

A NOTE ON THE ANNEALING OF OPTICAL GLASS.

BY

L. H. ADAMS and E. D. WILLIAMSON.

AN ideal optical glass would fulfil three principal requirements. (1) the glass must be colorless and transparent; (2) it must be chemically homogeneous, that is, free from striæ, "stones" and bubbles; and (3) it must be mechanically homogeneous—free from internal stress. The last of these requirements is a subject which occupied the attention of the authors during a portion of the period of the war-time participation of the Geophysical Laboratory in the manufacture of optical glass, and is the subject which we now propose to discuss. The prevention of internal stress in glass and its removal when present is a problem which requires, for its exact solution, a determination of certain thermal, optical, and elastic constants of the different glasses. As will be apparent later, the stresses are determined by the temperature gradients and therefore a knowledge of the relations between the various factors such as temperature gradients, rate of heating, stress, and annealing temperature is required. Moreover, since stress is usually measured by the change in an optical property—birefringence—the data in the stress-birefringence ratio must also be obtained. Certain of these phases of the subject have already been covered in previous publications from this Laboratory, and the Annealing of Glass is treated in detail in a paper which is now ready for publication in another journal. It has seemed desirable, however, to summarize briefly the salient features of this subject, in so far as they pertain to optical glass, and accordingly in this note the formation of internal strain in glass is discussed, and concrete directions for the practical annealing of optical glass are presented.

The Way in Which Internal Stress Arises.—When a lump of molten glass is cooled quickly it acquires internal stresses and is said to be "strained."¹ Excessive strain cannot be tolerated

¹ It is important to remember that "stress" denotes a force and "strain" the consequent deformation. Stress usually accompanies strain, but the two words, although often interchangeable, are not synonymous.

in any glass, since it renders the glass liable to break when handled or heated again, while in the case of optical glass even a moderate amount of strain causes troublesome warping of finished lenses and prisms. In order to understand how glass becomes strained, it is necessary to recall that at a sufficiently high temperature glass softens and that when soft, internal stresses are relieved by viscous flow. Moreover, any solid body when heated or cooled from the surface acquires a certain temperature gradient,² and this temperature gradient induces temporary stresses the direction and magnitude of which depend on the temperature gradient and the dimensions of the solid.³ Thus, for example, in a slab of glass the surfaces of which are being heated at a constant rate h (in deg. per min.), the stress F at any point is given by the equation

$$F = 4.6 h (a^2 - 3x^2) \quad (1)$$

in which F is in kg/cm² and is positive for a tension, a is the semi-thickness (in cm.) of the plate, and x is the distance from the middle. Along the middle, $x = 0$ and the equation reduces to

$$F = 4.6 ha^2 \quad (2)$$

Thus, in a slab or plate heated at a uniform rate there will be in the middle a tension in all directions parallel to the faces of the plate, and at the surface a corresponding compression, while at a distance from the middle equal to 0.578 of the semi-thickness is a neutral zone, that is, neither tension nor compression. Fig. 1 illustrates the distribution of stress in a slab of glass 2 cm. thick heated at the constant rate of 5° C. per minute.

The corresponding formula for the stresses in a plate due to a sudden change of surface temperature is more complicated. Its general form is the infinite series:

