S 572

CAUSE AND REMOVAL OF CERTAIN HETEROGENEITIES IN GLASS

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ABSTRACT

Precise measurements of index of refraction of six barium flint lens blanks from the same melt showed individual deviations from the mean which reached a maximum of 37×10^{-6}. This suggested an optical heterogeneity that might easily exceed, within a given blank, an index tolerance of $\pm7\times10^{-6}$.

By reannealing the blanks the maximum deviation from the mean index was reduced to 12×10^{-6}, and in every case the absolute value of the deviation was decreased. Furthermore, in four of the six cases the sign of the deviation was reversed. These results showed that thermal effects predominated in producing the heterogeneities. The use of the "annealing equilibrium coefficient of index," for this glass -0.00003 per 1° C. increase in annealing temperature, indicated that the variations in the indices after reannealing corresponded to a nonuniform furnace gradient averaging 0.4° C. per 15 cm.

A second and more thorough reannealing reduced the maximum deviation to 3×10^{-6}. Considering both reannealings, this high degree of homogeneity, without material change in average index, was gained by surrounding the glass symmetrically with good heat conducting material in order to reduce furnace temperature gradients, by preheating to decrease the differential effects of all previous heat history, and by cooling not too rapidly to that predetermined annealing temperature at which the initial physicochemical condition was reestablished after a sufficient treating time.

The results of this series of experiments are consistent, therefore, with the following conclusions:

1. Under conditions conforming to present good practice in production, differences in heat history cause optical density variations in practically strain-free glass which render its use questionable for the most exacting requirements.
2. Such variations are largely removable by reannealing after a preheating, provided the furnace temperature gradients are sufficiently low.
3. In properly selected glass, the maximum effects due solely to differences in chemical composition, if any exist, are small in the sixth decimal place of index of refraction.

CONTENTS

		Page
I.	Introduction	720
II.	Determination of certain properties of the glass	721
III.	Initial comparison of the blanks	723
IV.	Possible causes of the index variations	723
V.	Experimental methods and procedure	726
VI.	Discussion and analysis of data on the first reannealing	728
VII.	Second or confirmatory reannealing	733
VIII.	Concluding discussion	735

I. INTRODUCTION

In the execution of the design for an optical system of any high precision instrument one of the first factors demanding consideration is the quality of the glass to be used. Aside from the fundamental requirement of suitable values for the refractivity and the partial dispersions, it is desirable that the variations in these quantities be small. Even a lack of homogeneity not detectable after careful search by the methods usually employed in testing commercial optical glass may entail variations in the refractive index which will adversely affect the performance. Indeed, it is often found necessary, in order to avoid irregularities in the wave front transmitted by a lens made of such material, to effect a degree of compensation by carefully figuring the surfaces. This process is successfully accomplished only by the most expert workers of optical surfaces with the aid of frequent performance tests and it is obviously to be avoided so far as possible.

The extent to which optical heterogeneity [1] is compatible with satisfactory performance of an optical system will be considered at another time in connection with a discussion of the optical uniformity of glass. Briefly, however, on accepting Rayleigh's [2] tolerance of one-fourth wave length as the maximum phase difference to be permitted and on assuming the possibility of sufficiently perfect design and construction, it would seem that figuring to correct for refractive index variations would be unnecessary for glass paths not exceeding 1 cm in length, provided the total variation in index never exceeds 0.000014.[3] For some distributions of the optical heterogeneity this degree of uniformity is, perhaps, to be regarded as a sufficient rather than a necessary prerequisite in optical media; but, in view of the difficulty of insuring against unfavorable distributions, and since even more exacting limits [4] than that of Rayleigh have been named, it seems desirable that the maximum deviations from the mean index within a single blank (intrablank deviations) should be confined to ± 0.000007 divided by the thickness in centimeters.

Interblank differences may be several times larger in magnitude, in most instances, than the above tolerance and still be in themselves of little or no importance; yet, in the absence of direct knowledge concerning their cause, speculation about their origin will suggest at once the possibility of objectionable intrablank variations. Just such a possibility was revealed through some measurements on six lens blanks of European manufacture obtained to form one of three components of some apochromatic objectives.

