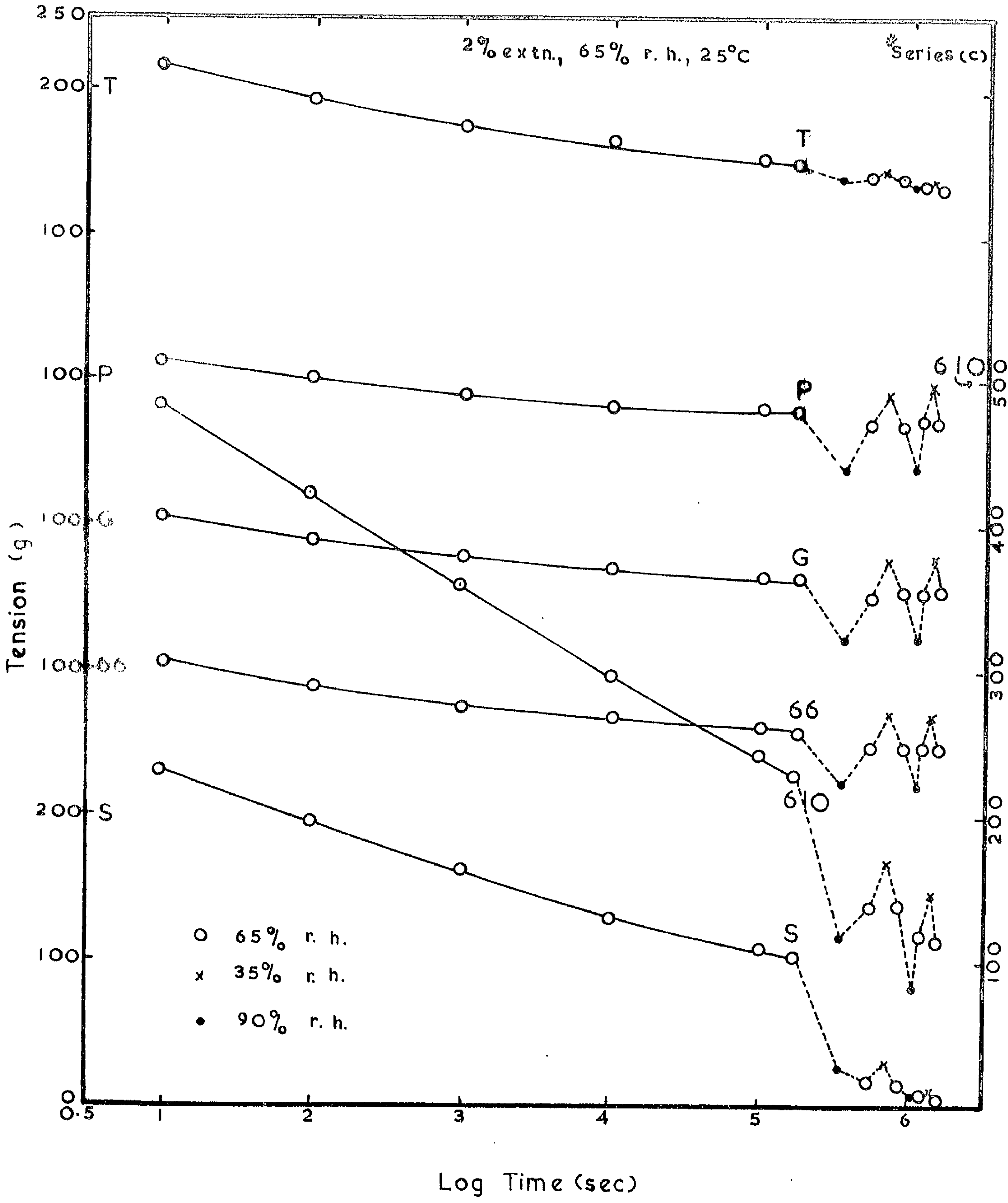

2% extn., 65% r. h., 25°C
*Series(b)
250
200-T
100-P
100-G
100-66
300-S
200
100
0
0.5
1
2
3
4
5
6
T
P
G
66
610
S
610
500
400
300
200
100
Tension (g)
Log Time (sec)
○ 65% r. h.
x 35% r. h.
● 90% r. h.

Fig. 19



2% extn., 65% r.h., 25°C
*Series (c)
250
200-T
100
100-P
100-G
100-66
200-S
100
0
0.5
1
2
3
4
5
6
500
400
300
200
100
T
P
G
66
610
610
S
○ 65% r. h.
x 35% r. h.
● 90% r. h.
Tension (g)
Log Time (sec)

Fig. 20

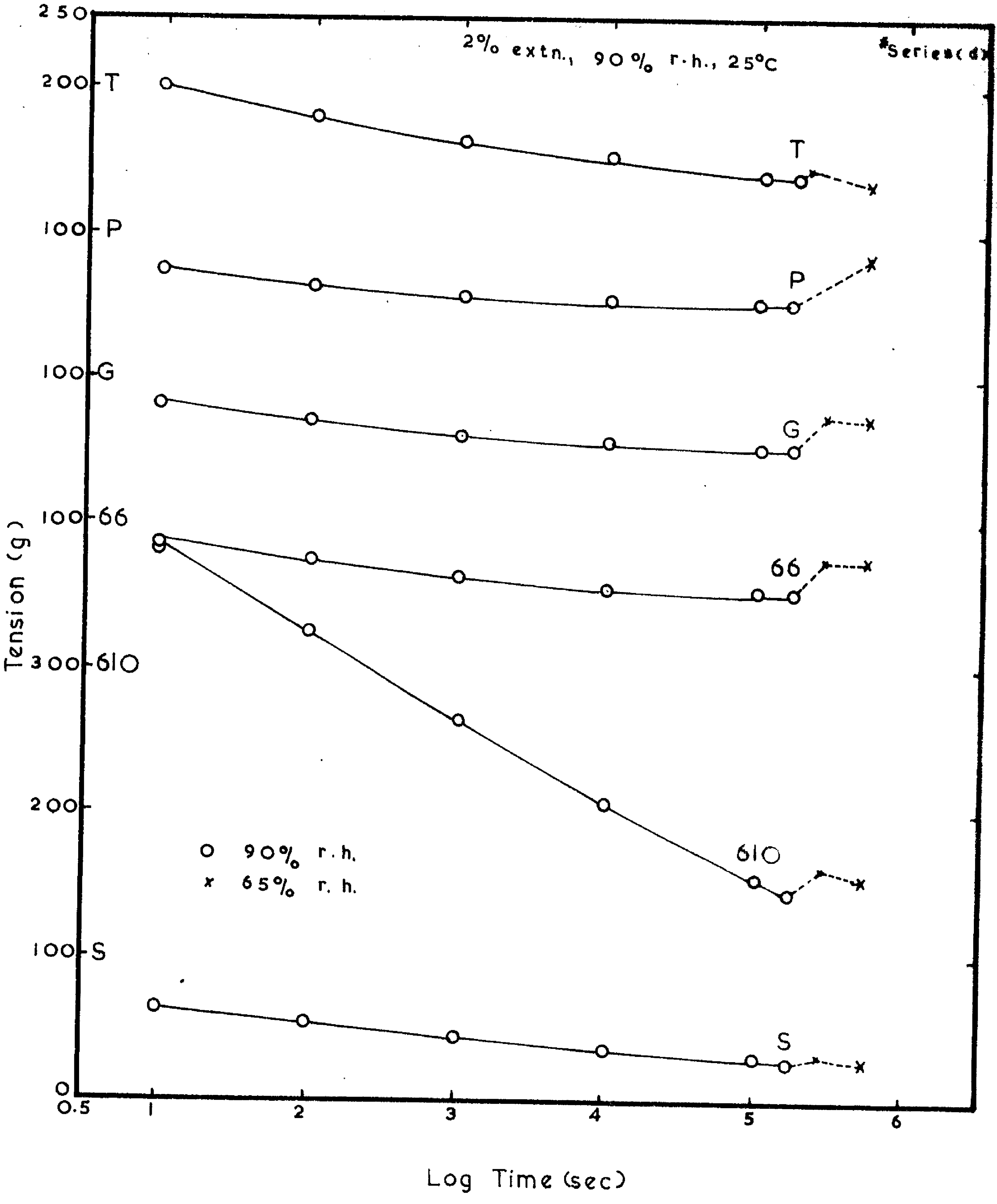

2% extn., 90% r.h., 25°C
*Series(d)
250
200-T
100-P
100-G
100-66
300-610
200
100-S
0
T
P
G
66
610
S
○ 90% r.h.
x 65% r.h.
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)

Fig. 21

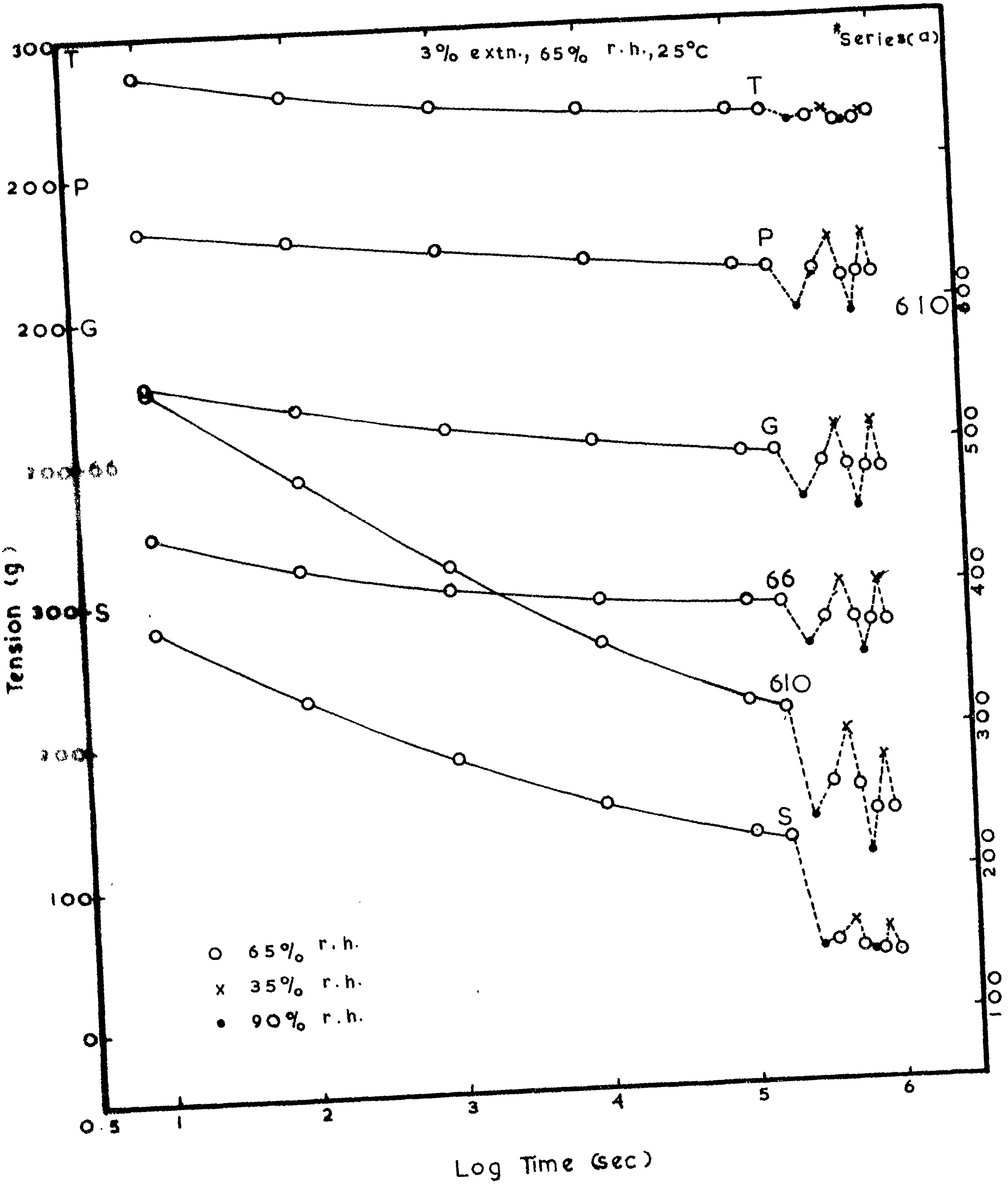
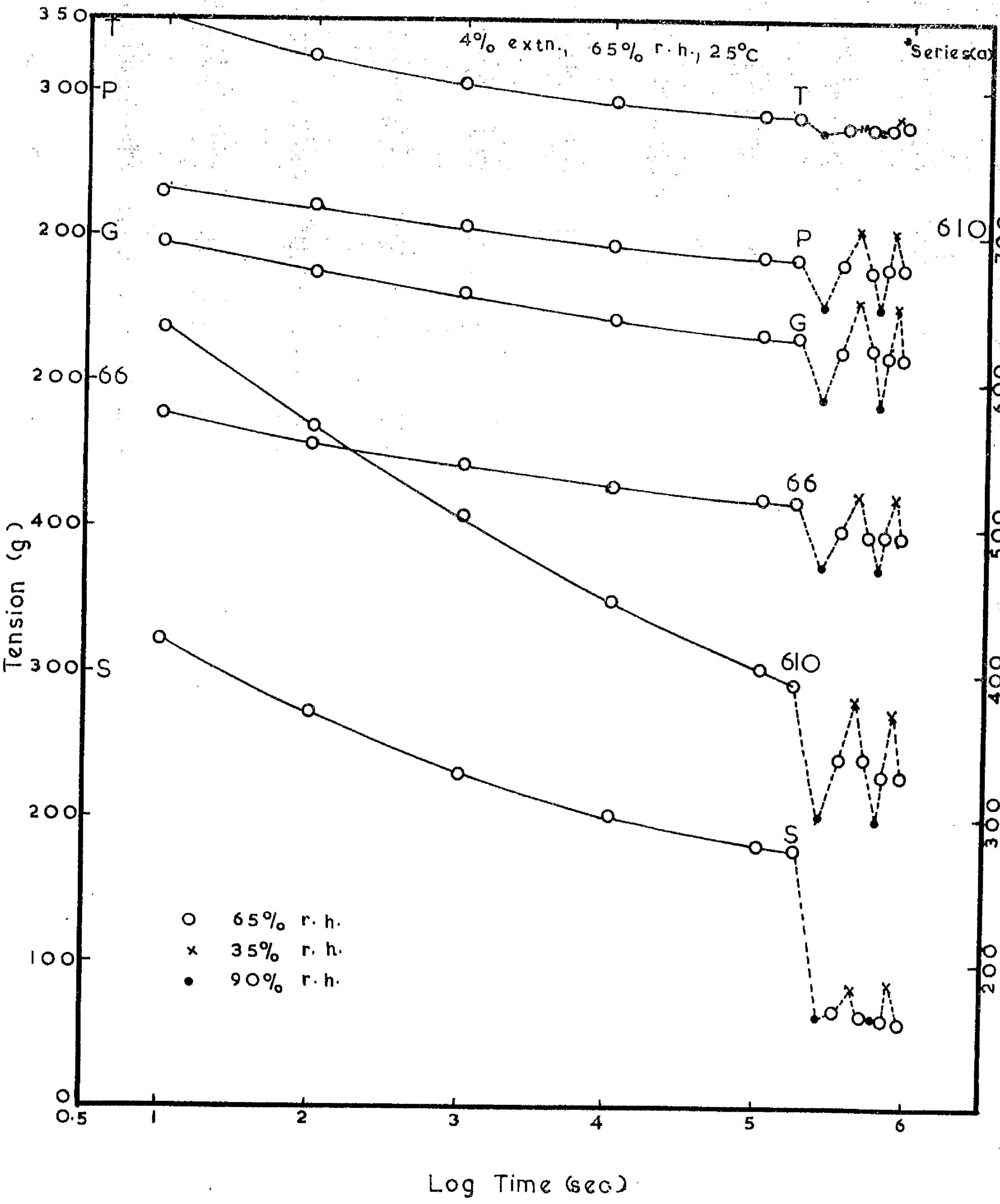
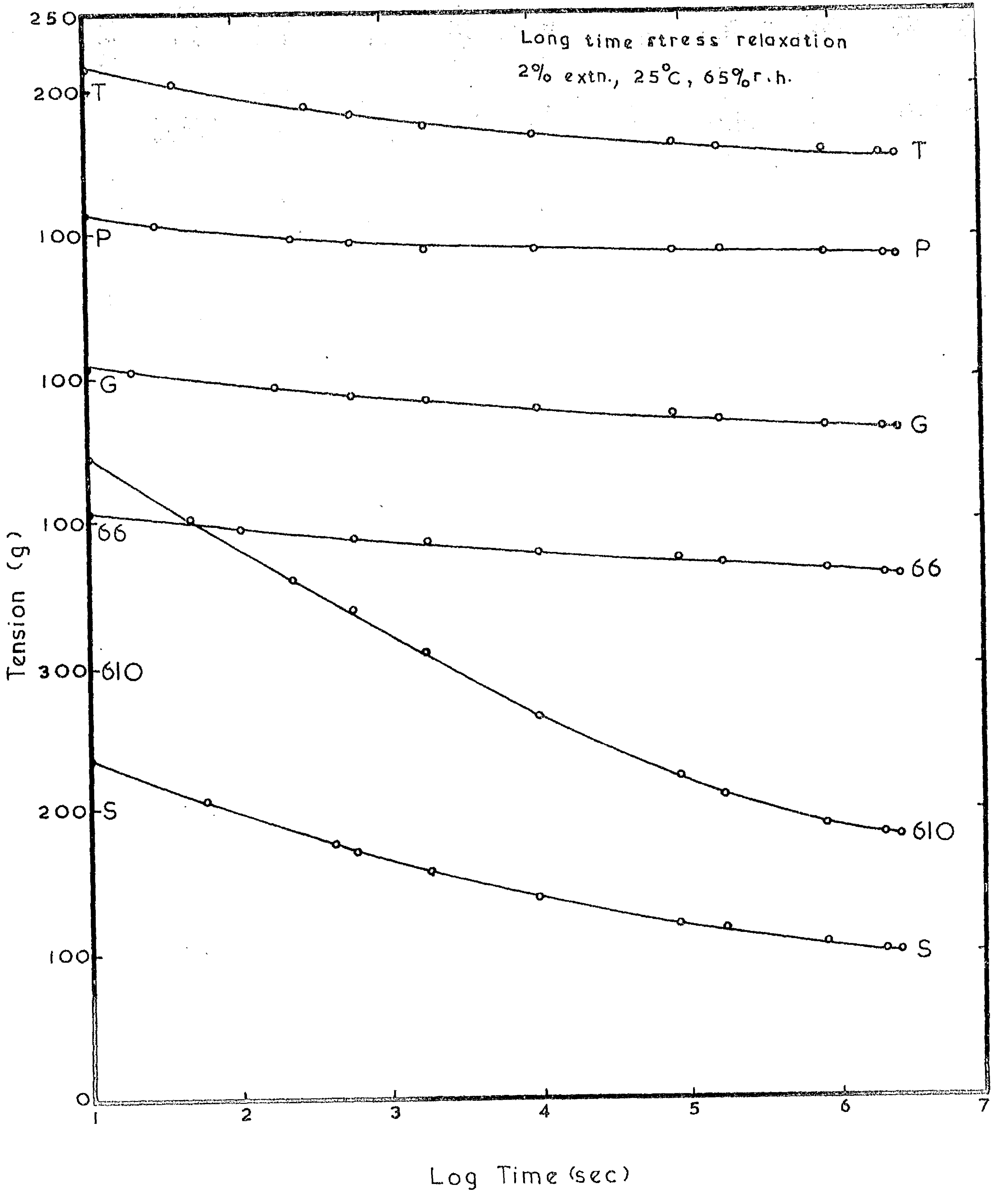

3% extn., 65% r.h., 25°C
*Series(a)
300 T
200 P
200 G
100 66
300 S
200
100
0
T
P
G
66
610
S
610
500
400
300
200
100
0.5
1
2
3
4
5
6
Tension (g)
Log Time (sec)
○ 65% r.h.
x 35% r.h.
• 90% r.h.

