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Annealing of Formed Perspex Structures

By

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The annealing of formed Perspex Structures

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SUMMARY

The relaxation of stress in plasticised perspex at annealing temperatures and at constant deformations occurs in two stages, the first rapid and the second slow. The temperature of this change, from one stage to the other represents the second-order transition lowered by the applied forces from its normal value to the experimental temperature. The temperature dependence and magnitude of the stress to produce this lowering of the second-order transition temperature are similar to those of other vinyl polymers. The tensile stresses in a specimen during annealing tend to a value below this critical value.

The annealing of complete structures should be performed when mounted in the complete metal framework. The relaxation data provide a minimum temperature and time of heating, other precautions and conditions are discussed. A heating period of not less than 3 hours at 65-70°C is recommended. Further work on unplasticised material is proposed.

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1 Introduction

In order that the maximum strength of perspex structures may be attained, it has been shown that crazing, surface scratches and other points of stress concentration must be avoided. Crazing consists of a system of fine cracks appearing in or beneath the plastic surface, it must be recognised as incipient failure. It may be induced in the material by the combined influences of stress and solvent vapour and in the extreme case when failure is imminent by high stresses alone. The importance of the removal and exclusion of all active solvents or their vapours cannot be over-emphasised. Each of these considerations has been dealt with in earlier reports.^{1,2}

The stresses to which a transparent plastic structure is subjected should be kept as low and as uniform as may be attainable. Stress concentrations may be caused by features of the design, and less obviously by the presence of stresses arising in polymerisation of the material or in its subsequent treatment. The shaping or forming of the curved structure, its assembly and mounting are each possible causes of such stresses. Polymerisation stresses are removed by the heat treatment required for shaping and are therefore of importance only in material used in its original cast form. The heat treatment of flat sheet for this purpose has been considered in a previous note.³

The annealing of complete shapings has, therefore, as its objective the reduction in the stress level in the original structure before it is subjected to service stresses such as aerodynamic loading. When such a structure consists of two separate shells cemented together with an interspace the exact geometrical fitting of the shells before cementing is improbable. This fact, together with clamping and shrinkage of the cement by loss of solvent, and non-uniform cooling after forming, are sources of initial stress. The solvent loss may occur either by evaporation or diffusion through the plastic or by polymerisation in the case of monomeric cements. When such a structure is subsequently mounted in its metal framework further stressing is probable. Hence annealing should, if possible, be performed on the complete mounted assembly.

2 Stress relaxation experiments at constant deformation

2.1 Material employed

Commercial methacrylate plasticised with 5 per cent of dibutyl phthalate was employed. In order to attain an outer fibre stress in bending of about 1000 lb/sq.in. at a convenient deformation sheets 3/16 inch thick were used and cut into strips 10 inches long and 1 inch wide. All the strips were heat treated at 140°C. and annealed at 80°C. as described in Technical Note Chem. 1088³, a procedure equivalent to the forming process on a curved structure. For a few experiments similar strips 1/16 inch and 1/8 inch thick were used.

2.2 Experimental procedure

For each experiment a strip was set up as a bent beam under a three-point loading system. It was inserted under two metal rods each 1/8 inch in diameter and 7 inches apart and a third such rod parallel to and equidistant from the other two was inserted beneath the specimen and raised on to a fixed stop to deform the latter by a constant amount. The force required just to lift the rod off the stop so as to break electrical contact between them was determined at any given time by direct weighing. The complete assembly was contained in an air oven at the desired temperature, the balance for the stress determination being mounted above it and connected to the central rod through a hole in the oven top.

The deformation under bending was arranged to give an initial outer fibre stress (see 2.31) of approximately 1000 lb/sq.in. This necessitated for the thickest specimens an initial load of the order of 2000 g. which could be determined readily to the nearest gram. The time was measured from the insertion of the sample in the assembly in the oven already at the required temperature. This caused a small initial disturbance after which the temperature was controlled to within $\pm 1^{\circ}\text{C}$. If over long periods of experiment the temperature varied outside these limits the results were rejected. Readings of the load necessary to maintain the deformation were taken at varying time intervals suitable for convenient plotting on a logarithmic time scale. Experiments were performed over the temperature range 55°C . to 75°C . in 5° intervals.