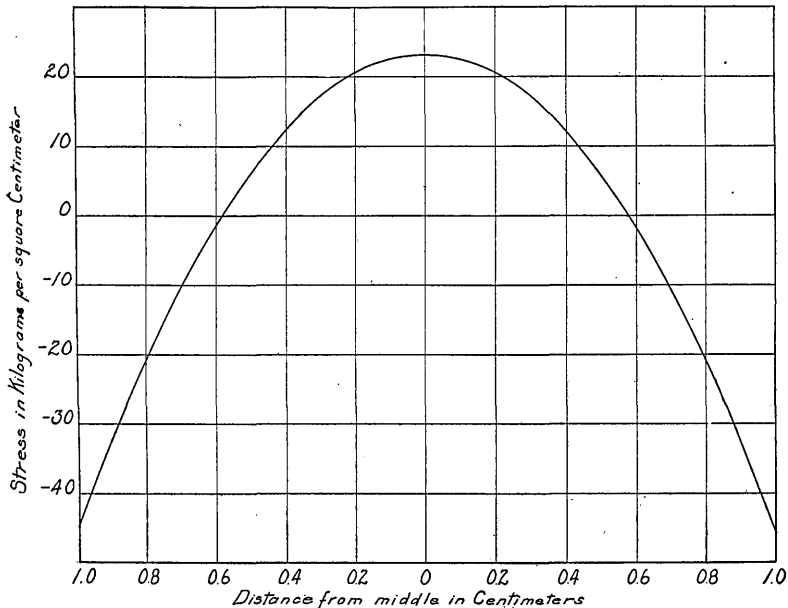
$$F = \frac{4 a (\theta_i - \theta_f)}{\pi C} \sum_{m=1}^{m=\infty} e^{-\frac{(2m-1)^2 \pi^2 \kappa t}{4 a^2}} \left\{ \frac{2}{\pi (2m-1)^2} - \frac{(-1)^{m+1}}{2m-1} \cos \frac{(2m-1) \pi x}{2a} \right\} \quad (3)$$

² E. D. Williamson and L. H. Adams. *Phys. Rev.*, 14, 99-114 (1919).

³ For a more detailed explanation the reader is referred to the above-mentioned paper on "The Annealing of Glass."

where m is any integer, θ_i is the initial uniform temperature of the plate, θ_f is the new temperature of the surfaces, C is equal to $\frac{1}{6R} + \frac{2}{9K}$, K being the modulus of compressibility and R the modulus of rigidity, and κ the coefficient of thermal diffusivity. In Fig. 2 is shown for several values of the time, the distribution of stress in a plate of glass 2 cm. thick, initially at 0° C. and suddenly plunged into a bath at 100° C.

FIG. 1.

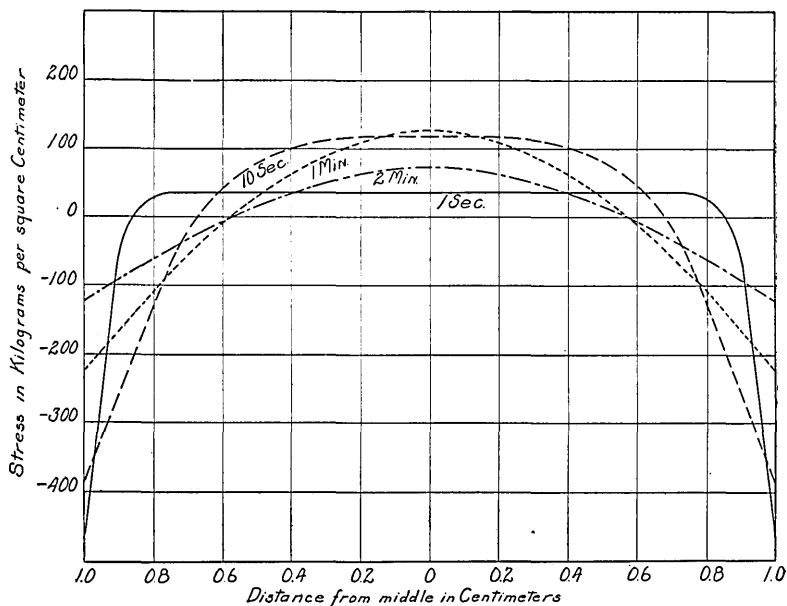


Curve showing distribution of stress in a plate of glass 2 cm. thick which is being heated at a constant rate equal to 5° C. per minute. Stresses are given in kg/cm^2 and are taken as positive for a tension and negative for a compression.