Fig 22



4% extn., 65% r.h., 25°C
*Series(a)
Tension (g)
Log Time (sec)
350
300
200
200
400
300
200
100
0
T
P
G
66
S
T
P
G
66
610
S
610
0.5
1
2
3
4
5
6
○ 65% r.h.
× 35% r.h.
● 90% r.h.

Fig. 23



Long time stress relaxation
2% extn., 25°C, 65% r.h.
Tension (g)
250
200-T
100-P
100-G
100-66
300-610
200-S
100
0
T
P
G
66
610
S
1
2
3
4
5
6
7
Log Time (sec)

Fig. 24

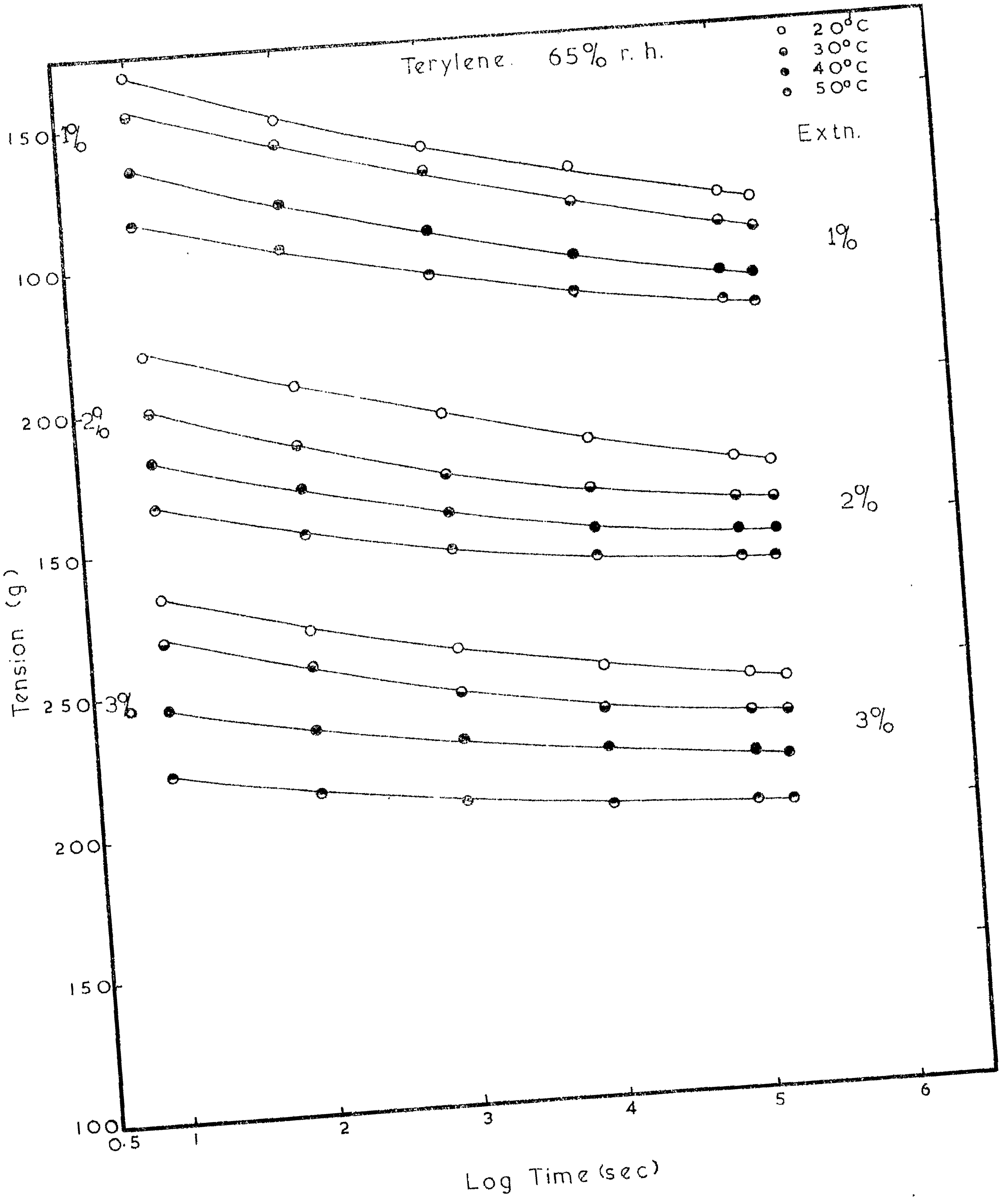

Terylene. 65% r. h.
○ 20°C
◐ 30°C
● 40°C
◐ 50°C
Extn.
1%
2%
3%
150 1%
100
200 2%
150
250 3%
200
150
100
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)

Fig. 25

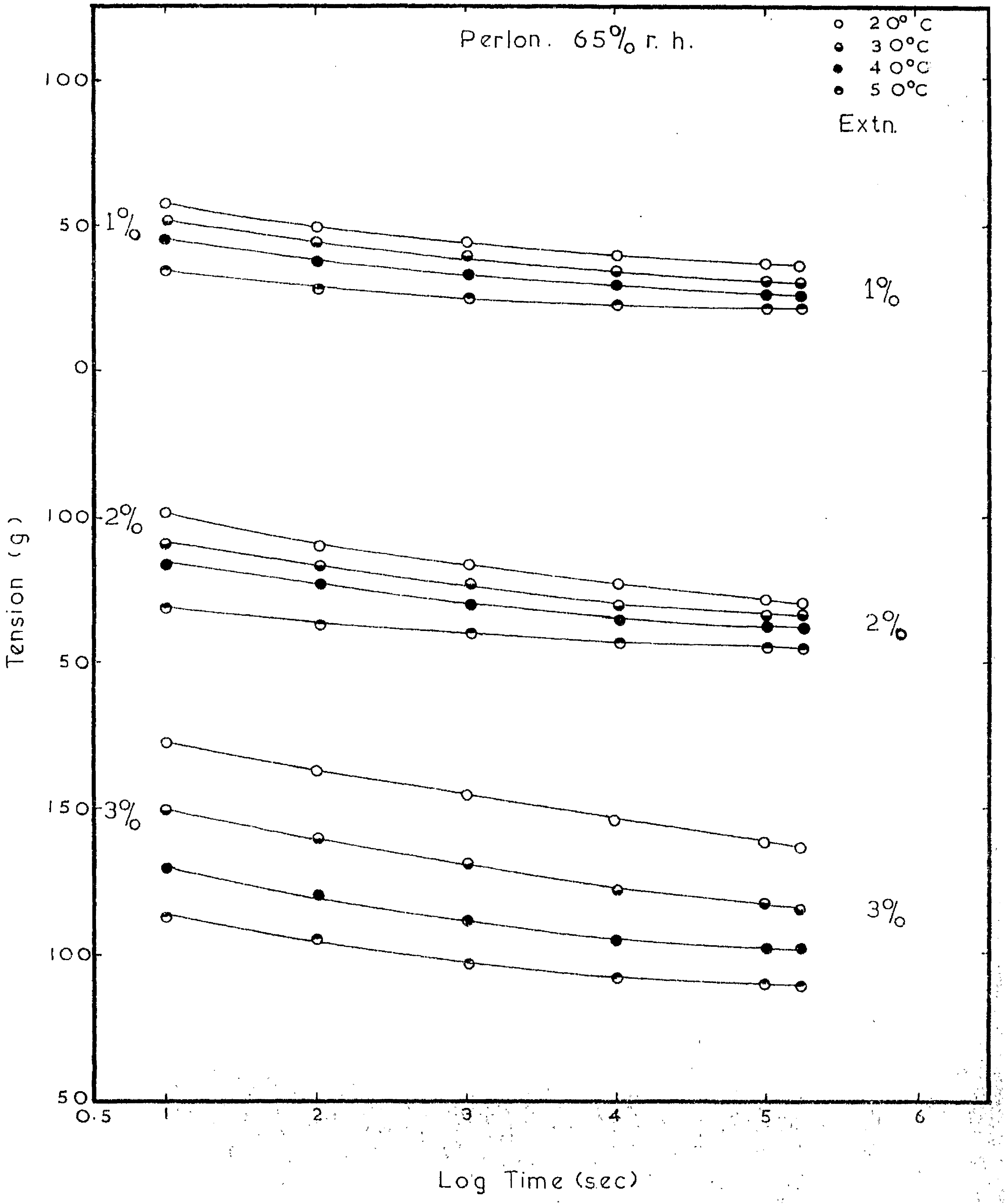
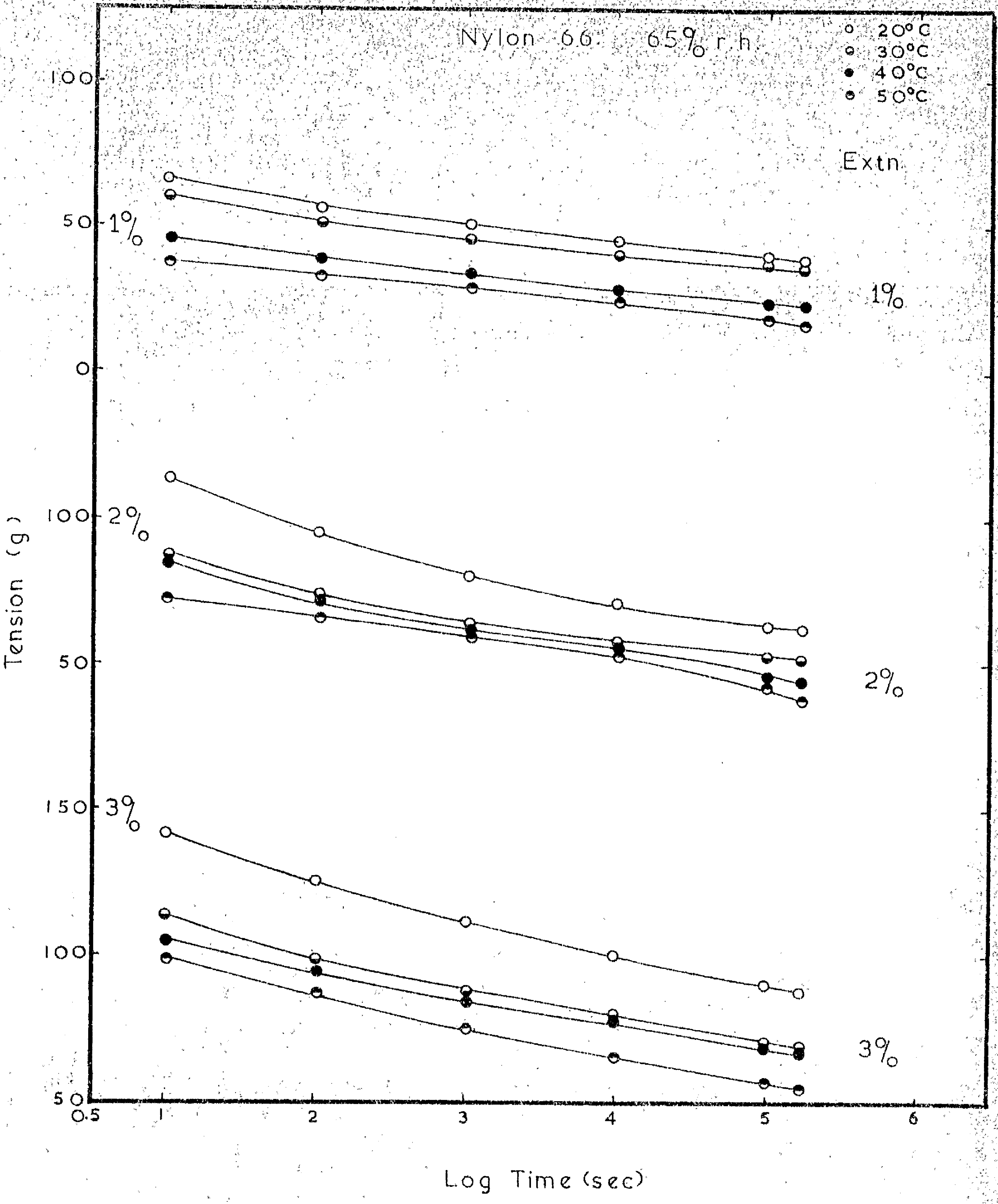

Perlon. 65% r. h.
○ 20°C
◐ 30°C
● 40°C
◒ 50°C
Extn.
1%
2%
3%
1%
2%
3%
100
50
0
100
50
150
100
50
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)

Fig. 26



Nylon 66. 65% r.h.
○ 20°C
○ 30°C
● 40°C
● 50°C
Extn.
1%
2%
3%
100
50
0
100
50
150
100
50
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)

Fig. 27

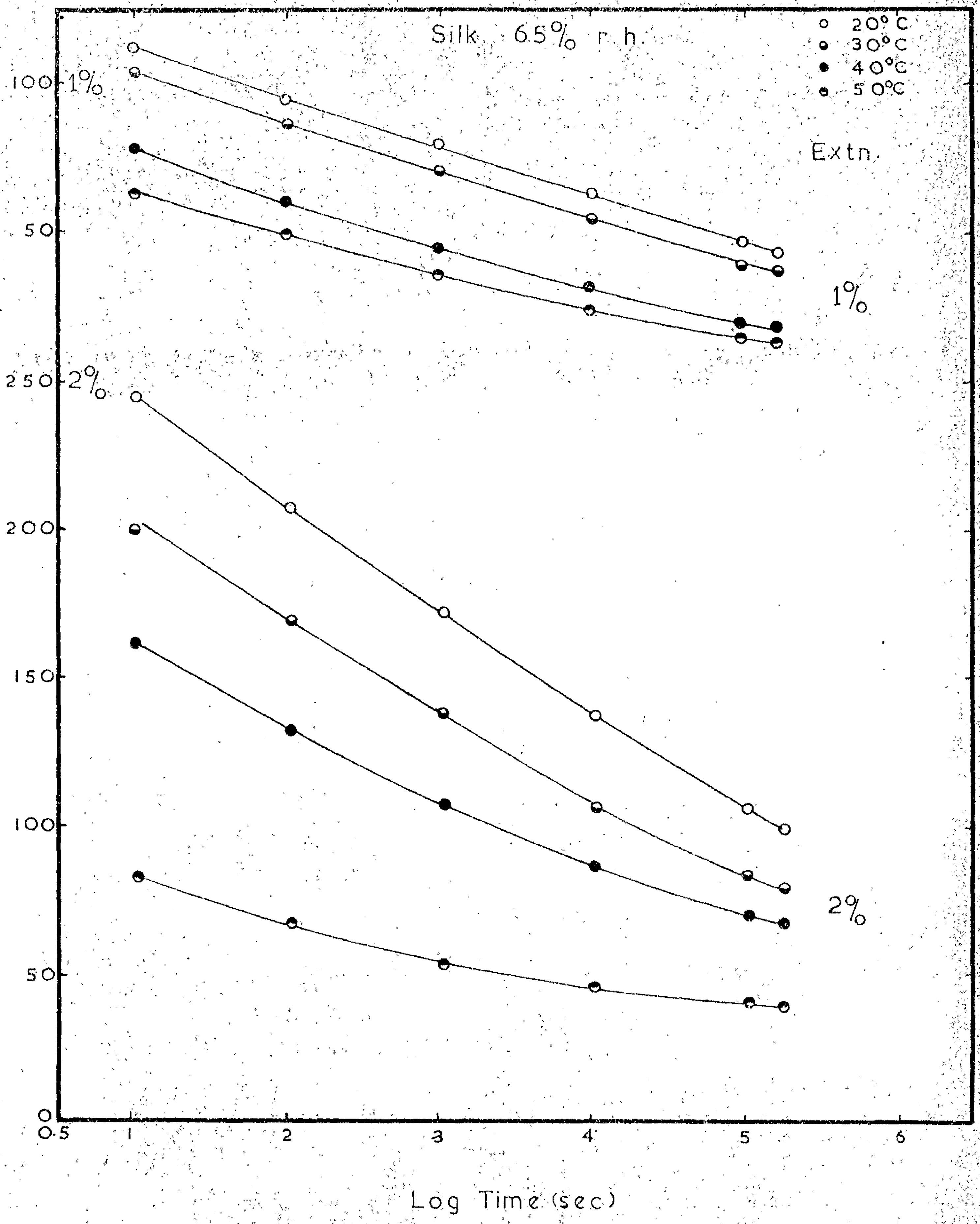
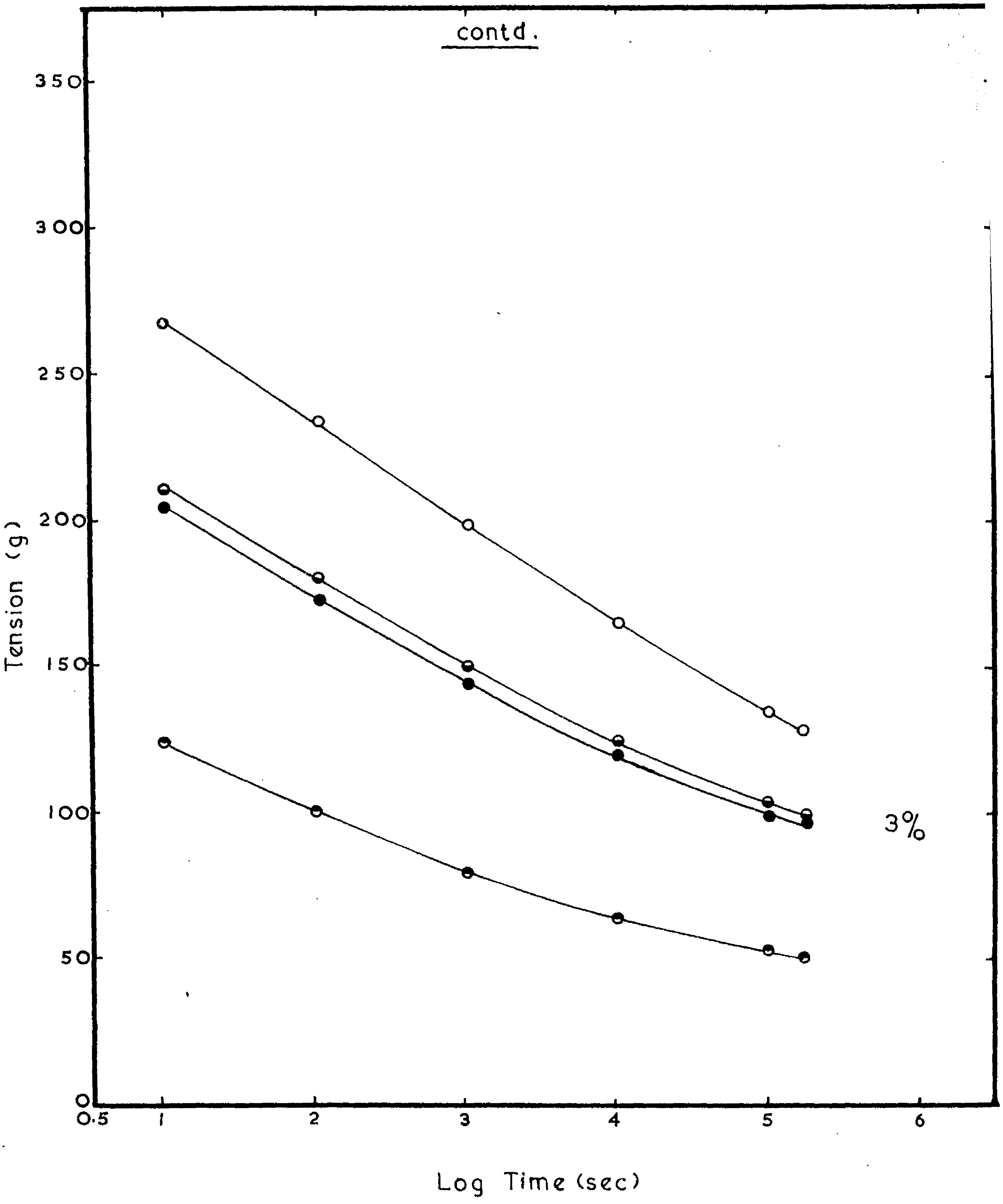