2.3 Results and discussion

2.31 The relaxation mechanism

Representative results are shown in Figs.1 (a) and (b) in which stress is plotted against time on a log scale. In order to correct the measured load for small variations in the dimensions of the sample the stress is calculated as an equivalent outer fibre stress. This is defined as the outer fibre stress to which the sample would have been subjected under the measured load if the stress gradient across the section of the beam had remained uniform. It is thus a method of averaging the stresses present and will be further examined below.

The decay of stress at constant deformation occurs in two stages. During the first the rate is rapid and is linear on the present method of plotting; in the second stage the rate is also linear but much slower. At very low stresses this line curves off asymptotically to the log time axis. For the rubber-like material polyisobutylene, Andrews, Hofman-Bang and Tobolsky⁴ have found that the decay of stress of material held in pure tension at constant elongation is linear in a similar plot over a wide range of log (time) and also curves off at low stresses. Polymethyl methacrylate differs from polyisobutylene only in the substitution of a $-\text{C}(\text{O})\text{OCH}_3$ for a $-\text{CH}_3$ group in the side chain. We may, therefore, reasonably assume a similar relaxation mechanism for the methacrylate when it is in the rubbery condition.

All the experiments were performed at temperatures below that at which the unstressed methacrylate becomes rubbery in character. External forces have been shown⁵ to lower this temperature - the second order transition point - for a range of polymers including polystyrene, Saran and polyvinyl chloride. Hence the intersection of the two straight lines (Figs.1 (a) and (b)) may be assumed to give the force required to reduce the transition temperature to that of the experiment. Above that stress the material is rubbery and stress decay is rapid; below it the relaxation is delayed as the molecular chains of the polymer are less mobile.

The temperature variation of the stress at which the transition is observed with the temperature of that transition is plotted in Fig.2. The $\log(\text{stress}) - \frac{1}{T}$ plot for the methacrylate is included for comparison with the published results; it is curved downwards in the manner found for Saran B. Over a short interval such as Boyer⁵ used for polystyrene a linear plot could be drawn. The two slopes and stress magnitudes are of the same order, which is evidence of the identity of the phenomena. As for Saran B a reasonably linear plot is obtained for all values of the stress against temperature. For the present data extrapolating to zero stress gives a temperature very close to the second order transition observed dilatometrically for the sample.

2.32 The stress distribution in the relaxing specimen

The variation of the stress distribution with time within the bent specimen will now be considered. The initial stress gradient across the section of the beam may be assumed to be uniform. The simplifying assumption will first be made that the central position of the neutral axis remains unchanged, i.e., that the stress decay is symmetrical about that axis.

For polyisobutylene it was shown⁴ that at low elongations the shape of the experimental curves is independent of elongation; the curves are superposable by multiplying the stress values by a simple factor which was proportional to the elongation and, therefore, also to the initial stress. Assuming the same law to hold for portions of the sample sufficiently stressed to be above the second order transition, in those portions of the sample remote from the neutral axis the stress decays more rapidly than in those near to it. The stress gradient in these portions diminishes with time but remains uniform as long as the chain mobility is retained. On the further assumption that the slow ratio of decay is also logarithmic the stress distribution may be determined graphically for given rates. The form of such curves is shown in Fig.3. Graphical integration to calculate equivalent outer fibre stresses as defined in 2.31 above gives curves of the form obtained experimentally. Fig.4 shows such curves calculated for 3/16 and 1/16 inch thick samples with approximate initial stress gradient used experimentally. The use of thinner samples gave increased slopes, a slightly higher stress at the transition and its later occurrence, as these curves indicate.

It will be noted that the true outer fibre stress is below the equivalent mean value as soon as the stress gradient across the section of the beam ceases to be uniform. The decay of the lower stresses in the inner portion being relatively slower than those near the surface, the former have an increasing influence on the value of the mean. The observed stress at the transition is one such value and is similarly too high. Altering the temperature is equivalent to altering the initial slopes of the curves (Figs.1 (a) and (b)); its relative effect on the stress at the transition was found graphically to be less than the experimental error of its determination.