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[1] The use of the term optical heterogeneity in referring to a medium of variable refractive index is in accord with the practice of certain writers on optics. See, for example, R. A. Herman, Geometrical Optics, 1900, pp. 304–319.

[2] Lord Rayleigh, Phil. Mag., **8**, p. 409; 1879.

[3] For light of maximum visibility traversing a glass path, g, 1 cm in length, this value of the limiting index variation, Δn, corresponds to Rayleigh's limiting variation in optical path, Δs, according to the relation $\Delta n = \Delta s / g$.

[4] F. L. O. Wadsworth, Astrophys. J., **16**, p. 279; 1902; A. W. Conrady, Montly Not. Ry. Astron. Soc. **79**, p. 591; 1919.

II. DETERMINATION OF CERTAIN PROPERTIES OF THE GLASS

The six disks of glass bore the same melt number and were identical in size, 1 cm thick and 9 cm in diameter. Although the chemical composition was not determined, the index of refraction, dispersion, density,[5] and thermal behavior are similar to those of a barium flint glass. The blanks were undoubtedly well annealed, in the usual sense, since the purchase order called for glass of first quality suitable for the construction of precision optical components and since an examination revealed a birefringence of the order of magnitude of not more than 1 millimicron per centimeter of glass path. The maker furnished some optical data for the glass but did not state conditions of temperature and air pressure, and, of course, gave no intimation of the variations which might be expected either within an individual blank or between the various blanks.

Since in the design of an apochromat an accurate knowledge of the partial dispersion ratios is of paramount importance, it seemed desirable to make careful determinations of the indices of refraction for various wave lengths on each one of the blanks. To accomplish this with a minimum glass waste and with a maximum portion of the glass involved in the measurements, it was necessary to grind and polish plane surfaces or windows [6] on the edges of the blanks as shown at AA' in Figure 1, thus forming the equivalents of prisms with refracting angles α. The light path in each blank was 8 cm long with a cross section of approximately 2.8 by 1 cm, so that each measured index should be, to a fair degree, characteristic of the whole blank. In one blank (No. 3) after a small 60° prism had been made from a very restricted peripheral portion, B in Figure 1, a second prismatic path (shown by dotted lines) was used. Index measurements on the small prism were necessary for the determination of the temperature corresponding to the equilibrium condition of the glass (see below), but it was also realized that the employment of different paths might show the presence of important intrablank variation in optical density.

A spectrometer was used for all index determinations, employing the minimum deviation method with all the precautions which experience has shown to be consistent with probable errors of a few units in the sixth decimal place.[7] All of the observations were made

[5] The density was found by E. E. Hill, of the volumetric section, to be 3.1558 g/cm³ at a temperature of 25° C.

[6] This method of preparing the samples is probably identical with that mentioned for large disks by M. J. Barot, Revue d'Optique, 2, pp. 502–505; 1923.

[7] The windows of the blanks, polished by E. L. Robinson of the optical glass shop, were flat to approximately 1/10 λ. The refracting angles, α, were all of approximately 37°. They were measured with an average probable error of ±1/4 second of arc, and it is thought that the systematic errors did not exceed ±1/2 second. These errors in prism-angle measurement are the only important ones concerned in the comparison of the various blanks and they correspond in index of refraction to magnitudes of $\pm 1\times 10^{-6}$ and $\pm 2\times 10^{-6}$, respectively. This comparison of blanks is not materially affected by the errors in measuring angles of deviation because light of three wave lengths has been used in all cases. The use of larger prism angles with more favorable tolerances in their measurement was impossible in the constant temperature prism housing, because the rather large size of the blanks would then have prevented the symmetrical use of their apertures. A general discussion of the apparatus and methods required in index determinations of this accuracy will be given in a later publication by one of the authors.

while the blanks were immersed in the stirred air bath of the constant temperature prism housing at 25.0° C. Corrections were made to a standard air pressure of 760 mm of mercury and to 0 mm absolute humidity.