Silk 65% r.h.
○ 20°C
◐ 30°C
● 40°C
◐ 50°C
Extn.
1%
2%
100
1%
50
250
2%
200
150
100
50
0
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)

Fig. 27



contd.
350
300
250
200
150
100
50
0
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)
3%

Fig. 28

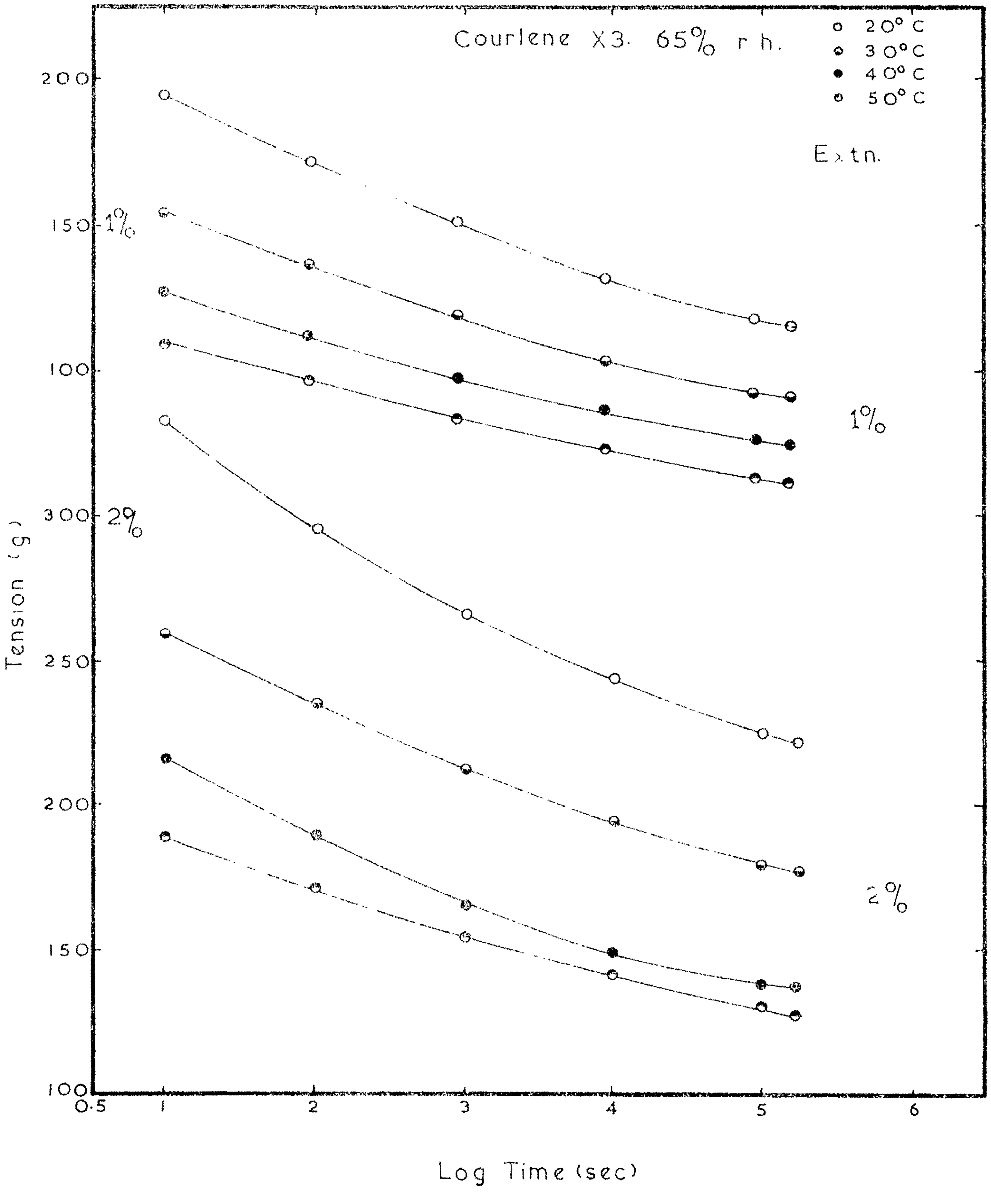

Courlene X3. 65% r.h.
○ 20° C
⊖ 30° C
● 40° C
⊗ 50° C
Extn.
1%
2%
1%
2%
Tension (g)
200
150
100
300
250
200
150
100
Log Time (sec)
0.5
1
2
3
4
5
6

Fig. 28

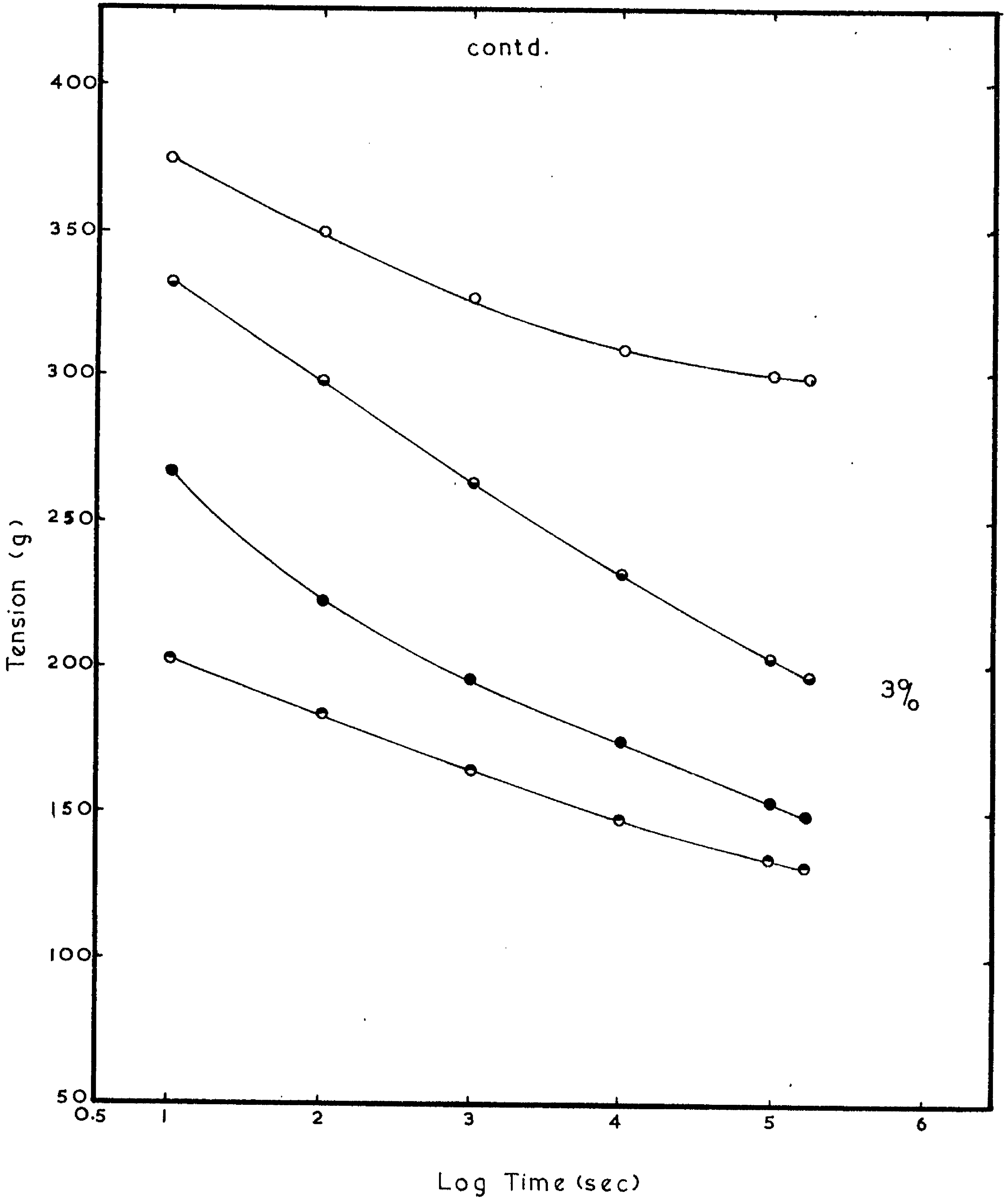
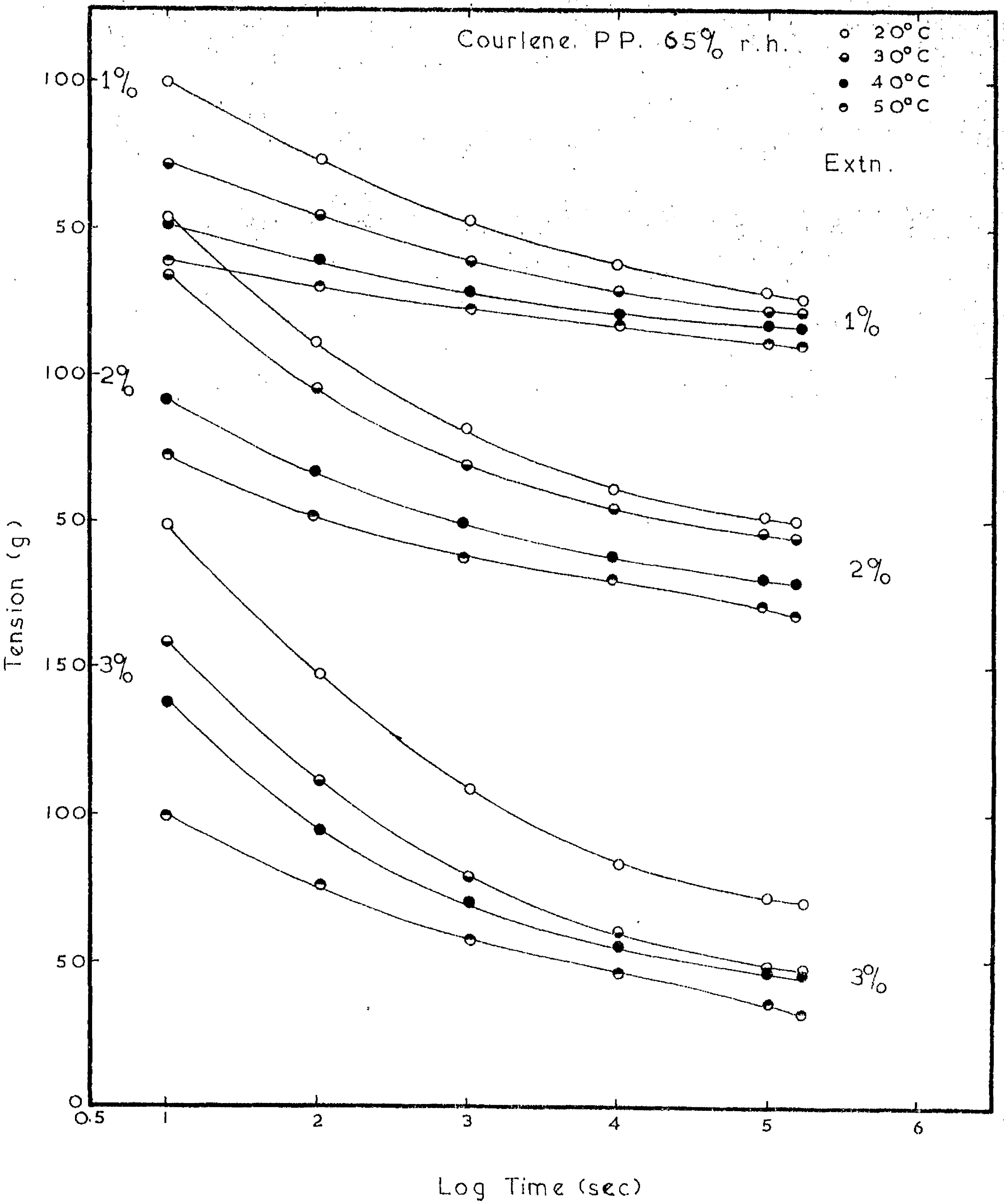

contd.
Tension (g)
400
350
300
250
200
150
100
50
0.5
1
2
3
4
5
6
Log Time (sec)
3%

Fig. 29



Courlene. P.P. 65% r.h.
○ 20°C
◐ 30°C
● 40°C
◒ 50°C
Extn.
1%
2%
3%
100
50
100
50
150
100
50
0
1%
2%
3%
Tension (g)
0.5
1
2
3
4
5
6
Log Time (sec)

Fig. 30

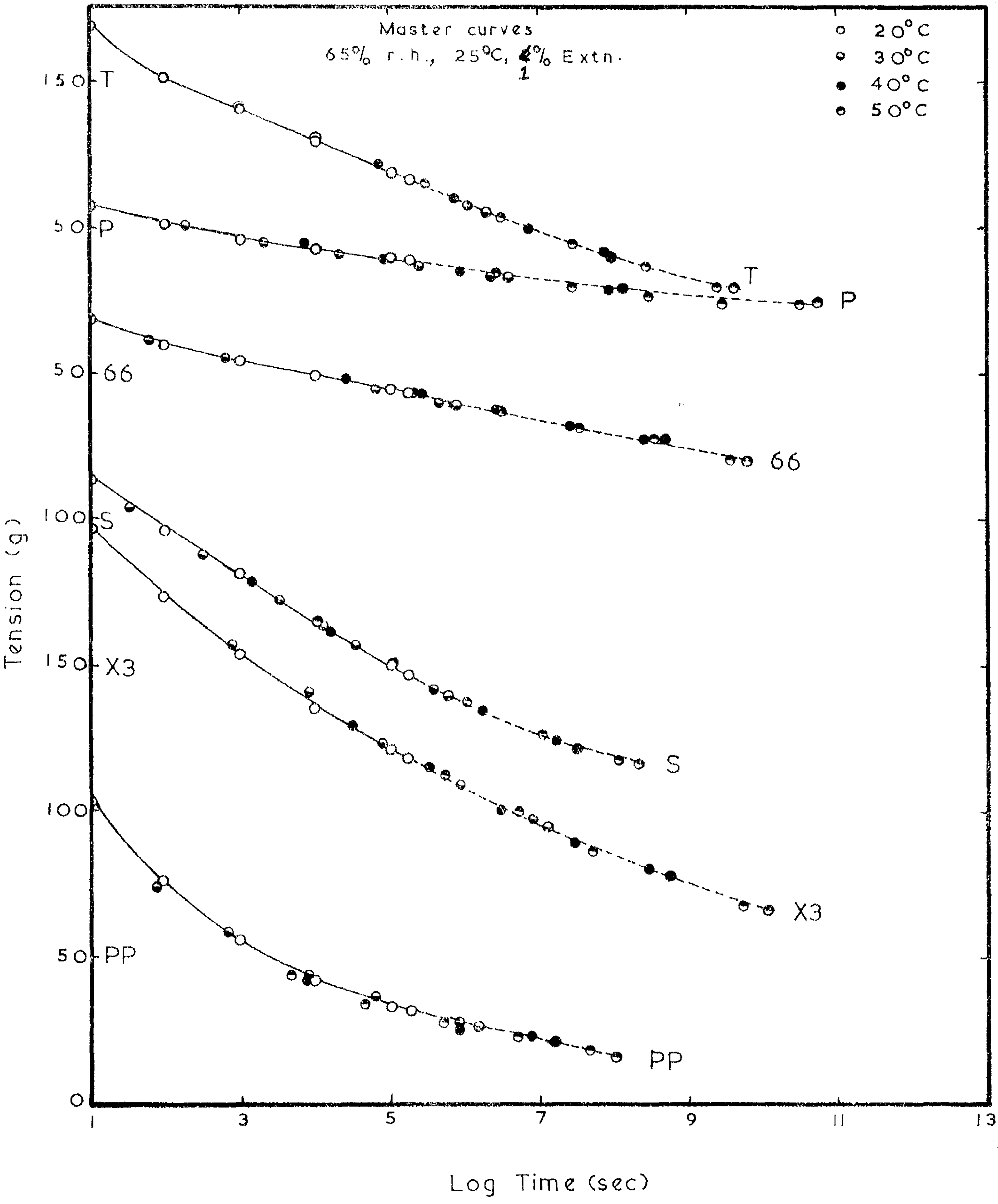
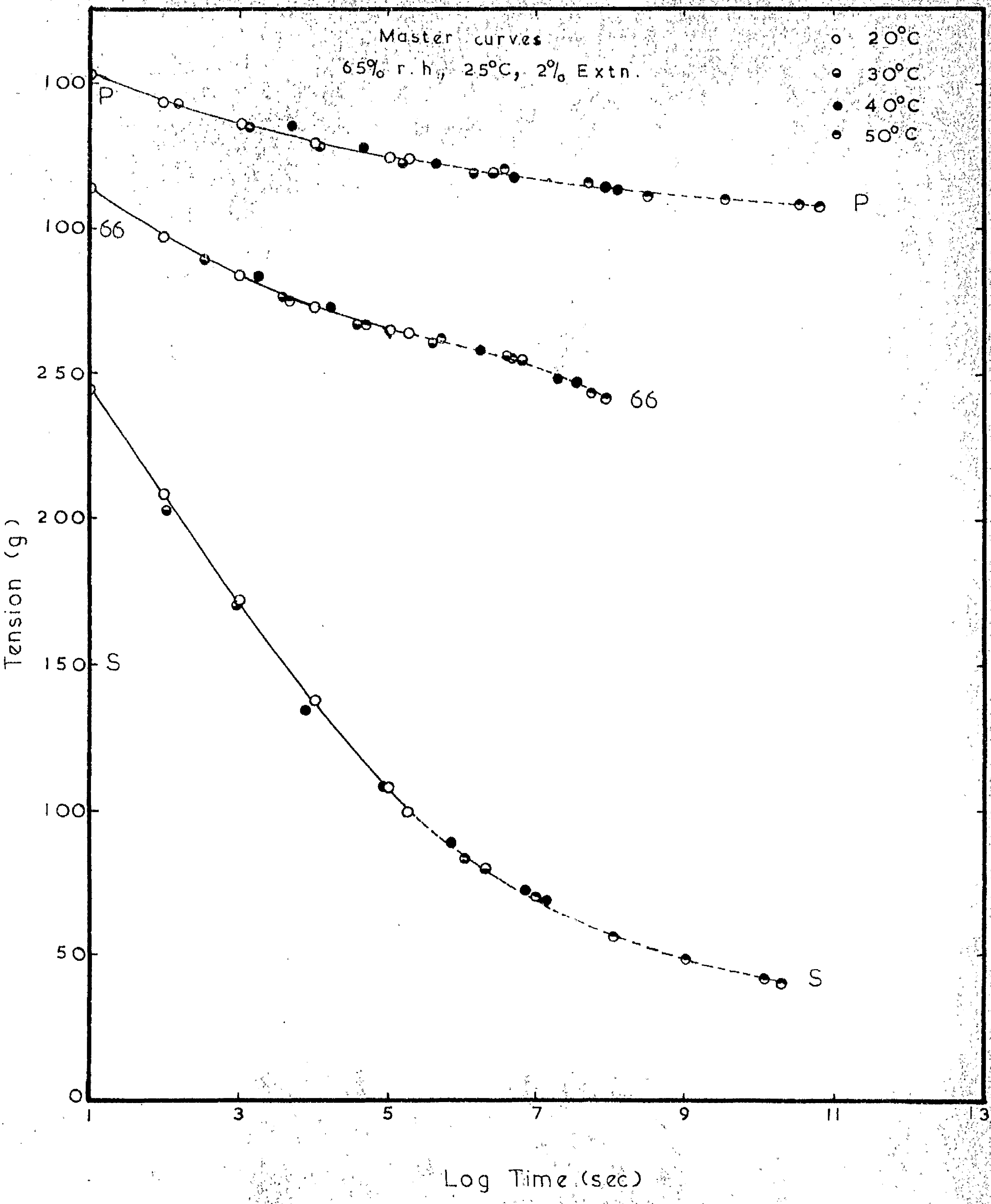