The graphical treatment indicates that the transition is observed at approximately the time at which the outer portions initially at the highest stress reach the true transition. This observation permits an estimate of the true stress at the transition to be made. The area A B C D indicated on Fig.3 is calculated as a function of the true value AB from the initial stress and the rate of stress decay below the transition. Since this area is equal to $\frac{1}{2} BC \times$ (observed stress at the transition) the value of AB is derived.

TABLE I
The stress to reduce the second order transition
to various temperatures

Temperature °C.	Equivalent outer fibre stress lb/sq. in.	Calculated stress lb/sq. in.
55	902	647
60	743	576
65	604	432
70	350	314
75	198	159

Table I shows these calculated mean values which are also included in Fig. 2 (dotted lines). The agreement in the calculated values between samples 3/16 inch and 1/16 inch thick was good.

If the decay in compressive stress differs from that in tension the neutral axis is virtually shifted towards the face at which the rate is slower since the system is in equilibrium. It can no longer be treated simply as in the above case. The important facts to be noted are that the equivalent outer fibre stress calculated from the experimental data is always above the actual stress present and that the tensile stresses tend to a uniform low value. Since the latter are of major importance in failure and the sole cause of crazing the value of annealing is underlined.

3 Annealing of shapings

The appropriate conditions for the heat treatment of complete structures may now be detailed. The chief factors to be considered are the method, temperature and time of heating and the conditions of cooling. For cleanliness and to maintain dryness in double shell hoods air is recommended; in any case no aqueous fluid should be used nor any liquid or gas liable to cause crazing under stress. Solvent vapours which may be present in cemented joints or have been absorbed in the plastic are removed with great difficulty under ordinary temperature conditions, but the greater part can be de-sorbed at annealing temperatures. To assist this desorption process enclosed spaces, such as interspaces, should be well ventilated with clean dry air preheated to oven temperatures. The temperature of annealing should be as high as is consistent with the avoidance of serious distortion of the structure. Distortion depends on the unknown stresses initially locked in the material and on the adequacy of the forming operation. If the latter has been conducted at too low a temperature the material exhibits an elastic memory and distorts towards its original cast condition. Material held in the deformed state at forming temperatures shows less distortion when annealed at a lower temperature than when cooled immediately after forming; hence also the rate of cooling influences the extent of this form of distortion. Thus the choice of temperatures for annealing depends on unknown factors and must be somewhat arbitrary. The data presented in this note suggest a minimum of 65°C. for perspex to Specification D.T.D. 339A (containing 5% of dibutyl phthalate); experience available at the present time suggests a maximum of 70°C.

The time of heating for annealing must be sufficient to permit the attainment of thermal equilibrium and, therefore, the desired fall in stress. Prolonged heating is not justified in that the stress decay is very slow in the later stages and at the recommended temperatures the stress remaining is small. A total period of three hours is proposed measured from the time at which the oven temperature recovers (if already hot when the structure is inserted) or reaches (if heated with the structure from cold) the required value. Cooling may be permitted to occur naturally to still air at room temperature. Since all the plastic is at temperatures below the second order transition point after annealing the ill-effects of irregular cooling are small. Negligible permanent stresses are set up and the only objective is to avoid excessive temperature gradients through the material. If desired the rate of cooling may be slowed by covering the structure in a suitable insulating material; this must be chosen to avoid scratching the surface of the glazing. Alternatively the oven may be switched off and allowed to cool before removing the shaping. Table II summarises the above recommendations.

TABLE II

Recommended conditions of annealing formed structures
of perspex to Specification D.T.D. 339A

Temperature	65 - 70°C.
Time	Not less than three hours
Ventilate all enclosed spaces with clean dry air at 65 - 70°C.	