The data supplied by the maker, together with the results of measurements made at this bureau are presented in Table 1. Considering that the samples were not identical and that the conditions

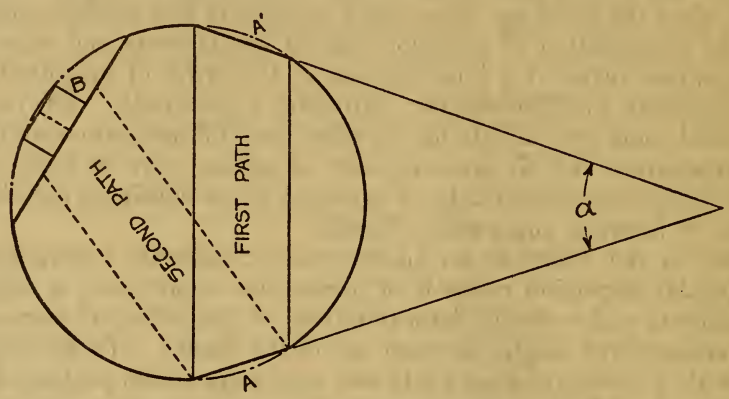

FIG. 1.—*Glass paths for index measurements*

In general, the first path only was used. For blank No. 3 the second path index exceeded the first by one unit of the sixth decimal place, while the index of a small 60° prism from the peripheral portion, *B*, proved lower by seven such units. This suggests the presence of residual effects from such a process as pressing, during which the edges cool much more rapidly than the central portion, and so have a lower optical density because of their correspondingly higher effective treating temperature.

of measurement for the maker's data were not supplied, the agreement is excellent.

TABLE 1.—*Optical data for the glass—original state*

	Maker's data	Bureau of Standards data [1]
Temperature	?	25.0° C.
Barometric pressure	?	760 mm
Absolute humidity	?	0 mm
n_D	1.56859	1.568597
ν	51.32	51.329
n_F-n_C	.01108	.011077
n_D-n_C	.003230	.003227
n_F-n_D	.00785	.007850
$n_{G'}-n_F$	.00643	.006440
$n_h-n_{G'}$	.00494	.004943
$n_C-n_{A'}$	----------	.003713
n_F-n_e	----------	.005116
n_h-n_g	----------	.005206

In the Bureau of Standards data, measurements on the D line correspond to settings on the unresolved sodium doublet while for A′ the settings were made midway between the lines of the potassium doublet. In addition to the other more usual notations, viz, C, F, and G′, for designating the hydrogen lines, the subscripts e, g, and h are used to refer to the mercury lines of wave length 5,460.7, 4,358.3, and 4,046.6 A. U., respectively. Measurements on blanks Nos. 1 to 3, inclusive, were made for all eight wave lengths, but only lines C, e, and F were observed for the remaining blanks.

III. INITIAL COMPARISON OF THE BLANKS

In Table 2, which facilitates a comparison of the results for the various blanks, neither the refractive indices, n_1, of individual prismatic paths, nor the average index, n_a, for all the first paths are given, but rather the quantities (n_1-n_a) which are characteristic of the deviations in the refractivities of individual blanks from the average for all. To give an idea of the degree of precision attained, the values are tabulated for each of three lines as well as for their average. The excellent agreement between the results for the first and second paths of blank No. 3 is a result of measurements which are entirely independent except that the paths cross.

TABLE 2.—*Initial index deviation*

Blank No.	Path	$(n_1-n_a)\times10^{-6}$			
		C	e	F	Average
1	First	−14	−18	−16	−16
2	do	−23	−20	−23	−22
3	do	+25	+27	+25	+26
3	*Second*	*+27*	*+27*	*+27*	*+27*
3	*Peripheral*	*+20*	*+18*	*+19*	*+19*
4	First	+23	+22	+28	+24
5	do	−36	−37	−39	−37
6	do	+24	+28	+27	+26

The last column, Table 2, gives an idea of the interblank differences in refractivity of the lens blanks as purchased, the maximum total spread being 63×10^{-6} or nearly five times the spread corresponding to the limit which has been tentatively stated above as permissible within any one blank. Thus it seemed entirely possible, under certain assumptions regarding the nature of the existing heterogeneity, that the blanks were not within themselves sufficiently uniform for good performance of the proposed objectives. The measurement on the small peripheral prism of blank No. 3 indicated a significant variation of this nature, but a thorough investigation carried out in this manner would have been unsatisfactory, not only because of serious encroachment upon the glass required for the lens components, but because no true comparison between edge and center can be so obtained. Furthermore, according to certain views now to be discussed, such a procedure, or even an examination by interferometric methods, seemed somewhat illogical and inadvisable because of the entire lack in such programs of features of a corrective or ameliorative nature.