Master curves
65% r.h., 25°C, 4% Extn.
1
○ 20°C
◐ 30°C
● 40°C
◑ 50°C
150 T
50 P
50 66
100 S
150 X3
100
50 PP
0
T
P
66
S
X3
PP
Tension (g)
1
3
5
7
9
11
13
Log Time (sec)

Fig. 31



Master curves
65% r. h., 25°C, 2% Extn.
○ 20°C
◒ 30°C
● 40°C
◓ 50°C
P
P
66
66
S
S
Tension (g)
100
100
250
200
150
100
50
0
1
3
5
7
9
11
13
Log Time (sec)

Fig. 32

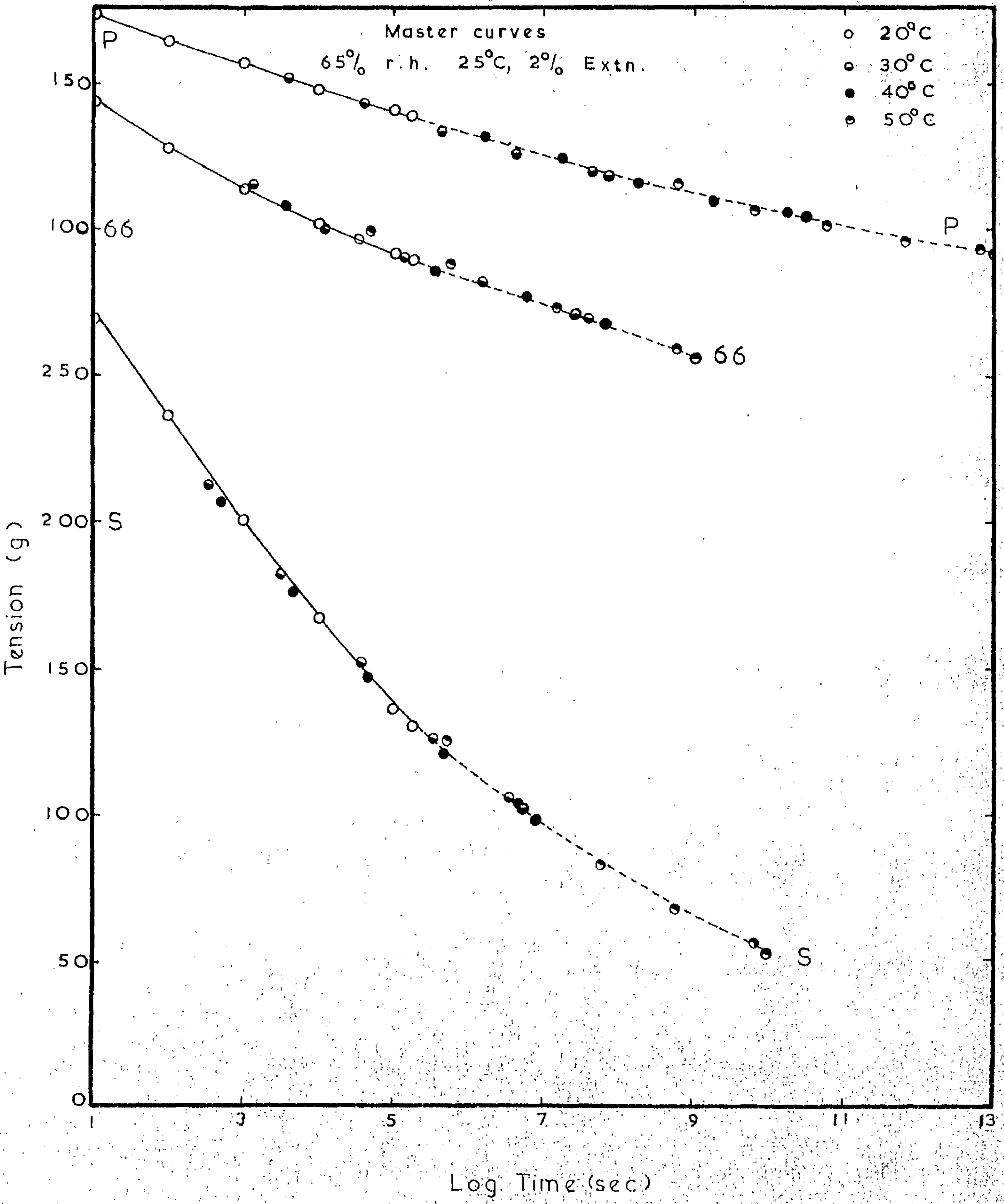
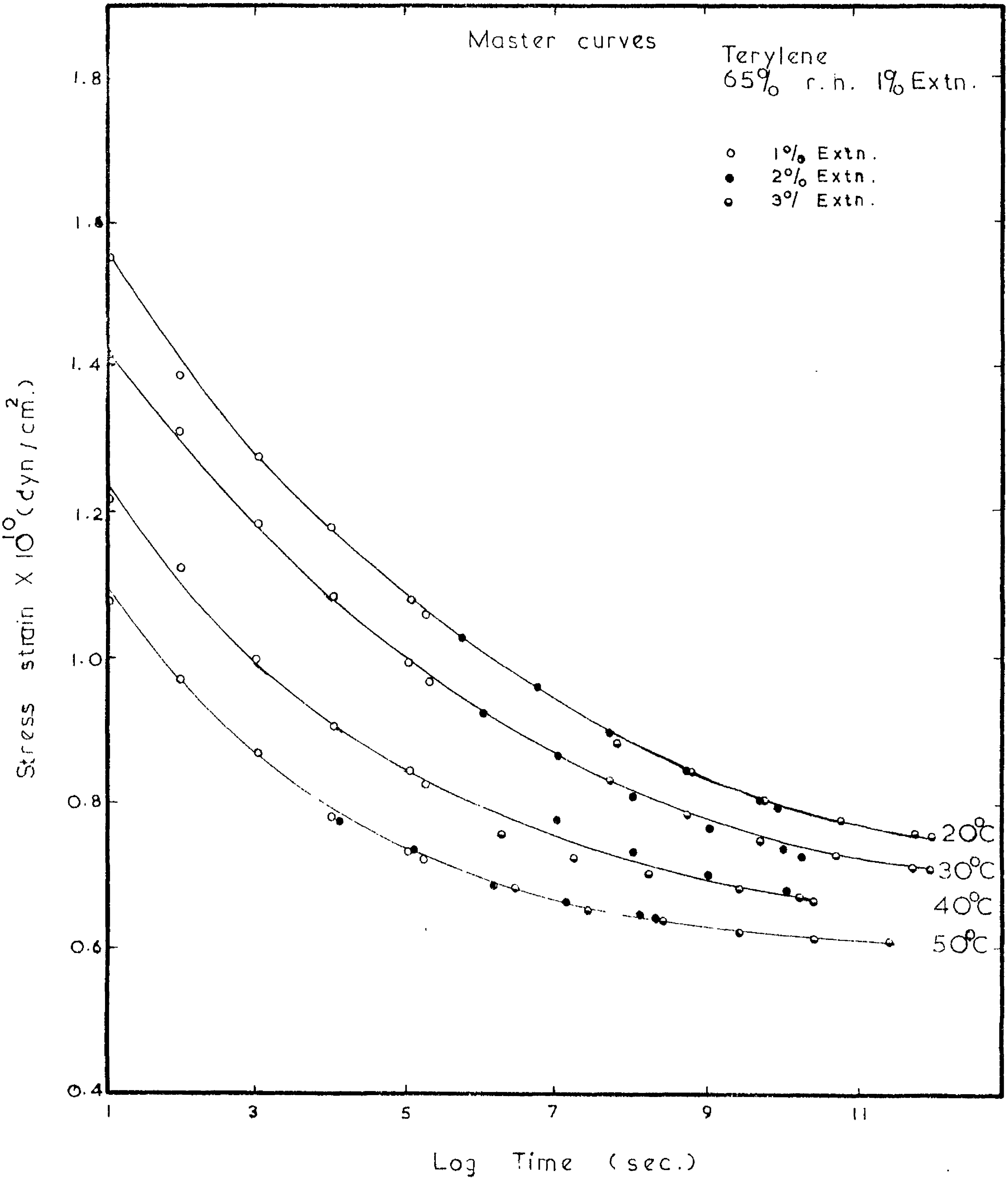

Master curves
65% r.h. 25°C, 2% Extn.
○ 20°C
◐ 30°C
● 40°C
◒ 50°C
P
P
66
66
S
S
150
100
250
200
150
100
50
0
Tension (g)
1
3
5
7
9
11
13
Log. Time (sec)

Fig. 33



Master curves
Terylene
65% r.h. 1% Extn.
○ 1% Extn.
● 2% Extn.
◐ 3% Extn.
Stress strain X 10^{10} (dyn/cm^2.)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
1
3
5
7
9
11
Log Time (sec.)
20°C
30°C
40°C
50°C

Fig. 34

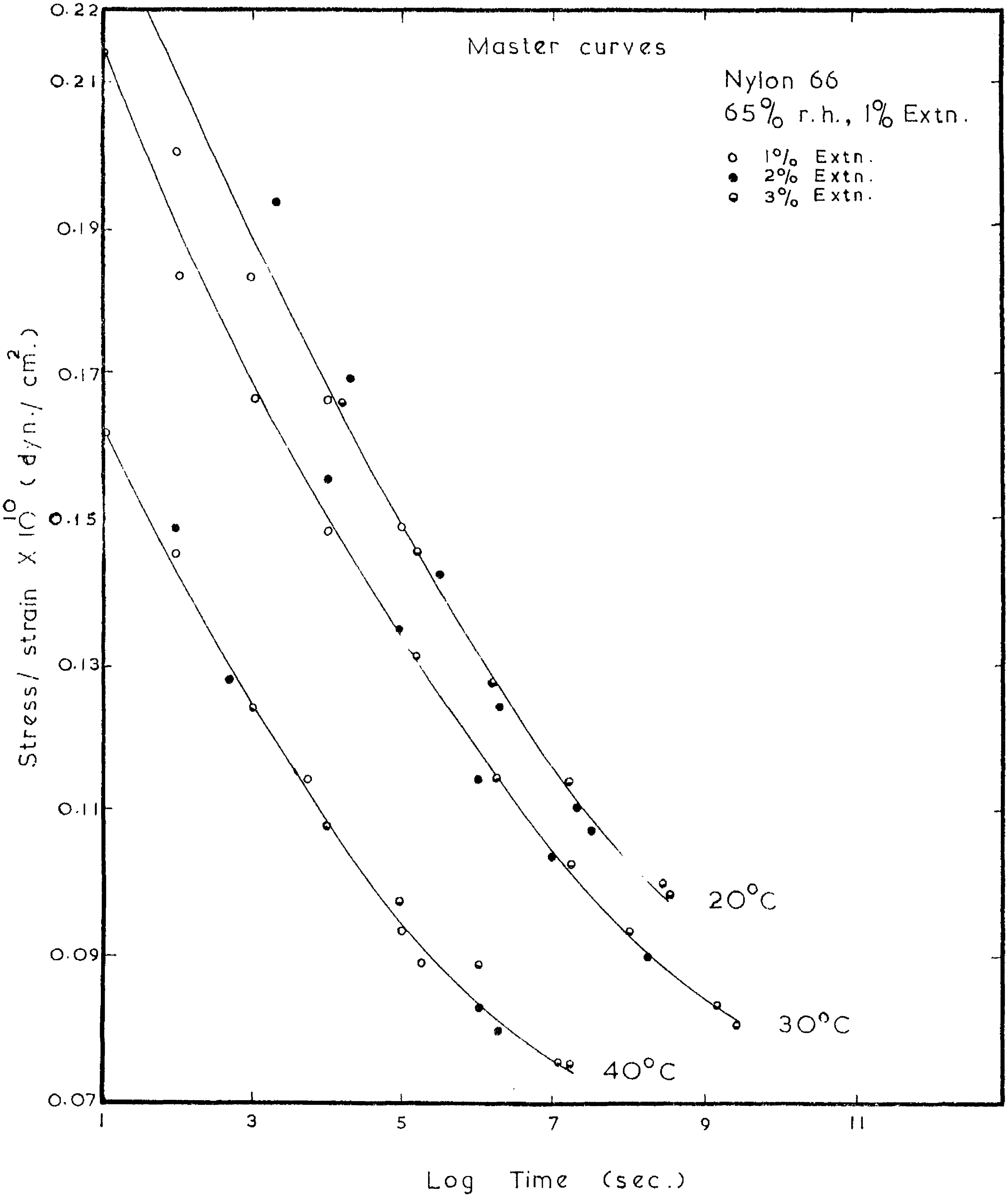
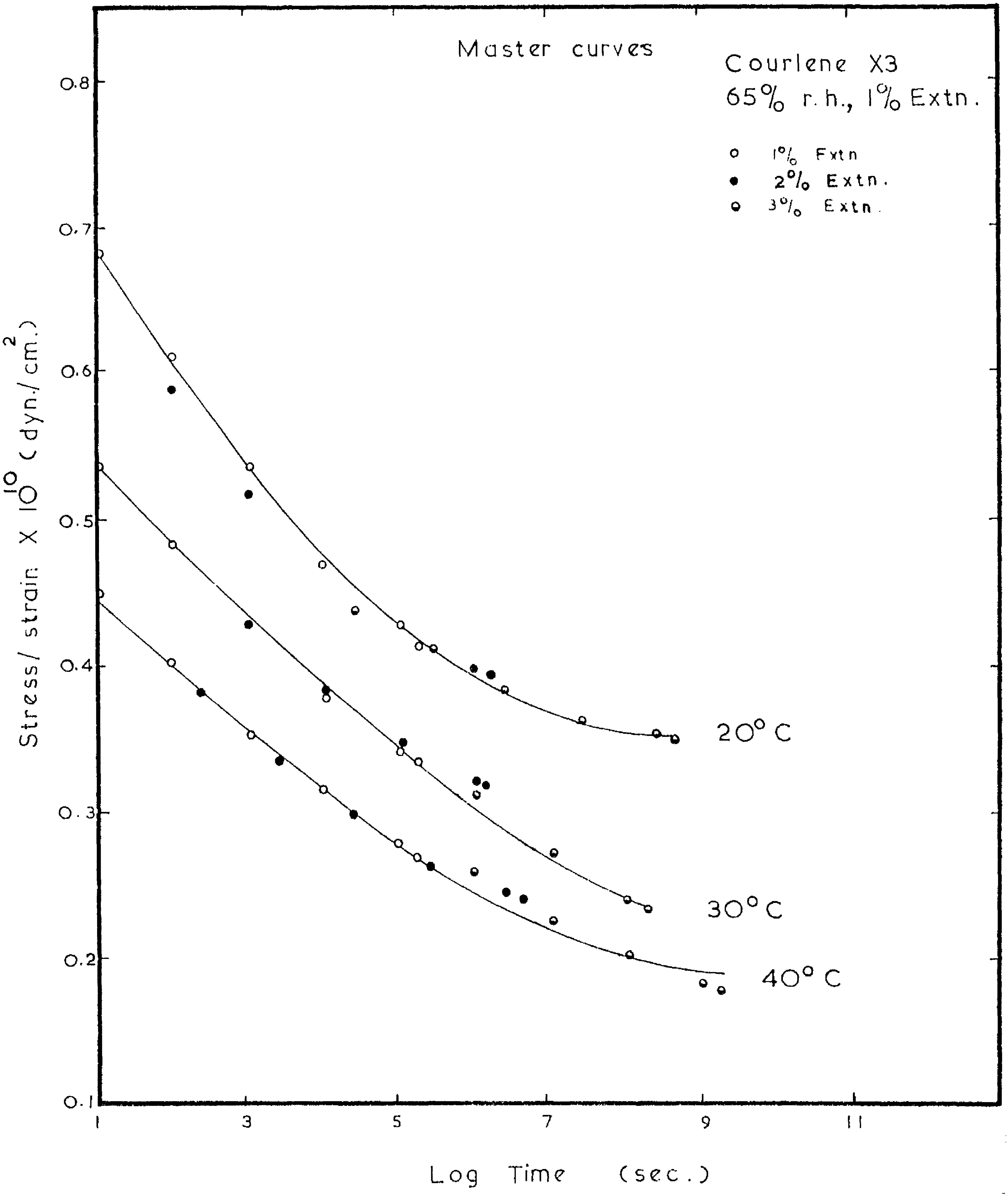
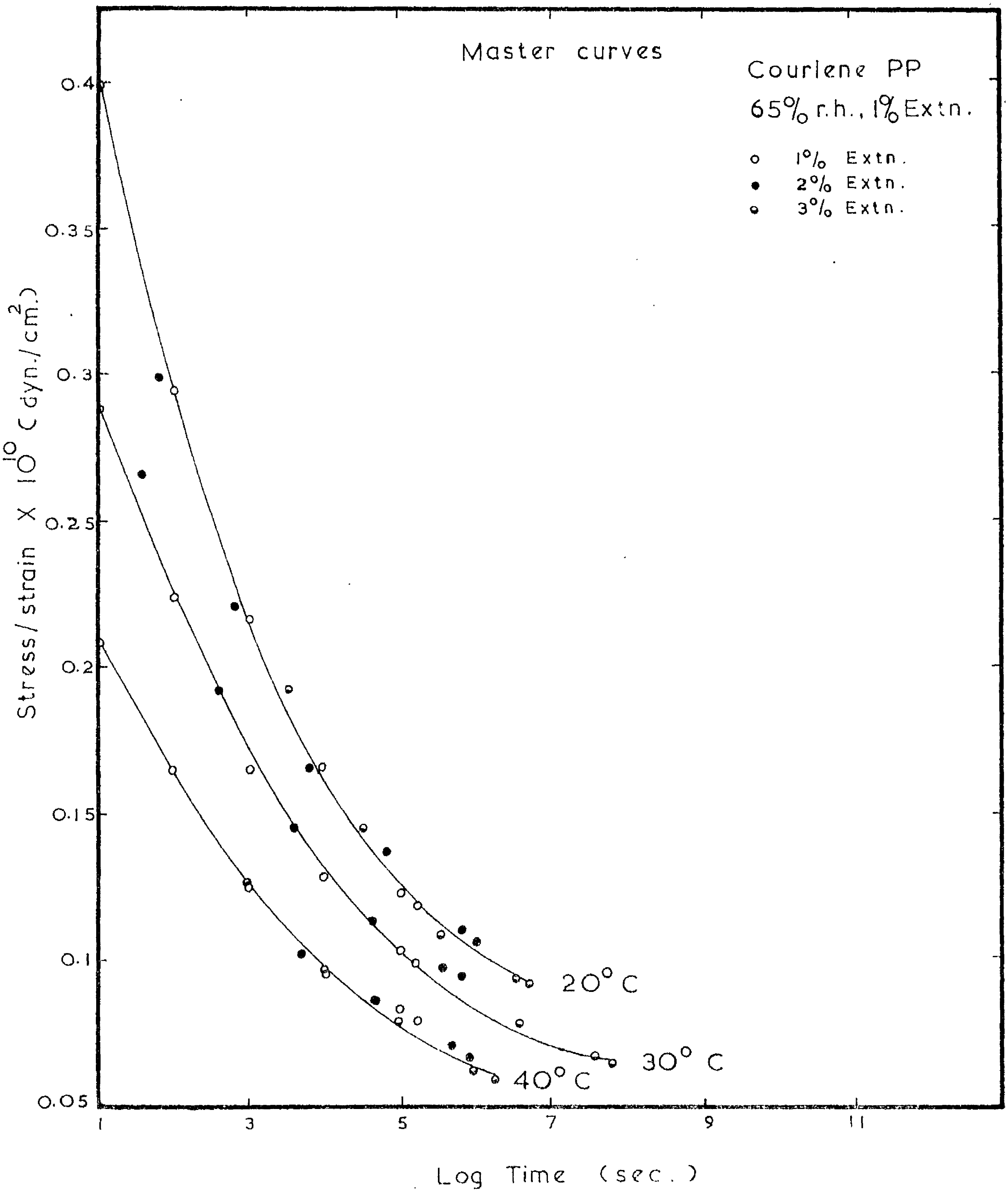