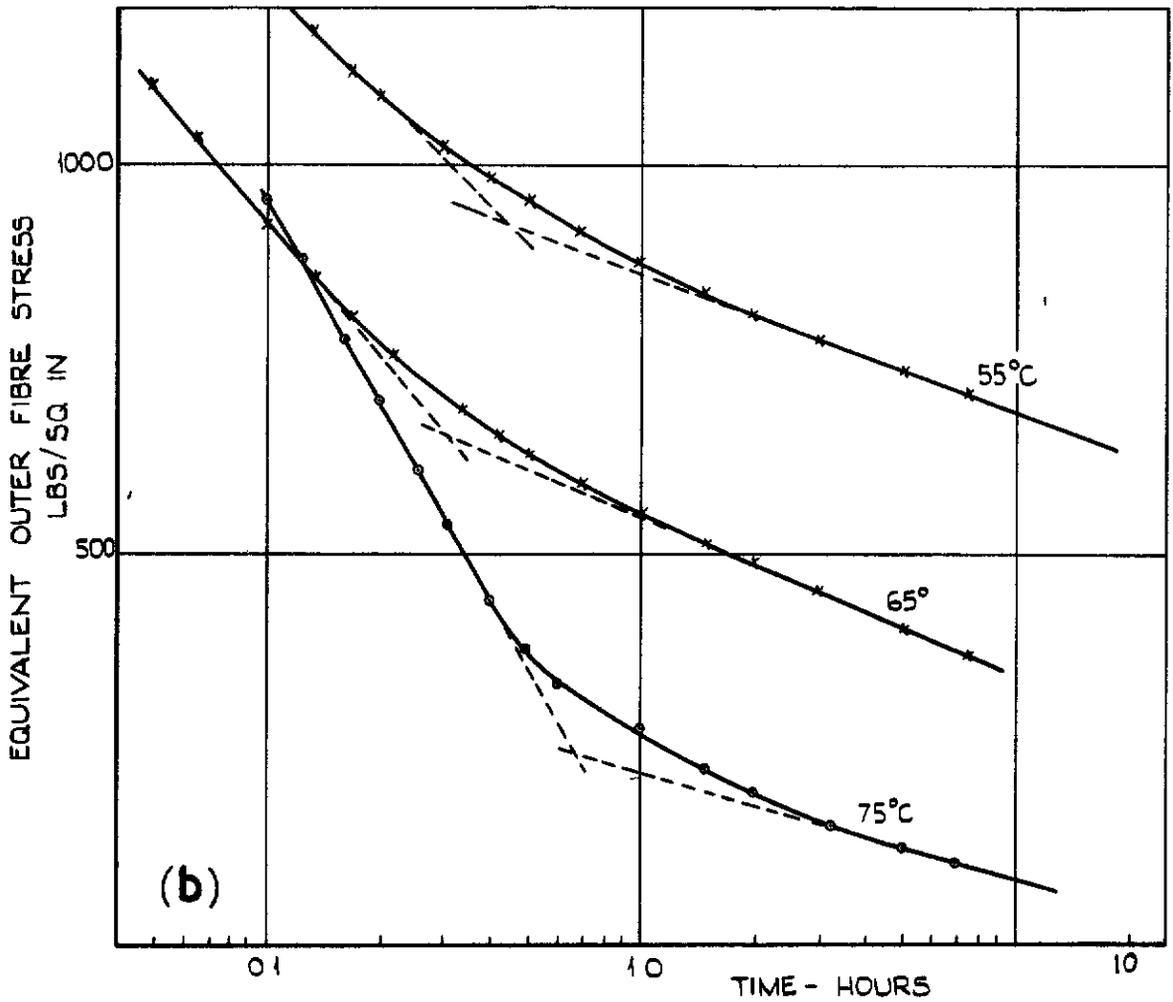