IV. POSSIBLE CAUSES OF THE INDEX VARIATIONS

That these interblank variations should have arisen from strain in the accepted sense was impossible, not only on account of the low value of the birefringence but because in this respect there was no

noticeable difference between the various blanks. Heat history may, however, have a very important bearing, since a number of investigators [8] have shown that heat treatment does have an influence on the properties of glass. Recent quantitative measurements of its effect on density [9] and refractivity,[10] including a quantity of unpublished data collected at this bureau, show that small differences in the effective treating temperature, of the order of 1 or 2° C., are quite sufficient to produce heterogeneities ranging from 20 to 100×10^{-6} in refractivity, depending on the type of glass. In addition to the probability of the general existence of annealing furnace gradients of the above-mentioned magnitude, there is the possibility that preheating temperatures in annealing schedules are not always high enough to remove heterogeneities induced by the relatively rapid surface cooling which occurs during the pressing or molding of blanks.[11] The whole question of heat history is then one of great importance in any inquiry concerning the causes of heterogeneities in glass.

Another possibility, according to quite generally accepted ideas, is that of differences in chemical composition which may develop from certain conditions incident to melting. Whenever homogeneity is lacking, volatilization from the surface layer, pot solution at sides and bottom, and faulty stirring are possible causes. Convection currents during cooling certainly produce partial mixing of the glass, as is shown by the final distribution of cords and strias.

Seldom, if ever, is it safe to proceed without considering the possibilities of mistakes of various kinds, and with this additional thought in mind the possible causes [12] for the particular interblank differences shown in Table 2 may then be outlined as follows:

1. Inadequate heat treatment, causing or failing to remove physicochemical heterogeneity due to—

(*a*) Differences in the effective annealing temperature which result from furnace gradients,

(*b*) Differences in the effective annealing temperature which result from lack of accurate temperature duplication, in separate annealings, or

(*c*) Residual effects of processing.

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[8] J. O. Reed, Ann. d. Phys. u. Chem., **65**, pp. 707–744; 1898; A. Q. Tool and J. Valasek, Meeting Am. Phys. Soc., Baltimore, Md., 1918; B. S. Sci. Paper (No. 358), **15**, pp. 537–571; 1920; A. Q. Tool and C. G. Eichlin, J. O. S. A., **4**, pp. 340–363; 1920; C. G. Peters and C. H. Cragoe, B. S. Sci. Paper (No. 393), **16**, pp. 449–487; 1920; A. A. Lebedeff, Trans. Opt. Inst., Petrograd, **2**, No. 10, pp. 1–18; 1921; F. Twyman and F. Simeon, Trans. Soc. Glass Tech., **7**, pp. 199–207; 1923; A. Q. Tool and C. G. Eichlin, J. O. S. A. and R. S. I. **8**, pp. 419–449; 1924; Fritz Eckert, Trans. Soc. Glass Tech. **9**, pp. 267–272; 1925; A. Q. Tool and C. G. Eichlin, J. Am. Ceramic Soc., **8**, p. 11; 1925; A. A. Lebedeff, Revue D'Optique, **5**, pp. 1–30; 1926; Die Glass Ind. **35**, p. 6–9, 1927.

[9] A. Q. Tool and E. E. Hill, Trans. Soc. Glass Tech., **9**, pp. 185–207; 1925.

[10] A. Q. Tool, L. W. Tilton, and E. E. Hill, Meeting Opt. Soc. Am., Ithaca, N. Y.; 1925; Abstract in J. O. S. A. and R. S. I., **12**, pp. 490–491; 1926.

[11] A. Q. Tool and C. G. Eichlin, J. O. S. A., **4**, p. 360; 1920; J. O. S. A. and R. S. I., **8**, p. 446; 1924.

[12] Concerning these causes it should be noted that only 1 (*b*) and 3, as designated in the outline, operate without also producing some intrablank heterogeneity.

2. Inadequate melting procedure, causing chemical heterogeneity of the melt due to—

(*d*) Faulty stirring of the melt, or

(*e*) Other unsatisfactory conditions during melting, or during cooling through the temperature ranges well above those of annealing.