Master curves
Nylon 66
65% r.h., 1% Extn.
○ 1% Extn.
● 2% Extn.
◐ 3% Extn.
20°C
30°C
40°C
Stress / strain X 10^10 (dyn./cm.^2)
0.22
0.21
0.19
0.17
0.15
0.13
0.11
0.09
0.07
1
3
5
7
9
11
Log Time (sec.)

Fig. 35



Master curves
Courlene X3
65% r.h., 1% Extn.
○ 1% Extn
● 2% Extn.
◐ 3% Extn.
20° C
30° C
40° C
Stress/ strain X 10^10 (dyn./cm.^2)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
1
3
5
7
9
11
Log Time (sec.)

Fig. 36



Master curves
Courlene PP
65% r.h., 1% Extn.
○ 1% Extn.
● 2% Extn.
◐ 3% Extn.
20° C
30° C
40° C
Stress / strain X 10^10 (dyn./cm.^2)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
1
3
5
7
9
11
Log Time (sec.)

Fig. 37

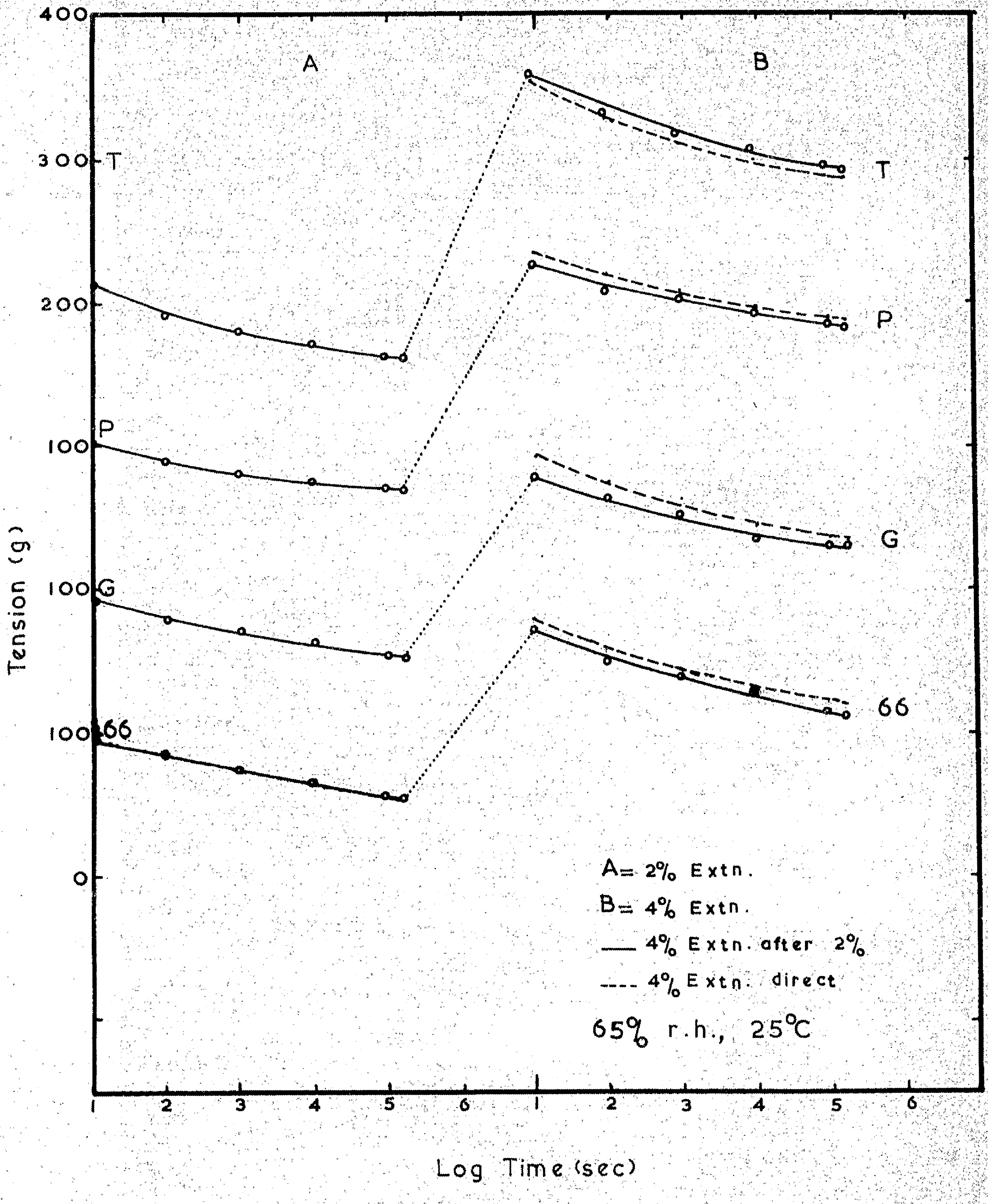
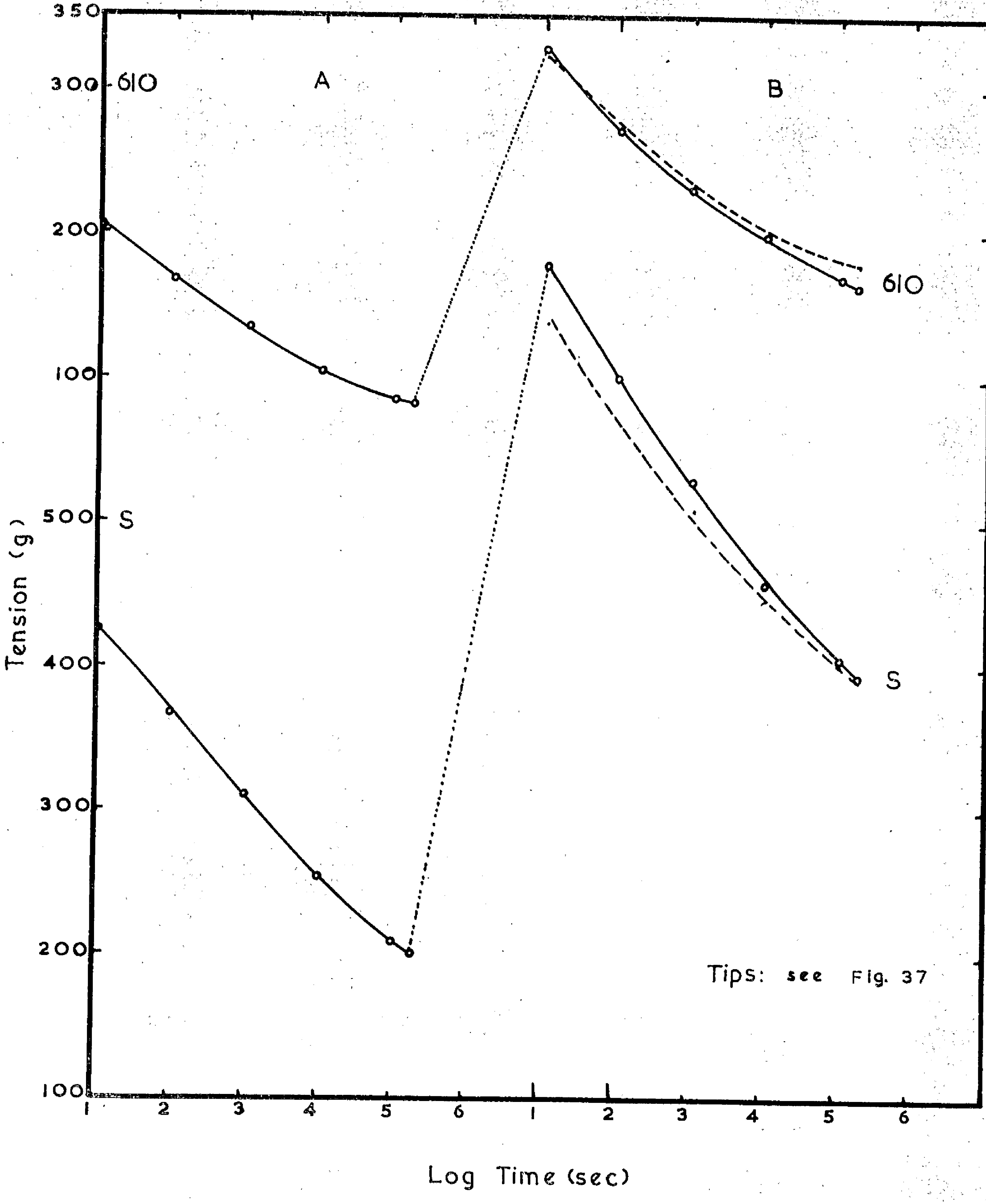
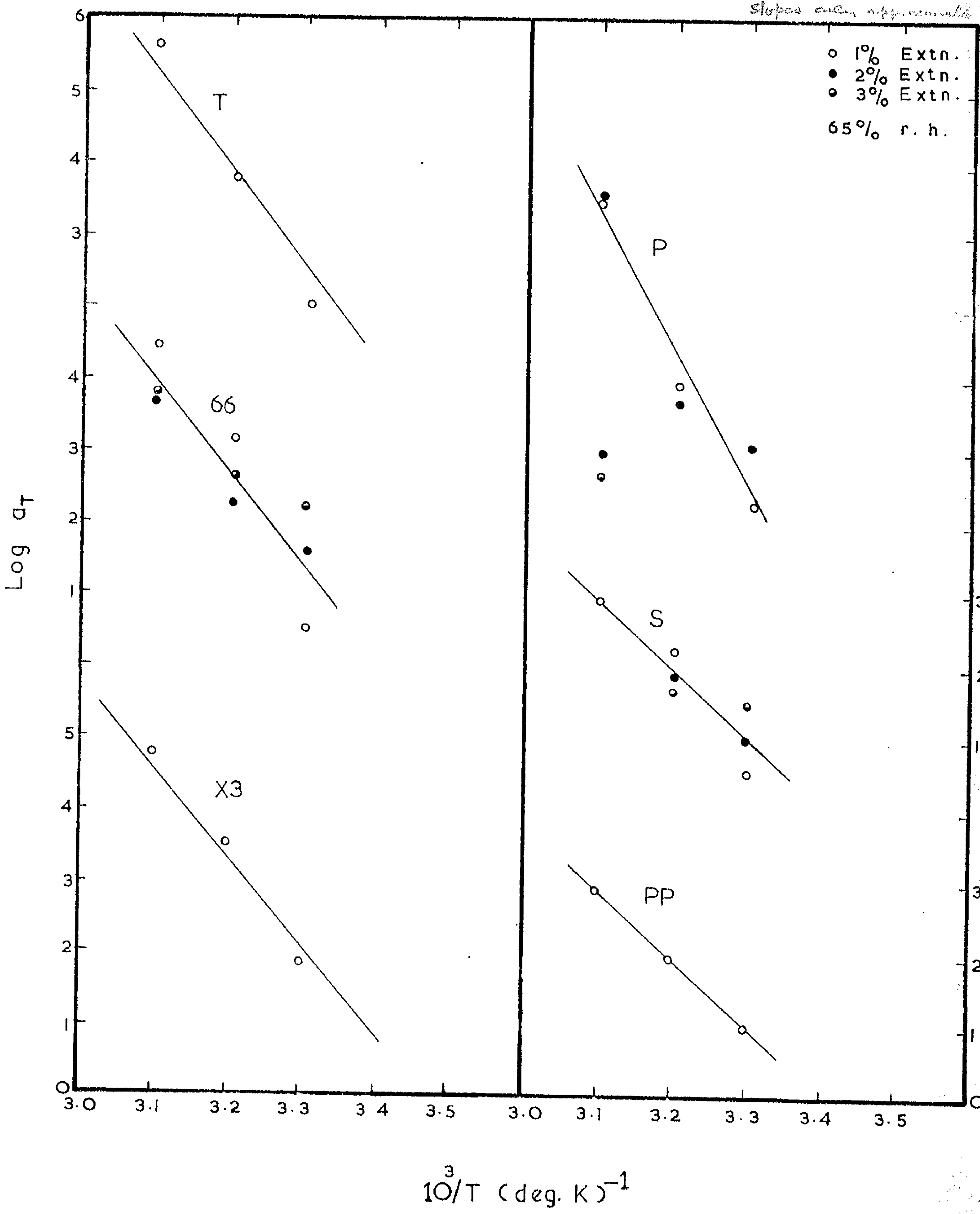

A
B
T
P
G
66
400
300
200
100
100
100
0
Tension (g)
1
2
3
4
5
6
Log Time (sec)
A= 2% Extn.
B= 4% Extn.
—— 4% Extn. after 2%
---- 4% Extn. direct
65% r.h., 25°C

Fig. 38



350
300
200
100
500
400
300
200
100
610
A
B
610
S
S
Tension (g)
1
2
3
4
5
6
1
2
3
4
5
6
Log Time (sec)
Tips: see Fig. 37

Fig. 39


Slopes only approximate

CHAPTER V

DISCUSSION OF RESULTS

1. Stress relaxation at standard conditions

From the present experimental results in Figs. 1 to 14, it is clear that in the case of Perlon, Grilon, nylon 66 and nylon 610, the initial tension and the shape in the mechanically conditioned specimen is nearly the same as that in its first run. This shows that all these synthetic monofilaments are fully recovered and there will be no temperature rise due to stretching.[17,107,17 There is no permanent set up to 2% constant extension. This has already been proved.[107,178] Terylene shows a slightl smaller initial tension in its mechanically conditioned run than in its first run. This indicates that Terylene shows very little permanent set at 2% extension which, here, has been found out to be roughly 0.01%. This agrees with the permanent set values obtained by Hsu.[107] Another multi-filament twisted material silk, shows considerable difference in the initial tension for the first run and the mechanically conditioned specimen. This is probably due to the increasing permanent set value of silk which is 0.15% at 2% extension and also due to the high twist (see Table 1). The permanent set of silk at 2% is about the same as obtained by Meredith.[178]

From Figs. 11 to 14 it can also be clearly seen that every sample shows a behaviour of curves very slightly convex towards the log time axis but it can be said that they are tending to straight line behaviour. This can be verified from the stress relaxation results (from 10 seconds) in Fig. 16, when the relaxation behaviour is entirely at constant conditions of temperature and humidity.

From Figs. 11 to 16 and 18 to 23 and Table 10, it is clear that Terylene and Perlon show the slowest rate of relaxation, Terylene being slightly slower than Perlon. The values of percent change of tension per decade of time from Figs. 11 and 12 differ from those obtained from Fig. 16 for 2% extension, i.e. values in first column A of Table 9 are different from those in column B because of the different relaxation time range and different duration of stretching,[171] and possibly experimental error and sampling variation.

From Table 10 it can be concluded that the average percent change in tension per decade of time is nearly constant for the constant extensions up to the first yield point, and beyond the first yield point the values decrease.

The general stress relaxation curves for nylon 6 are in agreement with the curves obtained by previous workers.[40,107] Also there is reasonable agreement of the general stress relaxation behaviour of Terylene with previous work.[107]

While considering the stress relaxation behaviou of synthetic fibres, e.g. Terylene and nylon, it seems that Terylene has much lower values of percent change in tension than those of nylons as shown in Table 10. The percent change in tension is nearly constant at 2% extension, and decreases with increase in percent extension up to 4%. This indicates that a master stress relaxation curve may possibly be obtained by shifting the stress/strain curves at different extension along the time axis to the curve at a particular extension (say 1% in present work). This has been done in Figs. 33 and 34 for Terylene and nylon 66 respectively.

2. Effect of fluctuating humidity

The stress developed under fixed extension at any time is dependent upon humidity or more accurately, on the amount of moisture absorbed by the fibre. From the experimental results for Courlene PP Fig. 17, it can be seen that this fibre does not show any fluctuations due to changes in humidity, because its moisture regain is zero. Courlene X3 also has zero moisture regain but it can be seen from Fig. 17 that it shows an appreciable initial drop in tension due to change of humidity from 65% to 90% and the tension varies slightly with fluctuations in humidity. This effect is probably due to the orange pigment which is present in this sample of Courlene X3. The pigment can attract moistur on to its polar groups.

It has already been shown,[179] that due to the oxidation of polyethylene in the atmosphere, it absorbs some moisture. This (very little) oxygen acts as a polar group and absorbs moisture at higher humidities and causes the changes in the tension due to fluctuating humidities.

Terylene has also a very low moisture regain (0.4% at 65% r.h. and 20°C) and it shows very little change in tension due to fluctuating humidity from 35% to 90%. Silk has the maximum moisture regain among the samples tested, and it shows a maximum initial drop in tension on changing to the high humidity (90% r.h.) but after this change, further changes in humidity have a relatively small effect. The different behaviours of various fibres will be discussed later.