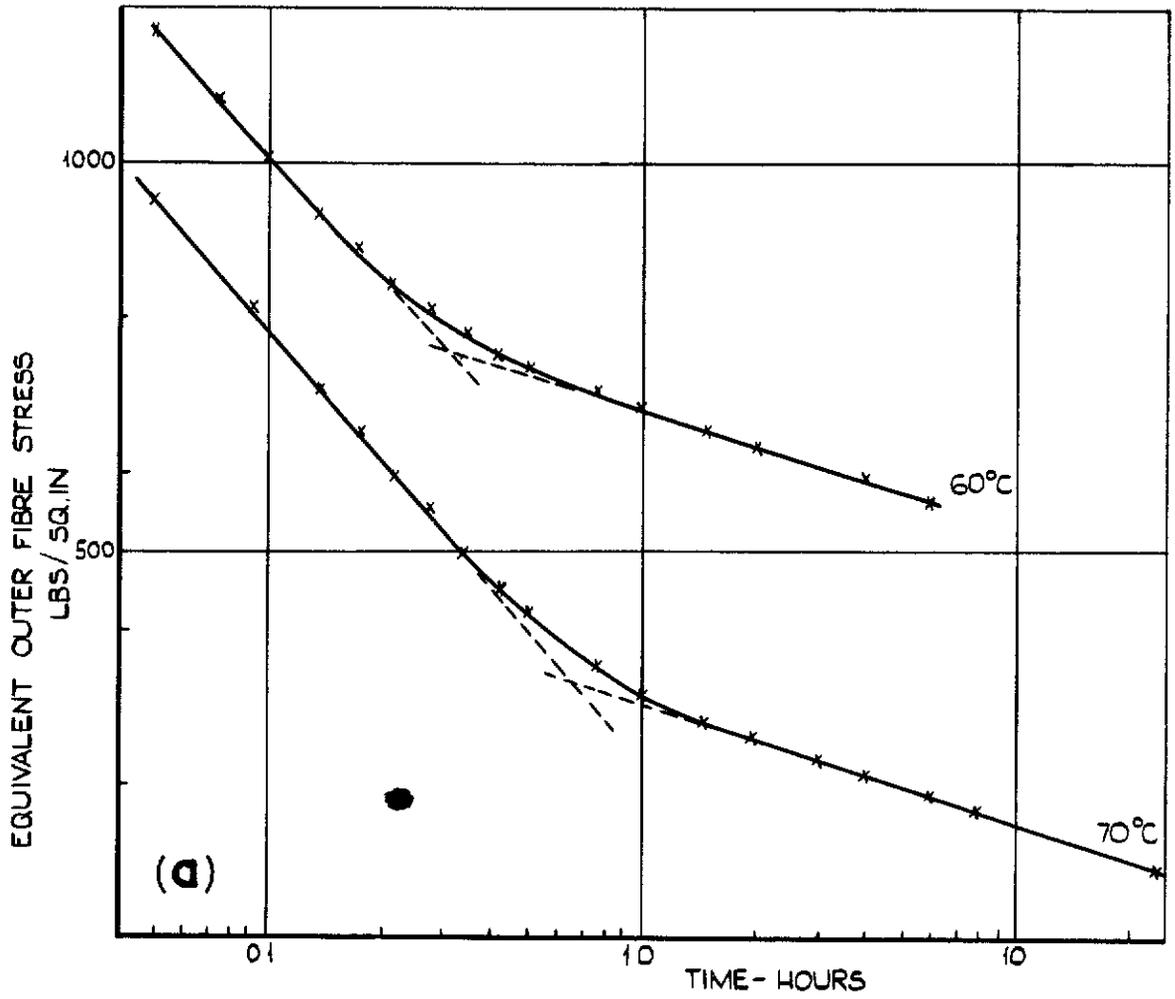
4 Conclusions