3. Mistakes causing confusion of glass from different melts.

It is evident that all of the effects listed under 1, because of their dependence on reversible processes,[13] should, to a considerable extent, be easily erased by the simple expedient of subjecting the glass to a very thorough heat treatment. That this might be the case and that the remedy mentioned might be of practical importance in the present instance was indicated to some extent by data recently published by Eckert [14] on variously processed glass from three practically identical melts of a barium flint glass somewhat similar to that discussed in this paper.

He found, for "fine annealed pressed" glass, average intramelt spreads in index of 7×10^{-5}, which is of the same order of magnitude as that shown in Table 2; but regardless of this spread and of the very much larger intramelt spreads which occurred in some "lens annealed pressed" samples of Eckert's glasses, a fine annealed product not previously pressed (a total of 16 samples) was found uniform to $\pm1\times10^{-5}$ within each one of the three melts. In other words, it appears that the purely chemical heterogeneities existing within any one of the melts which he examined did not produce deviations greater than $\pm1.5\times10^{-5}$ in the refractivity.

It thus seemed, in considering the causes mentioned above under 1 and 2, that relatively less weight should be attached to those listed under 2. Furthermore, the fact that the differences were very small made it unlikely that glass of other melts had been accidentally included, as mentioned under item 3. Consequently, attention was redirected to those causes listed under 1, and a rather marked grouping of the blanks, noticeable in Table 2, was interpreted as decidedly more favorable to item (*a*) or (*b*) than to (*c*). Between (*a*) and (*b*) there was little choice in this respect; but, since the deviations corresponded to such small differences in effective treating temperature, the former seemed the more probable cause. That cause (*c*) could not be fully ignored, however, was shown by a reconsideration of the indices of blank 3 as determined for the three paths employed. A smaller index had been found for the peripheral portion than for that of the whole blank. This is just the condition which would be occasioned by a failure to completely remove the effects of such a process as pressing, because the edges of the blank during the opera-

[13] A. Q. Tool and C. G. Eichlin, J. O. S. A. and R. S, I., 8, p. 443; 1924; A. Q. Tool, L. W. Tilton, and E. E. Hill, loc. cit., p. 490, "point" 4.

[14] Fritz Eckert, Ztschr. f. Tech. Phys. No. 6, pp. 282-287; 1926.

tion cool much more rapidly than the central portion, and so correspond to a higher effective treating temperature.

At any rate there was a decided possibility of considerably improving the optical uniformity of the blanks by reannealing. A highly favorable result would be acceptable as sufficient evidence of intrablank homogeneity also, and thus the necessity for further tests to establish it would be obviated. Even in the presence of small gradients during reannealing it was thought that the blanks, in addition to becoming more uniform, might no longer fall into the same groupings, thereby evidencing the absence of an appreciable chemical heterogeneity and giving at the same time definite information concerning the magnitude of the existing gradients. Should the differences persist in both magnitude and grouping, after an unquestionably ample reannealing program, further tests of intrablank homogeneity were, of course, recognized as necessary. This was particularly true in view of the fact that, according to current opinions, some of these blanks, presumably from the same melt, might have originated at or near the boundaries between rather sharply defined regions having slightly different chemical composition.

V. EXPERIMENTAL METHODS AND PROCEDURE

The first step taken was the determination of a suitable annealing schedule. The approximate annealing range and maximum permissible preheating temperature were determined from the thermal expansion [15] and heating [16] curves. As has been previously shown, such determinations are easily made. Both curves usually show the temperature range in which a glass begins to deform rapidly, and the increased expansivity in one and the heat absorption effect in the other permit an approximate determination of the annealing range.[17] These curves [18] for the glass in question are reproduced in Figure 2.

In addition to fixing the annealing range, it is sometimes desirable to locate that particular temperature which will permit a long reannealing without material change in the index of refraction. It was for this purpose, as previously stated, that a small prism was made from the periphery of blank No. 3. After measuring its index, this prism was treated at 500° C. and remeasured. Then two successive treatments at 480° C. were made with the corresponding index determinations. This data, together with a knowledge of the straight line tendency of such temperature-index relationships [19] (at least over short intervals), resulted in an estimate of 485° C. for

[15] C. G. Peters and C. H. Cragoe, loc. cit., pp. 484–486.