Hsu[107] found from his experiments that moisture plays an important part in the stress relaxation process He has also shown a linear relationship between force an moisture regain at 25°C at the start of stress relaxatio and at the end of one hour stress relaxation. He found that at the start, the relaxation may be affected by some variation in the rate of extension between differen experiments. This effect is again due to the increase in moisture regain of the fibre due to stretching.[121] Th at the end of one hour stress relaxation, it is definite that the stress relaxation behaviour is normal. For this reason the experiments carried out in the present investigations of the effect of fluctuating humidity on stress relaxation behaviour, the specimens are left at constant extension for 48 hours before changing the humidity so that the rate of relaxation reaches a steady state. This enables one to study more accurately the effect of humidity change on the stress relaxation.

Also, between humidity changes, a period of one day has been allowed in an attempt to bring about equilibriu conditions between the moisture in the fibre and that in the surrounding atmosphere.

For the fibres absorbing moisture, their dry condition study of stress relaxation is quite simple,[107] but the study of their stress relaxation at any humidity introduces complexities in the normal behaviour due to thermal agitation. Thus the moisture in textiles causes two relaxation processes instead of one. These two relaxation processes,[107,112] due to thermal agitation and other associated with moisture regain, superimpose upon each other, but the latter completes its relaxation earlier than the former, giving rise to a change of curvature in the relaxation curves of the moist fibres. It is reasonable to suppose that the relaxation process, due to thermal agitation (latter part of curve) will not be affected much if tested at different humidities. Therefore, the relaxation curves subsequent to completio of the process associated with moisture are essentially similar for all humidities.

From the experimental results shown in Table 11, it is clear that the change in tension with change in humidity is largely independent of extension up to 4% extension which includes the extensions below and above the lower yield points of all the specimensused (see Figs. 9 and 10). However, if we go into the details of each specimen and its behaviour due to fluctuating humidities, Terylene shows an average difference in tension increasing slightly with imposed extension, but since the differences are so small, they are of very little significance. These differences in change in tension could be possibly due to sample variations.

For Perlon, Grilon and nylon 66, the average difference in tension is largely independent of imposed extension. The constancy of the average difference in tension due to fluctuating humidity seems to be disturbe at 4% extension especially for Grilon. Such divergence may be accounted for by incomplete equilibrium of the moisture regain of the fibre. Nylon 610 shows increasi difference in tension with imposed extension, but this increasing difference is not proportional to the imposed extension, e.g. nylon 610 at 1% extension shows average change in tension 52(g) and if there is proportionality of this change in tension with extension, then at 2%, 3% and 4% extensions, it should show 104, 156 and 208(g) as average tension differences. But, in actual experiments they are 55, 65 and 77(g) showing no proper proportion. At 4% extension the rise in tension difference is only 50% greater than at 1% extension. This shows that the rise in tension is not in any proper order or proportion with the imposed extension.

Silk also shows an increase in average difference in tension with increase in imposed extension but the ris is again not proportional to the imposed extension, as shown in Table 11.

As the magnitude of strain does not affect the ultimate change in tension due to fluctuations in humidit let us consider the general sensitivity of tension for different fibres at 2% extension which will represent th behaviour up to 4% extension. Table 12 and Figs. 16 an 18 show the change in tension caused by change in relati humidity from 90 to 35% and also from 35 to 90% respectively. In general the values for the first set are a little lower than the values in second set. This is because in the first set there is possibility of an initial drop in tension as shown peculiarly by silk and even by nylon 610.

Terylene, having moisture regain 0.4% (at 65% r.h. and 20°C), shows least sensitivity to humidity change. Nylon 610 also has a low moisture regain of 2.6% (at 65% r.h. and 20°C) and takes next place in the ranking for the lowest sensitivity to humidity change. Nylon 66, Grilon and Perlon, with moisture regains 4.2%, 4.0%, 4.0% respectively, come next. Although Perlon shows slightly higher % change in tension than nylon 66 it shows slightly smaller values than Grilon. In these cases the above relationship between moisture regain and the corresponding sensitivity to humidity does not materialise. We may perhaps assume that this relationship is correct because there is not much divergence in the case of nylon 66, Grilon and Perlon, but if we look at the sensitivity of Silk (Tables 11 and 12) in Figs. 16, 18, 19 or even for 1%, 3% and 4% extensions in Figs. 15, 21, 22 also Table 11, we find that it is much less than that of the nylons. Silk having a moisture regain of 10% (at 65% r.h. and 20°C) shows, on an average, less change than even nylon 610 which has the smallest moisture regain of all the nylons

TABLE 18

Longitudinal Swelling Percentages

Fibre	Moisture regain %	% change in length at 90% r.h. (Positive change)		% change in length at 35% r.h. (Negative change)	
		From direct measurements A	From Fig. 40 B	From direct measurements A	From Fig. 40 B
Perlon	4.0	0.91	0.80	0.53	0.60
Grilon	4.0	0.79	0.80	0.43	0.60
Nylon 66	4.2	0.79	0.75	0.43	0.55
Nylon 610	2.6	0.27	0.25	0.14	0.25
Silk	10.0	0.20	0.20	0.30	0.30

A = percentage change in length taken on the basis of length at 65% r.h.

B = percentage change in length obtained as intercepts a and b in Fig. 40.

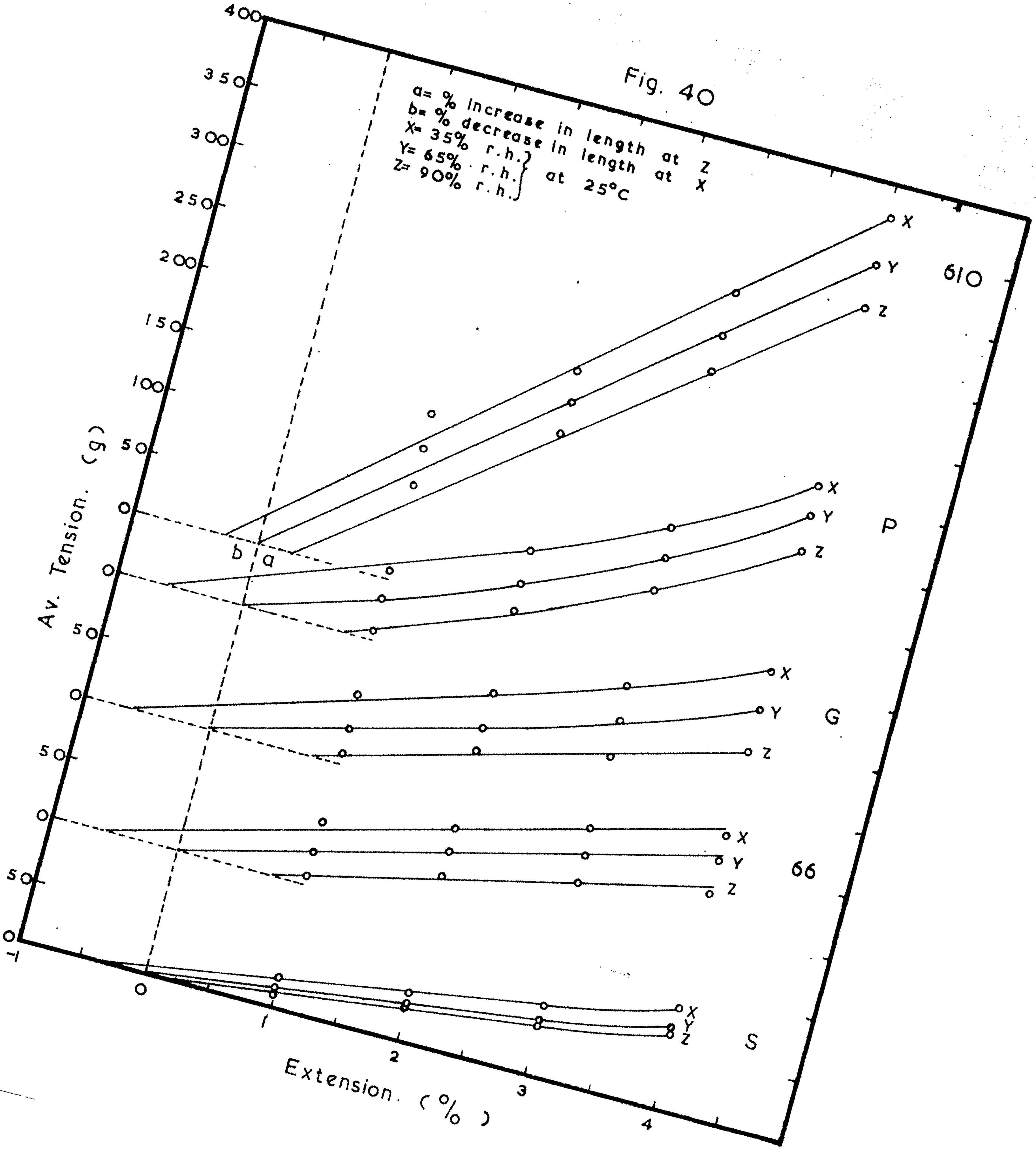

a= % increase in length at Z
b= % decrease in length at X
X= 35% r.h.
Y= 65% r.h.
Z= 90% r.h.
at 25°C
Av. Tension. (g)
Extension. (%)
400
350
300
250
200
150
100
50
0
50
0
50
0
50
0
50
0
-1
0
1
2
3
4
a
b
X
Y
Z
610
P
G
66
S

Fig. 40

Thus the phenomenon of sensitivity of tension to humidity change is not directly due to the moisture regain of the material, but could be due to the change in the equilibrium length of the specimen at different humidities. This brings us to the longitudinal swelling behaviours of nylons and silk.

From literature,[173] various workers have found that silk[180] in water has a longitudinal swelling of 1.3% - 1.7% on a dry length basis whereas that for nylon[181] even at 90% r.h. is 2.05% (the same authors have given lateral swellings in water as 19% and 3.2% respectively.)

The experimental results for change in length given in Table 18 agree with previous work.

Section A in Table 18 gives the results of per c change in length obtained by direct measurement of lengt with changing humidity after 24 hours at a given humidit These changes in length are taken as the average of absorption and desorption values for the materials. Th per cent change in length in Table 18 (column A) is on the basis of the average length at 65% r.h. Columns marked B in Table 18 shows the average per cent change in length due to humidity changes from 65% to 35% and 90 obtained from the intercepts a and b in Fig. 40. These curves are plotted as average tension against extension at ~~constant~~ the same humidity when the humidity is fluctuating. Curves X, Y, Z represent such curves at 35% r.h., 65% r. and 90% r.h. The intercepts a and b give estimates of the positive or negative change in equilibrium length of specimen according to high or low relative humidity. In Sections A and B the actual length measurements and the tension measurements show quite a good agreement as far as per cent change in equilibrium length, due to humidity, is concerned.

This experimental evidence shows that the fluctuations in tension due to changes in humidity are dependent on the degree of longitudinal swelling of the material in presence of moisture. The higher the longitudinal swelling, the greater is amplitude of fluctuations of the tension at any fixed extension. Perlon and Grilon seem to have higher degrees of longitudinal swelling (see Table 18), so they show slightly higher sensitivity to humidity change than nylon 66 (see Table 11) although there is not very much difference in their moisture regains.

The same arguments stand for the peculiar type of behaviour shown by silk in comparison to nylons. Thus silk is less sensitive to humidity change than nylons, although it has the higher moisture regain (10% compared with 4%). This extra moisture regain of silk is accommodated by lateral swelling (19% in water).

To sum up, the above discussions show that the longitudinal swelling of the material governs the sensitivity of the tension in fibres in the atmosphere of fluctuating humidity. This is confirmed by a set of experiments carried out as change of humidity from 90%

to 65% in Fig. 20 and individual fibre can be correspondingly studied as above.

The above discussion can also be well supported by the expected behaviour of Courlene X3 and Courlene PP Direct length measurements on Courlene PP (polypropylene shows no change in length with change in humidity and it also does not show any fluctuations in tension with humidity change.

Courlene X3 (high density polyethylene) which is supposed to have no moisture regain at 65% r.h. shows no measurable change in length for change in humidity below 65% r.h. but surprisingly shows + 0.035% change in lengt when humidity increases to 90% r.h. This change in length at 90% r.h. brings about small fluctuations in th tension due to fluctuating humidity.

Courlene X3 is high density polyethylene (densit 0.95), although it has better properties, it is inferior to standard 'Courlene' yarn from the point of view of photo degradation.[173] Moreover this photo degradation in polyethylene is accelerated by the catalysts used in the manufacture of high density polyethylene. Even introduction of pigment may perhaps increase the polar groups in it. Thus, the very little longitudinal swelling in the orange pigmented Courlene X3 used, may be due to photo degradation which introduces oxygen in it and perhaps due to the pigment present. Otherwise, the general sensitivity of Courlene X3 should be the same as that of Courlene PP.

TABLE 19

Increase in tension decay due to fluctuating humidity

	Tension decay (g)/decade of time (sec.)								B/A			
Extn.	1 %		2 %		3 %		4 %		1%	2%	3%	4%
Fibre	A	B	A	B	A	B	A	B				
Terylene	8.8	17.5	15.0	18.5	9.3	12.0	17.0	21.5	2.00	1.23	1.30	1.27
Perlon	4.0	5.5	8.5	12.5	9.0	12.5	10.0	14.5	1.40	1.40	1.40	1.45
Grilon	7.0	11.0	12.0	19.5	14.5	24.0	9.3	18.0	1.60	1.63	1.65	1.95
Nylon 66	7.0	12.0	10.0	16.5	14.5	25.0	14.8	32.5	1.71	1.65	1.72	2.20
Nylon610	45.0	89.0	52.0	106.0	57.5	112.0	53.0	110.0	2.00	2.04	1.97	2.04
Silk	16.0	25.5	27.0	51.0	39.0	67.5	35.0	65.0	1.80	1.90	1.70	1.86

A = Actual tension decay at 65% rh. and 25°C (during constant conditions)

B = Increased tension decay at 65% rh. and 25°C (during fluctuating humidity)

B/A = Ratio of increased rate of decay to actual rate of decay at 65% rh. and 25°C.

The evidence that Courlene X3 (orange pigmented) absorbs water was confirmed by measuring its moisture regain. It showed a moisture regain of 0% at 65% r.h. and 0.6% moisture regain at 98% r.h. That the degradation of polyethylene introduces water attracting polar groups, e.g. oxygen, has been already proved in literature.[179, 182, 186]

From Figs. 15, 16, 18, 19, 21 and 22, it can be seen that for constant extensions up to 4%, the rate of decay of tension increases when the relative humidity fluctuates between 35% and 90%. The extent of the increase in the rate of decay is roughly independent of the mode of change of humidity from 65% r.h. (Figs. 16 and 18) and also independent of the duration of exposure to different humidities (see Fig. 19), as long as the rate of decay is taken as an average line or curve passing through the tensions at 65% r.h. after every humidity change.

Another important behaviour found was that the degree of rate of decay at large is also independent of initial per cent extension imposed. This can be well judged visually from Figs. 15, 16, 21 and 22 and also from the Table 19 where column A shows the decay of tension in grammes per decade of time (sec.) and column B shows the decay of tension (g) during the fluctuating humidity. Ratio of B to A gives the ratio of the increase in rate of decay to the actual rate of decay at 65% r.h. and 25°C. This increase in rate of decay due to humidity change is roughly constant for extensions up to 4%. Terylene has a higher value of this increase in rate of decay at 1% constant extension. This could be possibly due to the slightly concave shape of its relaxation curve at 1% extension (see Fig. 15) as compared with the convex shape of the curves at other extensions in the Figs. 16, 21 and 22.

Thus the increase in rate of tension decay due to humidity fluctuations is approximately independent of the initial tension in the fibre up to 4% extension. This increase in rate of tension decay is in the increasing order as Terylene, Perlon, Grilon, nylon 66, silk and nylon 610.

Thus nylon 6 and nylon 66 are less affected by humidity change than is silk, as far as the rate of relaxation is concerned. This can be possibly due to initial large amount of drop in the tension of silk due to humidity change. Terylene is least affected due to its low moisture content.

A conclusion of practical importance is that when storing textiles containing strains resulting from mechanical processing, the strains will relax more quickly in an atmosphere with fluctuating humidity than in an atmosphere of constant humidity such as that obtaining in a testing laboratory, spinning room or weaving shed.

(3) Effect of temperature on the rate of relaxation

Polymers are high molecular weight substances and at high temperatures the molecules are engaged in Brownian motion. This motion is simply a manifestation of the thermal agitation, common to all matter. As a matter of fact it is the Brownian motion of the polymer molecules, superimposed on external forces which leads to simultaneous storage and dissipation of mechanical energy when a polymer sample is deformed. If the Brownian movement increases, the orientation tends to randomness.

Similarly when a polymer is deformed by mechanical forces, the situation is not different. Energy is stored, because orientation is imposed on the contorted molecules, while decreasing their entropy.

In the deformed state for a period of time, the orientations are erased by Brownian motion, and the free energy is dissipated as heat. The polymer molecules wriggle in various modes of motion and thus there results a broad spectrum of relaxation times. The understanding of complex motion of polymer molecules has been greatly advanced by theories of Rouse[64] and Bueche[65] which expres them as a series of characteristic modes of co-operative motions of molecular segments with different relaxation times.

All modes of molecular motion become faster with increasing temperature, because the monomeric friction coefficient is reduced qualitatively, the local viscous flow is cut down. All magnitudes of friction coefficien are proportional to the relaxation times, so relaxation times change by the same factor a_T, when temperature is changed from T_0 to T. This simple shift of relaxation spectrum along the log time scale is measured as $\log a_T$. The temperature dependence of all mechanica properties involving relaxation process in an amorphous polymer (e.g. polyisobutylene, polymethylacrylate) can thus be simply described by a plot of $\log a_T$ against temperature. This factor is always referred to some arbitrary standard temperature, often chosen as 25°C, curves for different polymers all cross to T_0, where $a_T = 1$ and $\log a_T = 0$, but vary widely in steepness. It is evident that enormous shifts of the time scale over many decades can be achieved by changing the temperature. Taking reference temperature T_0 different for different materials we can plot a_T against $T-T_S$ for different amorphous polymers, by using Williams, Landel, Ferry 1955 (WLF) equation,[63] who put arbitrary modification to Rouse Theory.[64]

The situation for polycrystalline polymers has been rather less well understood. Recently, however, evidence has been published for applicability of time-temperature superposition principle even to polycrystalline materials within certain restricted conditions. Yoshitomi, Nagamatsu and their co-workers[19] have applied it successfully to nylon 6 in torsional stress relaxation at low strains and to polytetrafluoroethylene in longitudinal stress relaxation[184] at strains below 0.7%. For low density polyethylene, Tobolsky[197] found that the time-temperature superposition principle was applicable to stress relaxation data but the results of experiments by Nagamatsu et al.[183] made at lower strains have not been amenable to treatment by this principle. The more recent study of stress relaxation of nylon 66 at various temperatures made by Dunell, Joanes and Rye[20] has shown a reduced master relaxation curve and also a straight line plot of log a_T versus reciprocal of absolute temperature.