The relaxation of stress in plasticised polymethyl methacrylate at annealing temperatures and at constant deformation has been shown to occur in two stages, the first rapid and the second slow. The temperature of the change from one stage to the other represents the second order transition lowered from its normal value to the experimental temperature by the applied forces. The temperature dependence and magnitude of the stress to produce this effect are similar to that of other vinyl polymers. The stress distribution through a sample in bending is considered; the tensile stresses tend to a uniform value below that required to lower the transition to the temperature in question.

The annealing of a complete structure is discussed. This should be performed when mounted in its final metal framework. On the basis of the relaxation data a time and minimum temperature are proposed for the heating cycle. Distortion limits the upper temperature that can be used and a value based on present experience is put forward. Further work is to be done on unplasticised methacrylate.

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FIGS. 1a & 1b THE RELAXATION OF STRESS AT VARIOUS TEMPERATURES.

FIG.2.&3.

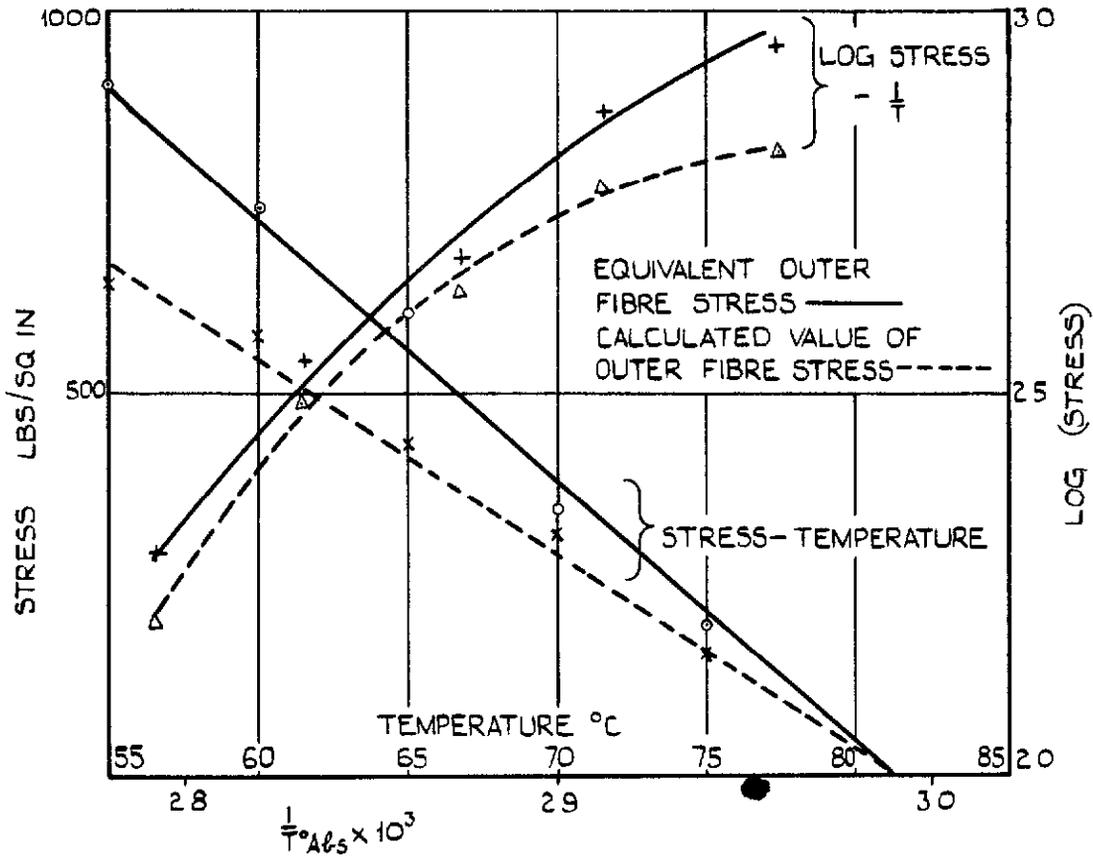


FIG.2. THE TEMPERATURE -DEPENDENCE OF THE STRESS AT THE SECOND-ORDER TRANSITION.