It is obvious that if a temperature gradient happens to exist in a block of glass which is unstrained, the removal of the temperature gradient will produce stresses equal and opposite in sign to those produced by introducing the same gradient. Now if we start with a lump of glass in the molten condition and suppose that it be cooled at a uniform rate, the stresses produced by the establishment of the temperature gradient disappear almost instantly, and as the cooling proceeds we have the condition of a temperature gradient without accompanying stresses. When room

temperature is reached, however, the cooling stops, the temperature gradient disappears, and hence, according to the rule laid down, the removal of the gradient produces a state of permanent stress, which is exactly the same as the system of temporary stresses caused by heating the originally cold and unstrained glass at the same rate. That is to say, if the glass be in the form of a plate, the inside will be in a state of longitudinal tension and

FIG. 2.



Set of curves showing the distribution of stress in a plate of glass 2 cm. thick which, initially at 0° C, is suddenly plunged into a bath at 100° C. The full line indicates the magnitude of the stresses throughout the glass after 1 second has elapsed; the broken line, after 10 seconds; the dotted line, after 1 minute; and the dot-dash line, after 2 minutes.

the outside in a state of longitudinal compression. The same kind of explanation holds for glass cooled at a variable rate and we may perhaps regard the stresses in unannealed glass as due to a temperature gradient (corresponding to a certain cooling rate) being "frozen in" as the glass hardens.

Detection of "Strain."—Glass when subjected to stress becomes birefracting. The usual method for detecting strain takes advantage of this fact, the presence or absence of strain being determined by observing the glass in polarized light between

crossed nicols. A small amount of strain causes a lightening of the field;⁴ a larger amount produces the higher colors of the Newton scale, and by comparing the colors with a proper chart a quantitative measure of the optical path difference is obtained. A better method consists in using a graduated quartz wedge⁵ in which the path difference can be read directly in $\mu\mu$.

In any one kind of glass the birefringence is proportional to the stress; that is,

$$\Delta n = BF \quad (4)$$

where F is the stress in kg/cm^2 , Δn is the birefringence, and B is a constant. The values of B for nine kinds of optical glass⁶ are given in the fourth column of Table I. For most kinds of glass a uni-directional stress of 1 kg/cm^2 produces a maximum birefringence which does not differ much from about 2.8×10^{-7} , that is, about $2.8\mu\mu$ per cm. For heavy flint glasses, however, the value of B is smaller, and for the heaviest flints is of the opposite sign.

TABLE I.

For converting strain from optical to mechanical units. The first three columns describe the glass, and the last column gives the birefringence-stress ratio.

Kind of Glass	Refractive index n_D	Constringence ν	Birefringence due to 1 kg/cm^2 B
Borosilicate Crown.....	1.516	62	2.85×10^{-7}
Ordinary Crown.....	1.523	59	2.57×10^{-7}
Light Barium Crown.....	1.574	57	2.81×10^{-7}
Heavy Barium Crown.....	1.608	57	2.15×10^{-7}
Barium Flint.....	1.606	44	3.10×10^{-7}
Light Flint.....	1.573	42	3.20×10^{-7}
Medium Flint.....	1.616	37	3.13×10^{-7}
Heavy Flint.....	1.655	33	2.67×10^{-7}
Extra Heavy Flint.....	1.756	27	1.22×10^{-7}

Moreover, by determining the sign of the birefringence, that is the α and γ directions,⁷ we may know the direction and sign

⁴ For detecting a small amount of strain, greater sensitivity is obtained by using a sensitive-tint plate similar to that ordinarily used on the petrographic microscope.

⁵ See for example, F. E. Wright. The methods of petrographic microscopic research. Carnegie Inst., Washington, Publication No. 158 (1911).

⁶ See L. H. Adams and E. D. Williamson. *J. Wash. Acad. Sci.*, 9, 609-623 (1919).

⁷ α is the lesser refractive index, and in a positive uniaxial crystal is for light vibrating perpendicular to the axis.

of stress; thus having determined the α and γ directions (in any ordinary glass), we know that there is either a tension parallel to γ or a compression parallel to α (or both).

Taking the average value of B as $2.8\mu\mu$ per cm., and substituting by equation (4) in equation (2) we have

$$\Delta n = 13 ha^2 \quad (5)$$

(in which Δn is in $\mu\mu$ per cm., h is in deg. per min. and a in cm.) for the birefringence along the middle, due to heating a plate of glass at a constant rate.