Below the glass transition temperature, though configurational changes play a minor role in amorphous polymers, viscoelastic responses exist which are usually attributed to motion of side chains and cover a wide spectrum of relaxation times. Such internal motions of amorphous polymers can certainly not be described in terms of a monomeric friction coefficient, but if it is assumed that all the relaxation times concerned have the same temperature dependence, reduced variables can be applied to the glassy zone as an entirely separate calculation. Below the glass transition temperature, the free volume treatment and the WLF equation[63] cannot be expected to be applicable. In fact the temperature dependence of a_T follows an equation[8] of the simple Arrhenius form,

$$\log a_T = \left(\frac{\Delta F}{R}\right) \frac{1}{T_o} - \frac{1}{T} \qquad (1)$$

where a_T = shift factor; ΔF = activation energy;
R = gas constant (1.987 cal/mole/degree;
T_o = reference absolute temperature;
T = absolute temperature

with moderately low value of ΔF e.g. for polymethylmethacrylate ΔF = 29 kcal/mole. Thus temperature dependence of responses below glass transition temperature bears no relation to what would be extrapolated from the behaviour above glass transition temperature, where F is enormous and increasing rapidly with decreasing temperature

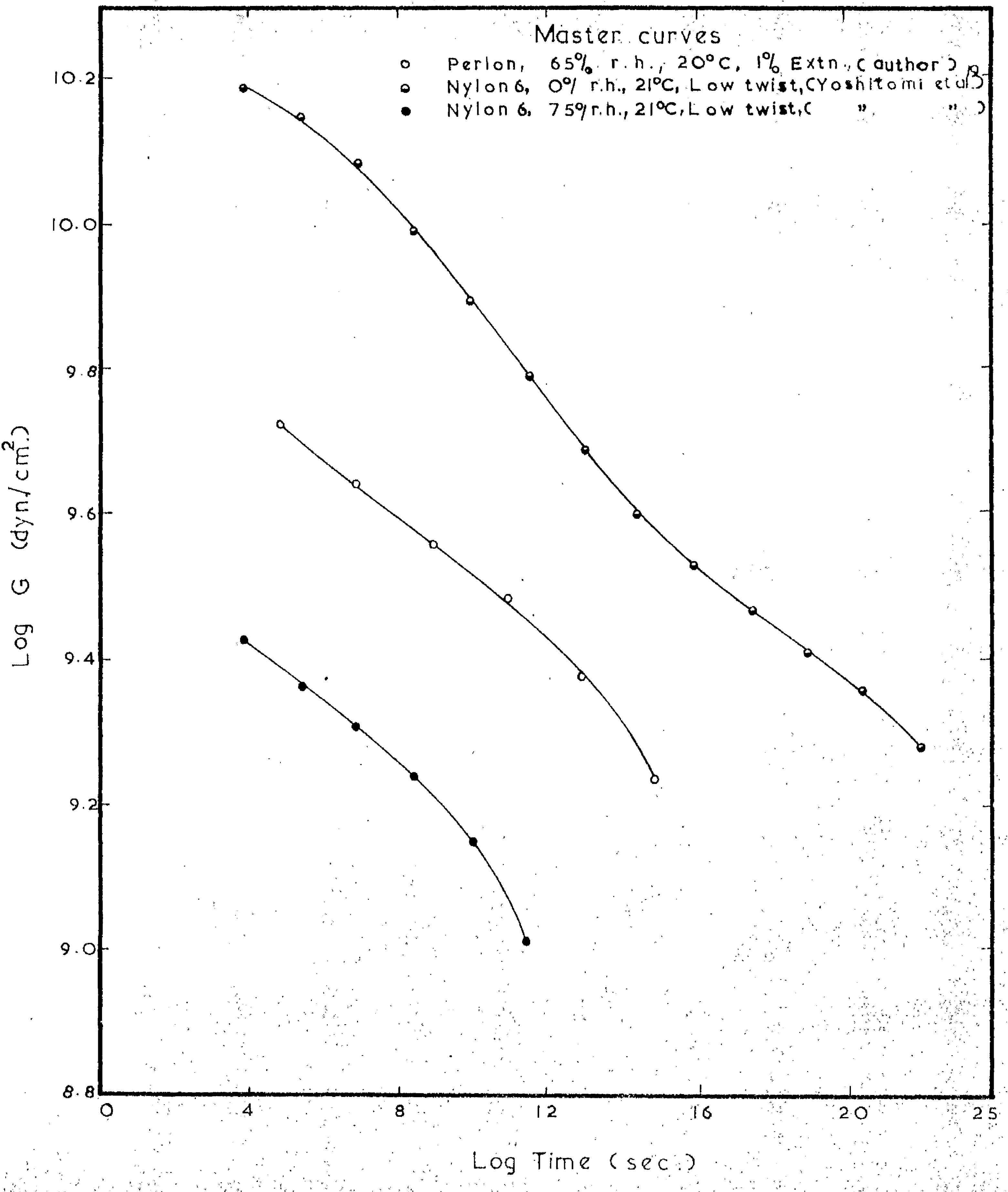
Similarly, for highly crystalline polymers the amorphous segments between crystallites are too short to permit any motions describable in terms of a monomeric friction coefficient. However, at temperatures so far below the melting point that the degree of crystallinity has reached its maximum value consistent with steric limitations so that further decrease in temperature will not be accompanied by crystal growth and alteration of internal structure, it can again be assumed that the relaxation times concerned in whatever motions do occur have the same temperature dependence as a glass. Application of reduced variables on this basis has been successful for a number of highly crystalline polymers, including nylon 6[19] and nylon 66[22] high density polyethylene,[14] polychloro-tri-fluoroethylene.[186] The temperature dependence of a_T again followed by above equation (1) and they found[19,20,145,1] activation energies as 88, 31, 30 and 125 kcal/mole respectively.

From the present experimental results for stress relaxation of Terylene, Perlon, nylon 66, Courlene X3 and Courlene PP, it is found that the above equation (1) is at least applicable at low extensions of one percent.

When the stress relaxation curves at 30°C, 40°C and 50°C at constant extension and humidity (65% r.h.) in Figs. 24 to 29 are shifted along log time axis to superimpose the similar curve at $20^{\circ}C$ they give quite a good fit of all curves on the $20^{\circ}C$ curve giving a master curve at $20^{\circ}C$ and 1% extension (see Fig. 30): similarly at 2% and 3% constant extensions the master curves (Figs. 31 and 32) could be obtained in the case of Perlon, nylon 66 and silk with little approximation. The values of shift factor in the form of log a_T for the shift of curve at every temperature are tabulated in Table 14. The master stress relaxation curves thus obtained at $20^{\circ}C$ are in quite good agreement with the actual behaviour of the materials observed over one month and shown in Fig. 23, by putting in correction because the curves in Fig. 19 are at $25^{\circ}C$ instead of 20° as in the master curves in Fig. 30, 31 and 32.

Yoshitomi et al[19] were able to obtain for nylon 6 similar types of master stress relaxation curves at 0% r.h. and 75% r.h. They studied the relaxation of torque at constant twist. The present master stress relaxation curve for Perlon (nylon 6 type) at 1% constan extension was converted to shear modulus values by assuming E[19,187] = 3G. The values of log G from the presen work for Perlon at $20^{\circ}C$ and 65% r.h. are plotted against log time in Fig. 41. The master curve plotted in this manner agrees well with the curves plotted by Yoshitomi[19] as shown in Fig. 41. The activation energy value from his results[8,19] is 88 kcal/mole and may be compared with the activation energy of 83 kcal/mole obtained from the present experiments, calculated from Fig. 39(P).

Fig. 41


Master curves
○ Perlon, 65% r.h., 20°C, 1% Extn. (author)
◒ Nylon 6, 0% r.h., 21°C, Low twist, (Yoshitomi et al.)
● Nylon 6, 75% r.h., 21°C, Low twist, (" ")
Log G (dyn./cm.²)
10.2
10.0
9.8
9.6
9.4
9.2
9.0
8.8
0
4
8
12
16
20
25
Log Time (sec.)

This activation energy value was obtained by use of equation (1). Thus, by plotting a graph of log a_T against $\frac{1}{T}$ (where T = absolute temperature), all the fibres gave approximately a straight line passing through an average path made by the points plotted for 1, 2 and 3% extension as shown in Fig. 39. The slope of these lines, according to equation (1) should represent the activation energy divided by the gas constant.

Thus the activation energies can be calculated from slope x 2.303R (where R = gas constant = 1.987 cal/mole/deg.) The activation energies thus calculated from Fig. 39 are 60 kcal/mole, 58 kcal/mole, 42 kcal/mole, 55 kcal/mole and 41 kcal/mole for Terylene, nylon 66, silk, Courlene X3 and Courlene PP respectively. These values can be approximately compared with the values obtained in the literature by comparing the values at the same conditions of temperature, humidity and also strain. Faucher[145] obtained values of activation energy for Marlex-50 (crystalline polyethylene) and crystalline polypropylene as 30 kcal/mole and 50.5 kcal/mole respectively. But if his results are considered at the temperature range of our experiments i.e. 20°C to 50°C, the values for polyethylene and polypropylene become 45 kcal/mole and 39 kcal/mole, which can be compared with the present results of 55 kcal/mole and 41 kcal/mole respectively.

From Fig. 39, it can be seen that in the case of Perlon, the points for 3% extension results are missing.

This is because Perlon at strains over 0.3g/den. is very much affected by temperature change,[190] thus it gives higher values of log a_T which shows higher value of activation energy when compared with those obtained from an average plot through 1% and 2% extension results.

Thus the validity of Ferry's reduced variable method below glass transition temperature at low extensions can be proved from the approximate straight lines obtained in the plots of log a_T against reciprocal of absolute temperature. The approximation is taken in drawing the straight lines because the points were not enough to show definite behaviour. However, the results seem to be reliable as they are not very far from those obtained by the other workers.[8,19,20,145]

4. Effect of magnitude of strain

Figs. 37 and 38 show the effect of a sudden rise in extension on the stress relaxation behaviour. From all these curves (Figs. 37 and 38) for Terylene, Perlon, Grilon, nylon 66, nylon 610 and silk it is found that the general slope of the curves at 2% extension is not much different from the general slope of curves at 4% extension, particularly at the later stages of stress relaxation. This has already been shown by Kubu[123] for wet nylon 66 up to 15% extension, wet silk up to 10% extension and wet wool up to 20% extension.

These curves at 4% extension are also compared, with the dotted line curves, which are actual curves obtained at 4% extension, 65% r.h. and 25°C. These curves nearly coincide with the experimental curves and so the stress relaxation behaviour at extensions up to 4%, at least, is independent of the previous stress relaxation history at lower extension. This is in agreement with Anderson[59]: he found that for cellulosic fibres the tension at any extension is independent of its previous stretching history at lower extensions. The stiffness increases due to previous stretchings but if the extension is increased for same specimen, the stiffness will decrease as soon as the extension exceeds the previous extension.

If stress relaxation data at constant temperature and relative humidity at different extensions be plotted as stress/strain against log time, there is a possibility of obtaining a composite stress relaxation curve. Meredith[125] found that such curves for viscose rayon and cellulose acetate appeared to be part of a common sigmoidal curve, which he called a "composite curve". Hsu[107] also obtained such a curve for Terylene.

From Figs. 33 and 34 it can be seen that such composite curves have been approximately obtained at 1% extension, 65% r.h., and at 20°C to 50°C for Terylene; at 20°C to 40°C for nylon 66, Courlene X3 (polyethylene) and Courlene PP (polypropylene). The curves at higher extension of 2%, 3% and 4% extension are shifted along log time axis till they superimpose the curve at 1% extension. For Courlene X3 and Courlene PP curves at 4% extension were not available, so shift of only 2% and 3% extensions are made.

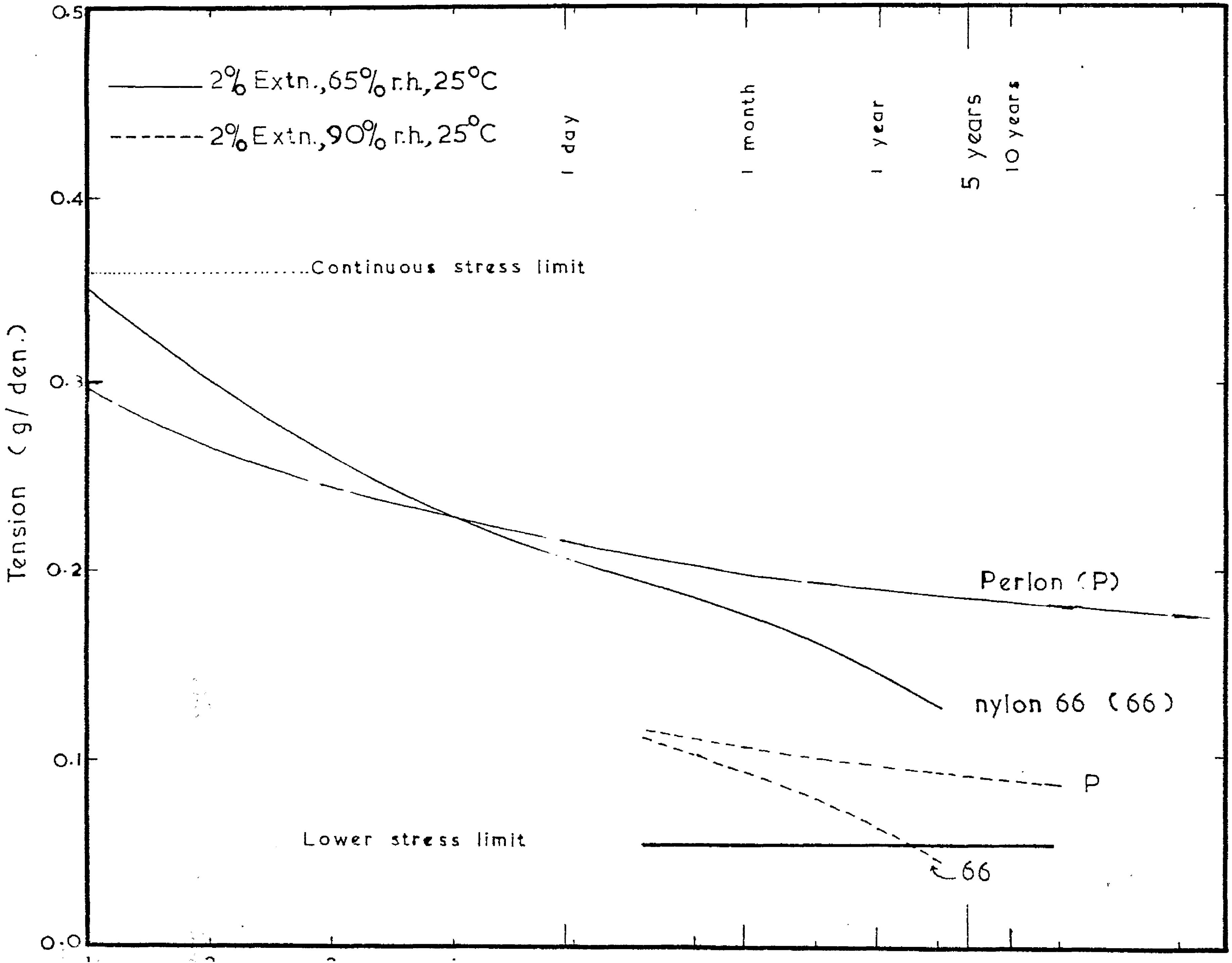
The practical significance of the experiments in which the extension was raised to 4% after relaxation at 2% extension lies in the indication they give concerning the effect of a tightening bar that can be operated when a sieve becomes slack after prolonged use.

It has been found in practice that a sieve used in flour milling becomes unsatisfactory when the tension per inch (measured along the frame) falls below 1½ lb. wt. Now tightening bars complicate the structure of the frame and therefore if a material could be found that maintains sufficient tension in use, this would be an advantage. The indications of the present work are that such a material is available and this is demonstrate in the following paragraphs.

The conditions to be satisfied are that the material must maintain a tension greater than 1½ lb./inch over a period of 5 years or so under conditions of fluctuating humidity and temperature, the stress on the mounting frame must not be too high and the abrasion resistance of the fabric must be high. Fig. 42 shows that Perlon (nylon 6) fulfils these conditions but nylon 66 does not.

The stress relaxation curves shown in Fig. 42 are for nylon 6 and nylon 66 at 2% extension, 65% r.h. and 25°C. They are, in fact, the master curves of Fig. 31. The dashed lines represent the effect of increasing the relative humidity to 90%, and it will be seen that the dashed curve for nylon 66 crosses the lower stress limit line before 5 years have elapsed, whereas that for nylon 6 remains above this limit.

Fig. 42


2% Extn., 65% r.h., 25°C
2% Extn., 90% r.h., 25°C
1 day
1 month
1 year
5 years
10 years
Continuous stress limit
Tension (g/ den.)
0.5
0.4
0.3
0.2
0.1
0.0
Perlon (P)
nylon 66 (66)
P
66
Lower stress limit

For a typical sieve cloth woven from 350 denier monofil nylon the number of filaments per inch is 35, so that $1\frac{1}{2}$ lb./inch represents a stress of $(1.5 \times 454)/(350 \times 35) = 0.055$ g./denier and this lower stress limit has been shown in Fig. x.

Now the results obtained with fluctuating humidity indicate that the rate of stress relaxation will be accelerated compared with the rate under constant humidity so that the performance of both nylons would be worse than shown but nylon 6 would still be satisfactory.

The data obtained for the effect of temperature on rate of relaxation show that from 20 to 50°C temperatu has relatively little effect so the main conclusion still holds good. The great value of the experiments at different temperatures is the fact that they enable the relaxation at very long times to be predicted and it is necessary to know the tension that will remain after as long as 5 years because the abrasion resistance of nylon permits the sieves to last that long. Silk sieves wear out in a much shorter time. Terylene would maintain tension better than nylon but has less abrasion resistanc in this kind of application.

There is an upper limit to the amount of stretch that can be applied continuously to the mounting frames. The continuous stress limit marked in Fig. x corresponds to a force on each side of a 24" frame equal to $(24 \times 35 \times 0.36 \times 350)/454 = 234$ lb. wt.

5. Relaxation of stress in dry viscose rayon

Nissan,[126] has developed a theory of the rheologica behaviour of hydrogen bonded solids. He has used the master stress relaxation curve for viscose rayon at 65% r.h., given by Meredith[125] (p.49) to demonstrate that almost the complete relaxation curve can be ascribed to a single mechanism, i.e. a co-operative reaction between several bonds breaking simultaneously. The number of bonds involved comes out to be about six, and this same number of bonds are considered to be ruptured at 65% r.h. by the addition of one molecule of water. It was suggested that interesting results should come out from repeating Meredith's work at low regain where the autocatalytic effect is small. Accordingly, experiments were made to find the master relaxation curve of viscose rayon at 0% r.h.

By shifting the stress/strain relaxation curves plotted from Table 17 along the log time axis it was possible to produce a continuous master relaxation curve for dry viscose rayon as shown in Fig. 43. The overlap of the individual sections of the master curve is not really sufficient to establish the master curve beyond all doubt, but the curve appeared to be sufficiently good to proceed with an analysis of the type carried out by Nissan. Additional curves at intermediate extensions are required but time did not permit their determination.

The data used in deriving log n_2 which is plotted in Fig. 44 against log t are given in Table 20. The

TABLE 20

Values of log n_2 for dry viscose rayon, obtained from master relaxation curve for 1% extension.