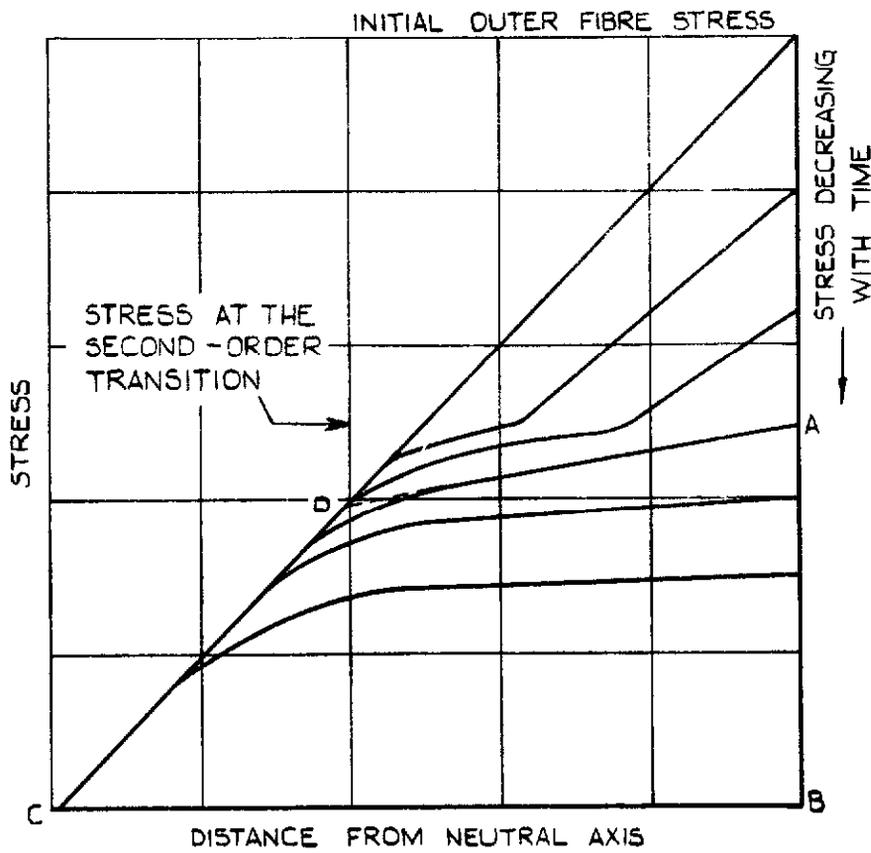


FIG3. VARIATION OF STRESS DISTRIBUTION WITH TIME - GENERAL FORM.

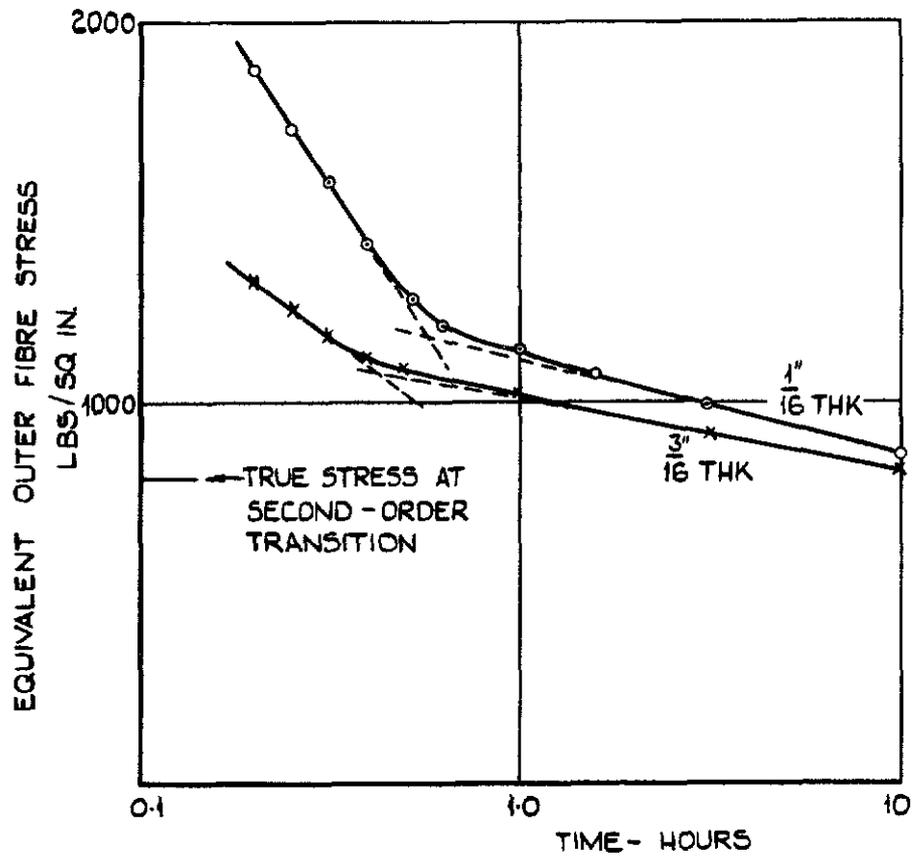


FIG.4. THEORETICAL FORM OF RELAXATION CURVES.

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