Removal of Strain—Annealing.—At a sufficiently high temperature the internal stresses relieve themselves by internal movement and thus gradually disappear. If the glass be then properly cooled it will be found to have very little internal strain. We have proposed to call glass “annealed” when the optical path difference⁸ as measured along the middle of a slab is not greater than $5\mu\mu$ per cm. The “annealing temperature” is defined as the temperature at which the strain is reduced from 50 to $5\mu\mu$ in a specified time, and the “annealing range” is defined, also quite arbitrarily and solely for convenience in referring to this range of temperature, as that 150° interval lying immediately below the “annealing temperature” for 1 minute. Temperature changes below the annealing ranges do not readily affect the permanent strain.

Experimental Determination of Release of Strain.—In order to measure the rate at which stress disappears in various glasses and at various temperatures, rectangular plates of each glass were placed in an electric furnace which was provided with a small hole at either end so that the path-difference (and hence the strain) could be determined *in situ*. The plates were about 2 cm. thick and 8 to 10 cm. long and had the two ends ground flat and then polished.

With each kind of glass measurements were made at several temperatures—usually three—which were measured with a

⁸ The standard of annealing proposed by F. E. Wright and adopted during the war for the inspection of optical glass was $20\mu\mu$ per cm. *maximum* path difference. The maximum in a slab is found at the outside surface, and is usually about twice that in the middle (where it is easier to measure the strain). Thus $20\mu\mu$ at the surface would correspond to $10\mu\mu$ in the middle. We have preferred the lower value, $5\mu\mu$, because the standard is an arbitrary one in any case, and no difficulty is encountered in annealing glass to that degree of excellence.

platinum-platinrhodium thermocouple in conjunction with a potentiometer. Glass was first strained by rapid cooling from a high temperature and the temperature of the furnace was held constant within 1° while, at frequent intervals of time, the birefringence along the middle of the slab was read by means of a graduated quartz wedge. For further details, including a diagram of the furnace and optical system, the reader is referred to the above-mentioned paper on the Annealing of Glass.

It was found that the release of stress at constant temperature proceeds according to the empirical equation

$$\frac{1}{\Delta n} - \frac{1}{(\Delta n)_0} = At \quad (6)$$

in which $(\Delta n)_0$ is the original birefringence, Δn is the birefringence at the time t , and A is a constant, which we may call the "annealing constant" for a particular glass at a particular temperature, and which is a measure of the rate at which glass anneals when held at constant temperature. Since by differentiation, $-\frac{d(\Delta n)}{dt} = A(\Delta n)^2$, it is to be noted that the equation (6) is equivalent to the statement that the rate of release of stress at constant temperature is proportional to the *square* of the stress.

The dependence of the rate of annealing on the temperature θ , that is, the relation between A and θ , is expressed by another empirical equation

$$\log A = M_1\theta - M_2 \quad (7)$$

where M_1 and M_2 are constants. The experimental results are summarized in Table II by giving the values of M_1 and M_2 for

TABLE II.

Constants, M_1 and M_2 of Equation 7, and annealing temperatures for various times.

Kind of Glass.	M_1	M_2	Annealing temperatures.							
			1 min.	5 min.	10 min.	1 hr.	5 hr.	1 day	1 week	1 mo.
Borosilicate Crown	0.030	18.68	598	575	565	539	515	493	464	444
Ordinary Crown029	17.35	573	548	538	511	487	464	434	414
Light Barium Crown032	20.10	605	583	574	549	527	506	480	461
Heavy Barium Crown038	24.95	637	619	611	590	572	554	532	516
Barium Flint028	16.28	555	530	519	491	466	442	412	390
Light Flint033	15.92	460	439	429	406	385	364	338	320
Medium Flint038	18.34	463	445	437	416	398	380	358	342
Heavy Flint037	17.51	453	434	426	405	386	368	345	329
Extra Heavy Flint033	15.03	433	412	403	379	358	337	312	292