Time (Sec.)	Tension 10^8 dyn/cm^2	E 10^{10} dyn/cm^2	n $\times 10^{18}$	n_2 $= n - n_1 \times 10^{18}$	$\log_{10}$
10^0	12.7	13.66	7440	7392	21.87
10^2	11.7	12.66	5910	5862	21.77
10^4	9.5	10.46	3340	3292	21.52
10^6	7.2	8.16	1580	1532	21.18
10^8	5.2	6.16	680	632	20.80
10^{10}	4.0	4.96	355	307	20.49
10^{12}	3.3	4.26	225	177	20.25
10^{14}	2.6	3.56	132	84	19.92
10^{16}	2.2	3.16	92	44	19.64
10^{18}	1.9	2.86	68	20	19.30
10^{24}	1.6	2.56	$48 = n_1$	0	-

n_2 = no. of bonds per cm^3 taking part in the cooperative type of reac

Fig. 43

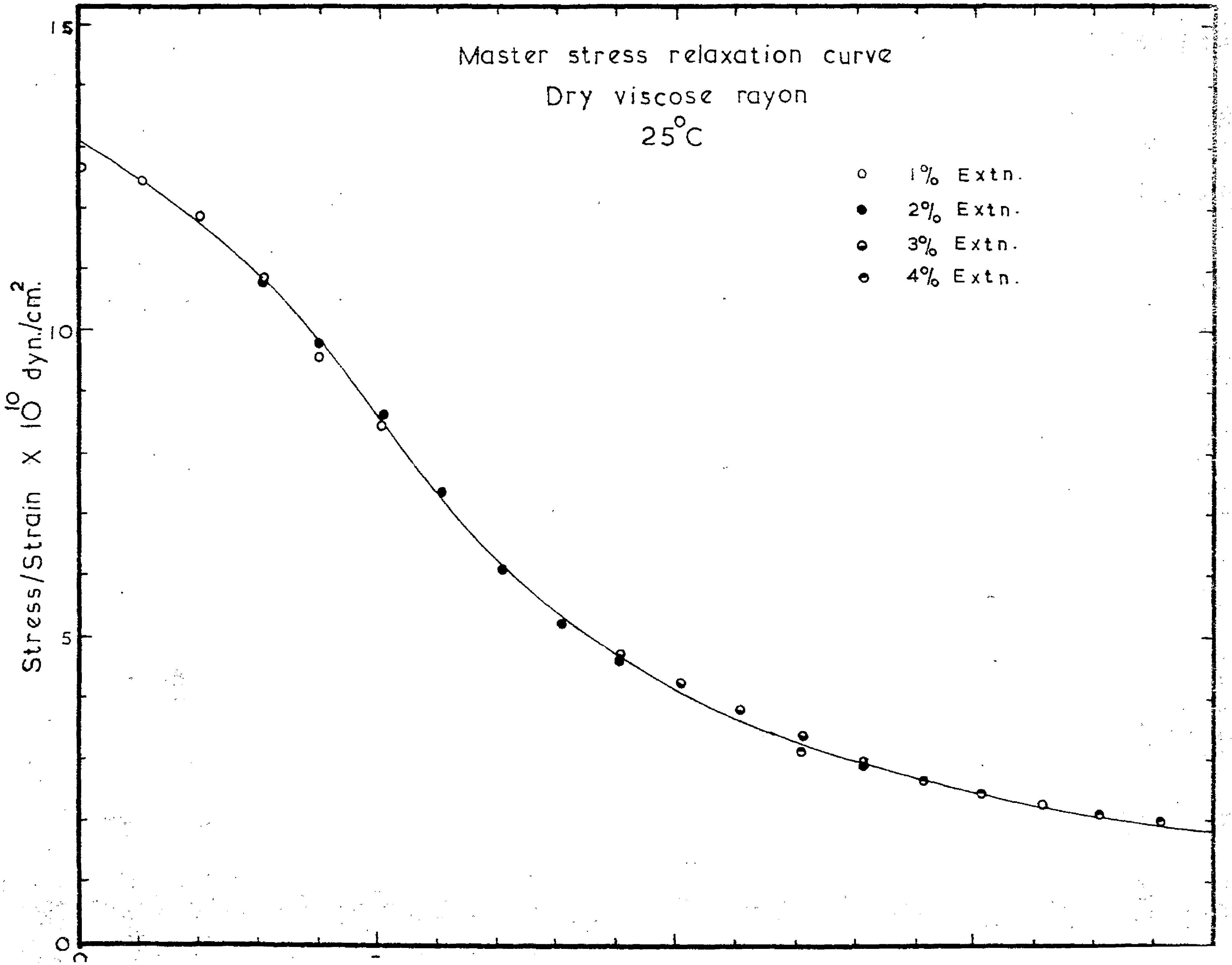
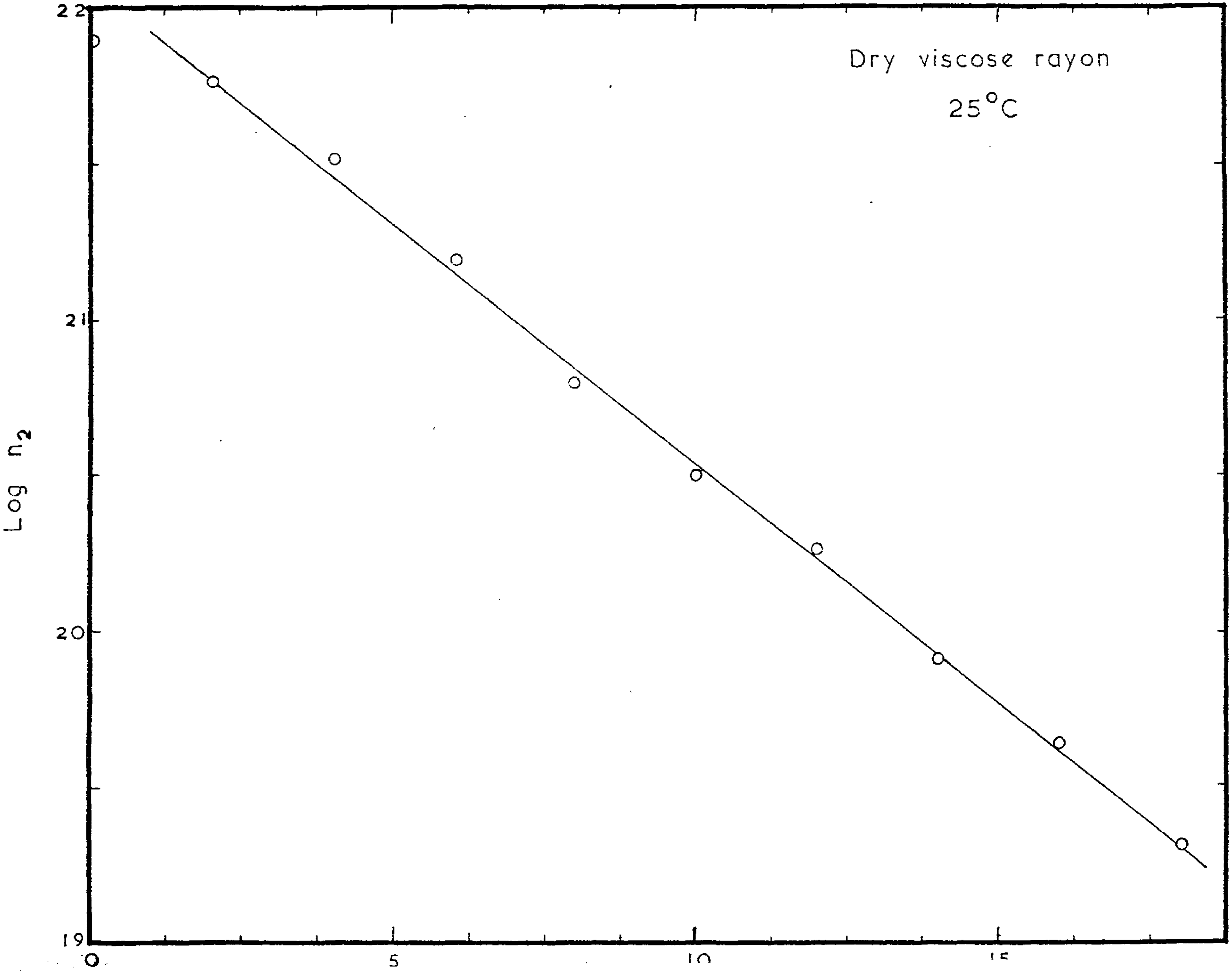

Master stress relaxation curve
Dry viscose rayon
25°C
○ 1% Extn.
● 2% Extn.
◐ 3% Extn.
◐ 4% Extn.
Stress/Strain X 10^{10} dyn./cm.^{2}
15
10
5
0

Fig. 44



second column gives the tension at various times for the master relaxation curve for 1% extension. Values of Young's modulus E in column 3 are derived from column 2 according to Nissan's formula $f = E\sigma - uK\sigma^2$ where f is stress, σ is strain, K is a second coefficient of elasticity and has a value equal to 1.1×10^{12} dynes/cm.^{2} and is a universal constant for hydrogen bonded materials u is a correction term involving the strain and a parameter of the Morse function for the strain energy (for $\sigma = 0.01$, $u = 0.873$).

The number of bonds per cm^3 taking part in the straining process is n, given in column 4 and is derived from the modulus, E, according to the relation $n = 2.92 \times 10^{-12} E^3$. If n_1 is the number of bonds per cm^3 taking part in a bimolecular reaction which occurs spontaneously and takes place at all times even when the material is under zero strain, it is assumed to be given by the value of n at very small values of strain, i.e. at times $> 10^{20}$ second (see foot of column 4), then n_2, the number of bonds per cm^3 which take part in the co-operative type of reaction, postulated to occur by Nissan, is given by $(n - n_1)$ and is recorded in column 5.

The plot of $\log_{10} n_2$ against $\log_{10}$time shown in Fig. 44 gives a straight line of which the slope is

$$\frac{d \log n_2}{d \log t} = -0.15$$

The object of this analysis is to find a value for the number of bonds (m) which move simultaneously and co-operatively into new positions of equilibrium when flow takes place inside the fibre under strain. It is assumed that this implies a reaction of order m or

$$d\ (n_{2/N})/dt \ = \ -k\ (n_{2/N})^{m} \qquad (2)$$

where N is Avagadro's number and k is the rate constant of the reaction.

Now a slope of - 0.15 means that

$$n_2/n_{2.1} = t^{-0.15} \qquad (3)$$

where $n_{2.1}$ is the value of n_2 at time t = 1 second, so that

$$\frac{1}{N} \cdot \frac{dn_2}{dt} = \frac{1}{N} \cdot n_{2.1}\ (-0.15)\ t^{-1.15}$$

But

$$t^{-1.15} = \left(\frac{n_2}{n_{2.1}}\right)^{\frac{1.15}{0.15}} = \left(\frac{n_2}{n_{2.1}}\right)^{7.67}$$

$$\therefore \qquad \frac{1}{N} \cdot \frac{dn_2}{dt} = -\ 0.15\ (n_{2/N})^{7.67}/(n_{2.1/N})6.67$$

$$\frac{d(n_{2/N})}{dt} = -\ 0.15\ (n_{2.1/N})^{-6.67}\ (n_{2/N})^{7.67}$$

$$(4)$$

and equation (4) is now the same form as equation (2), so that

$$m = 7.67$$

and

$$\begin{aligned} k &= 0.15\ (n_{2.1/N})^{-6.67} \\ &= 0.15\ (7392 \times 10^{18}/6.02 \times 10^{23})^{-6.67} \\ &= 8.4 \times 10^{11} \end{aligned}$$

But $$K = \frac{\bar{k}T}{h} \exp \frac{(-\Delta F)}{RT} \qquad (5)$$

where $\bar{k}$ is Boltzmann's constant $= 1.379 \times 10^{-16}$ erg/degre

h is Plank's constant $= 6.556 \times 10^{-27}$ erg sec.,

R is the gas constant $= 1.987$ calories per degr

T is the absolute temperature,

ΔF is the free energy of activation (kcal/mole)

Therefore, $$e^{-\frac{\Delta F}{RT}} = \frac{8.4 \times 10^{11}}{6.2 \times 10^{12}} = 0.1353$$

$$\frac{\Delta F}{RT} = 2.00$$

$$\therefore \quad \Delta F = \frac{\underline{1.987 \times 298 \times 2.00}}{1000} \quad \text{kcal/mole}$$

$$= \underline{1.18} \quad \text{kcal/mole}$$

Since $\Delta F = \Delta H - T\,\Delta S$

and assuming ΔF is 4.5 kcal/mole for the H-bond

then $T\,\Delta S = 4.5 - 1.18 = 3.32$ kcal/mole.

and $$\frac{T\,\Delta S}{\Delta H} = \frac{3.32}{4.5} = \underline{0.74}$$

Now Wakeham[188] has given data for the contribution to E of internal energy and entropy of regenerated cellulose fibres calculated from the temperature dependence of the stress at constant strain. His values for dry rayons at 1% extension give an average value of 0.51 for the ratio of entropy to energy terms which may be compared with the value of 0.74 evaluated above.

The value of m = 7.67 for dry viscose rayon may be compared with m = 6.0 for viscose rayon at

65% r.h. The number of bonds that must be activated together, on the average, for relaxation to proceed which is higher in the dry state than at 65% r.h. seems reasonable.

CHAPTER VI

CONCLUSIONS

Terylene shows the slowest rate of relaxation in comparison with other fibres e.g. Perlon, Grilon, nylon 66 nylon 610, silk, Courlene X3 and Courlene PP. Perlon is very close to Terylene in this behaviour of stress relaxations. Terylene shows a slightly concave shape of stress relaxation curve at 65% r.h., 25°C and at 1% consta extensions, whereas all other fibres show almost a straigh line or a curve convex to the log time axis. This peculi behaviour of Terylene at 1% extension is in agreement with investigations made by Hsu,[107] who predicted the possibility of obtaining a master stress relaxation curve by shifting the curves at higher temperatures to superpose on the curv at room temperature. From the present investigations, th has been successfully proved, and the master stress relaxation curve for Terylene at 1% constant extension is obtained at 25°C and 65% r.h. Similar approximate master curves have also been obtained for Perlon, nylon 66, silk, Courlene X3 and Courlene PP.

At 2% and 3% extensions Terylene, Courlene X3 and Courlene PP did not give such master curves, but Perlon, nylon 66 and silk gave satisfactory master curves at thes constant extensions. At 3% extension Perlon showed pecul behaviour, showing values of shift factor log a_T surprisin high and thus the activation energy values obtained at 3% extension were higher than those obtained at 1% and 2% extensions. This behaviour of Perlon at 3% extension is in agreement with the fact that Perlon, beyond 0.3g/den. tension, is much affected by temperature.[190] On the whole the plots obtained for log a_T versus 1/T give approximately straight lines through the points for 1%, 2% and 3% extensions from 20°C to 50°C. The activation energies obtained from these plots are in quite good agreement with previous results when considered over the same range of experimental temperature conditions.

Courlene PP shows the highest rate of decay. Courlene X3 is very near to the rate of decay of nylons, which in turn have slower rate of relaxation than silk. Considering the rates of decay at various extensions, it seems that for various fibres, in general, the increase in magnitude of strain (below lower yield strain) does not affect the rate of decay. Beyond the lower yield strain the rate of stress decay decreases with increase in magnitude of strain.

Increase in temperature, in general, decreases the rate of decay for small extensions, and master stress rela ation curve could be obtained at those extensions. Such behaviour of fibres is, in general, below the lower yield strain of the stress strain curve of the material. Beyond the lower yield strain the viscoelastic behaviour of the material becomes non-linear and there is change in crystallinity and structure of the material due to the increase in temperature. The validity of Ferry's reduced variable method, for crystalline polymer below the glass transition temperature of the material is supported by the results obtained in this work.

Terylene is least affected by fluctuating humidity Courlene X3 and Courlene PP, in general, can be taken as not affected by the fluctuating humidity. Silk shows peculiar behaviour of more initial tension drop due to change of humidity to 90% r.h., and then further fluctuations of humidity do not affect its tension to much extent. Nylons in general show very high sensitivity of tension to humidity when compared with similar behaviour of silk.

Magnitude of strain up to 4% extension does not seem to have effect on the values of change in tension due to fluctuating humidity.

On the whole, there is a general tendency for increase in rate of decay of the tension due to fluctuatin humidity, when the rate of decay of tension at constant humidity (65% r.h.) and the rate of decay at 65% r.h. during cycles of humidity change are compared. This accelerated stress decay, in general, is independent of the magnitude of strain up to 4% extension. Terylene shows very little increase in rate of tension decay. Perlon, although it shows very much change in tension due to fluctuating humidity, shows only slightly higher values of increased rate of tension decay. The maximum increase in rate of tension decay is shown by silk and nylon 610.

From the present experimental evidence it can be concluded that the effect of fluctuating humidity or tension is due to the different longitudinal swelling of different fibres. Nylons show more longitudinal swelling than silk, so they are more affected by humidity change. Terylene, having least moisture regain, shows minimum longitudinal swelling, so is least affected.

By comparing the different fibres in the present investigations, it can be suggested that Terylene and Perlon are the best of all, as far as the industrial use is concerned. They are least sensitive to fluctuating humidity. More over, when other physical properties are considered, Perlon may be given preference due to its better abrasion properties. Thus Perlon (or even Terylene can be recommended for use in sieves, it is necessary for tautness to be maintained under conditions of fluctuating humidity.

As suggested by Nissan, the composite stress relaxation curve for dry viscose rayon was studied. It was found that the value for m was 7.67 for dry viscose rayon. This value of m is comparable with m = 6.0 obtained by Nissan for viscose rayon at 65% r.h. This shows that the numbers of bonds that must activate together, on the average, for relaxation to proceed, is higher in the dry state than at 65% r.h., which seems quite reasonable.

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STRESS RELAXATION IN FILAMENTOUS MATERIALS: THE EFFECT OF HUMIDITY, TEMPERATURE AND STRAIN ON MAN-MADE FIBRES AND SILK.

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ABSTRACT

The relaxation of tension in strained filaments of Terylene, Perlon, Grilon, nylon 66, nylon 610, polyethylene, polypropylene and silk has been studied at strains up to 4% extension, at constant relative humidity of 65% and with humidity fluctuating between 35% and 90% r.h., and at constant humidity with the temperature varied from 20° to 50°C.

Single unit and six unit stress relaxometers are described together with the necessary auxiliary equipment for maintaining constant conditions of humidity and temperature.

Comparison of the rates of relaxation under standard conditions of 65% r.h. and 20°C with extensions of 1, 2, 3 and 4% showed that Terylene had the slowest rate of relaxation, that of Perlon was slightly higher. The highest rate of relaxation was shown by polypropylene. In general, there was no effect of magnitude of strain on the rate of relaxation.

Repeated variation of the relative humidity from 35% to 90% at a constant temperature of 25°C accelerated the rate of decay of tension. The sensitivity of the tension in the different materials to fluctuating humidity has been satisfactorily explained. The results of the

experiments with fluctuating humidity are of considerable practical importance.

The effect of temperature on stress relaxation under strains of 1, 2 and 3% at constant humidity were used to produce master curves using Ferry's reduced variable method. The success achieved in applying this method to partly crystalline polymers has enabled the tension that would remain at very long times to be predicted from short time measurements at elevated temperatures.

Experiments have also been made on viscose rayon in the bone dry condition over a wide range of extensions and from the resulting master relaxation curve it has been possible to calculate the number of hydrogen bonds which relax simultaneously according to Nissan's theory of the role of the hydrogen bond in determining the modulus of hydrogen bonded solids.