each of the nine varieties of optical glass. By means of equation (7) the value of A at a given temperature can be calculated, and from A , by means of equation (6) the "annealing time" for a given temperature can be computed. Thus, recalling that the annealing time is that time in which the birefringence is reduced from 50 to $5\mu\mu$ per cm., we have by equation (6) that the annealing time

$$t = \frac{\frac{1}{5} - \frac{1}{50}}{A} = \frac{0.18}{A}.$$

The annealing temperature for a given annealing time can be obtained in a similar manner. In making computations by equations (6) and (7) t is to be taken in minutes, Δn in $\mu\mu$ per cm. (10^7 times the true birefringence) and θ in degrees on the Centigrade scale.

Cooling Procedure.—The strain having been removed by holding the glass for a sufficient time at the proper temperature, the next step in the practical annealing of glass consists in cooling it down to ordinary temperatures without reintroducing an excessive amount of strain. This is, from the theoretical standpoint, a much more complicated process than that of removing the stress. The usual method of annealing glass heretofore has been as follows: The glass is heated at a moderate rate to a temperature at which the strain disappears almost instantaneously (with ordinary crown glass, for example, this temperature would be about 570°), and is then cooled very slowly down to room temperature. The permanent strain acquired by the glass in this case depends on the rate of cooling, and can be calculated fairly closely by equation (5) if h is taken as the *cooling* rate (in deg. C. per minute). Thus, if a plate of glass 3 cm. thick is to be cooled from a high temperature at such a rate that along the middle not more than $5\mu\mu$ per cm. birefringence is introduced, the cooling rate would be

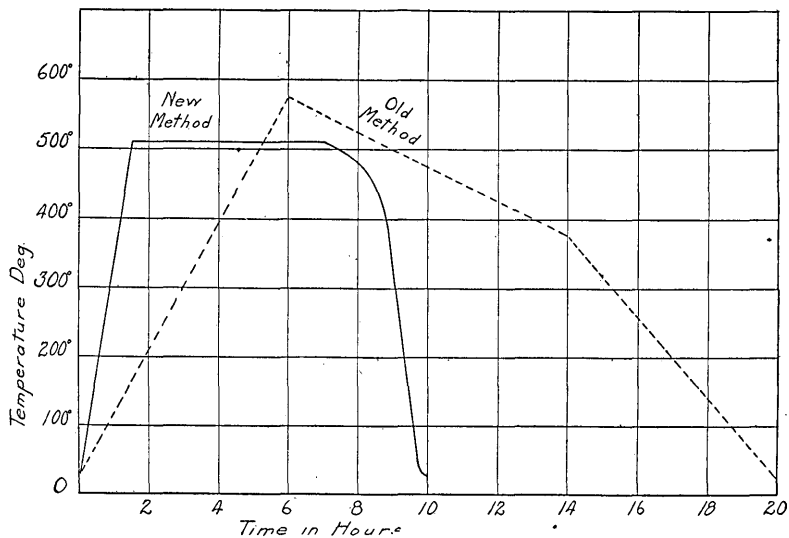
$$\frac{5}{13 \times \left(\frac{3}{2}\right)^2} = 0.17 \text{ deg. per min.}$$

or about 10° per hour. Other things being equal, the cooling varies inversely as the square of the thickness.

So much for the usual method of annealing glass. A procedure which is believed to be much better is as follows: Instead

of heating the glass to a rather high temperature for a short time, we hold it at a much lower temperature for a longer time. In this case the cooling rate can be much greater than with the usual method, a circumstance which compensates for the extra time spent in holding the glass at the annealing temperature. The two methods are compared graphically in Fig. 3. This improved method was used during the war in the annealing of some hundreds of thousands of pounds of glass, and the satisfactory

FIG. 3.



The broken line indicates graphically the usual method for annealing optical glass, and the full line the procedure similar to that recommended in this paper for ordinary crown glass 2 cm. thick. By this newer method the glass is heated very rapidly, is then held for some hours at a rather low annealing temperature, and is then cooled at a rapidly increasing rate.

results obtained indicated that this procedure has many advantages over the ordinary method.

In the first place, it is much easier to hold an annealing kiln at a constant temperature than to cool it at a given constant rate. The newer method requires a fairly constant temperature for some hours, but the subsequent cooling takes place in a short time and does not need careful control, so that on the whole the chances of failure, particularly when unskilled workmen are employed to regulate the burners, are less than with the older method which involves the difficult operation of cooling at a constant slow rate.

Another advantage of annealing at the lower temperature is that it minimizes the danger of overheating the glass. This is of especial importance when annealing valuable optical glass, large batches of which in several cases known to the authors have been spoiled, on account of the fact that the temperature in the annealing furnace was accidentally allowed to become about 50° too high. The sum of the time spent in annealing and the time spent in cooling is somewhat less for the second method, and by the newer method there is a saving of time spent in heating the glass up to the annealing temperature.

Annealing Schedules.—Mathematical analysis of the problem (which is too lengthy to be given here) shows that when following the newer procedure best results are obtained by annealing the glass to one-half the allowable strain (say $2.5\mu\mu$ per cm.) and allowing the additional $2.5\mu\mu$ to be incurred during the cooling process. The analysis also shows that for a slab 2 cm. thick a minimum time is required when the annealing temperature is such that the annealing constant, A , is about 0.0038. This corresponds to an annealing time of about one and three-quarters hours. We allow a factor of safety equal to two, and therefore anneal the glass for three and a half hours at the temperatures—for various kinds of glass—given in the second column of Table III. These temperatures are calculated from equation (7), the values of M_1 and M_2 being taken from Table II, and A being taken as 0.0038.

TABLE III.

Directions for annealing optical glass. Heat very rapidly up to annealing temperature; hold for the appropriate time, $3\frac{1}{2}$ hours for plates 2 cm. thick and 12 hours for plates 4 cm. thick; and cool at an increasing rate which except at the start doubles for every 20° drop in temperature.

Kind of Glass.	Annealing temperature for plate 2 cm. thick. Initial cooling rate 24° C. per hour.	Annealing temperature for plate 4 cm. thick. Initial cooling rate 6° C. per hour.
Borosilicate Crown.....	542	522
Ordinary Crown.....	515	494
Light Barium Crown.....	553	534
Heavy Barium Crown.....	593	578
Barium Flint.....	495	474
Light Flint.....	409	391
Medium Flint.....	419	403
Heavy Flint.....	408	392
Extra Heavy Flint.....	382	364

As for the cooling rate, it can be shown that minimum strain is introduced by cooling in a certain specified time if the cooling rate follows the relation

$$h = \frac{h_0}{2} \left(1 + 2 \frac{\theta_0 - \theta}{20} \right)$$

in which h_0 is the initial cooling rate, θ_0 is the annealing temperature and θ is any temperature. Except at the beginning this is nearly equivalent to the statement that the cooling rate doubles for every 20° drop in temperature.⁹ Furthermore, it so happens that the time spent in cooling is approximately equal to the time required at the annealing temperature.

In the third column of Table III are given the annealing temperatures for a slab 4 cm. thick, and at the head of the second and third columns are given the proper initial cooling rates for the two thicknesses. For the 2 cm. slab the cooling rates in the successive 10° intervals of temperature would be 24° (per hour), 29° , 36° , 46° , 60° , 79° , etc., and for the 4 cm. slab, 6° , 7° , 9° , 12° , 15° , 20° , etc. In general, doubling the thickness of the glass requires a 20° diminution in the annealing temperature, a multiplication by four of the annealing time, and a division by four of the initial cooling rate.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

⁹ It is obvious that if the cooling rate be thus increased in geometrical ratio, the rate eventually becomes very great; indeed, so great that the glass would be fractured. It turns out, however, that by the time this excessive rate is reached the temperature would usually be below the annealing range, so that the cooling rate would then be without much effect on the final strain or on the total time required for cooling.