[16] A. Q. Tool and J. Valasek, loc. cit.

[17] The results by these direct methods are preferable to estimates based on the composition of a glass because so little is known of the relation between composition and annealing characteristics.

[18] The curve showing the expansivity was determined by G. E. Merritt, of the interferometry section.

[19] A. Q. Tool, L. W. Tilton, and E. E. Hill, loc. cit.

that annealing temperature which should produce zero change in index.[20] These preliminary tests also made possible a rough estimate of the required treating time and yielded a value of about −0.00003 per 1° C. increase in the treating temperature for the annealing equilibrium coefficient of the index of refraction.

The furnace in which the glass was annealed is the one in which all of the fine annealing of optical glass is done at this bureau. The box, or chamber, in which the glass is placed is made of chrome-

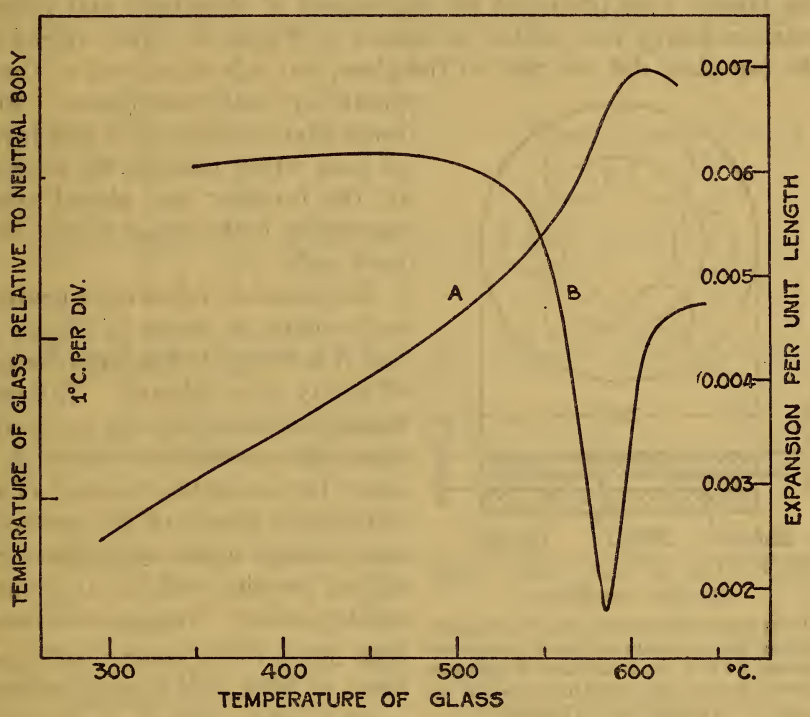

FIG. 2.—*Curves used to locate annealing range*

A, thermal expansion curve by interferometric method. *B*, heating curve by differential thermocouple method. Both these curves show that the glass begins to change rapidly at approximately 545° C. For annealing large pieces the holding temperature should be chosen at least 50° below this point; that is, at 495° C. or lower.

nickel steel; its walls are approximately 1 inch thick and its inside diameter and depth are 32 and 6 inches, respectively. Heating elements are symmetrically placed on the top and under the bottom of the box, and the whole is completely surrounded with about 8 inches of diatomaceous earth contained in a sheet-iron shell. The heat transmission of the insulation is such that 750 watts will maintain a constant temperature of about 500° C.

[20] This method employing index of refraction is analogous to that previously mentioned for obtaining the same result by a number of heating curves. See A. Q. Tool and C. G. Eichlin, J. Am. Ceram. Soc., 8, p. 15; 1925.

Temperature is measured by two chromel-alumel thermocouples,[21] one in the top and one in the bottom of the box, and a portable potentiometer with constant cold junction. The couples are placed in holes drilled 2 inches into the metal, and are brought through the insulation and shell in pyrex tubes closed at the inner end. All treating temperatures are believed to be correct to ±5° C., while small differences are considered as probably correct to ±1° C.

Realizing the necessity of guarding against temperature gradients, the blanks were protected by thin sheets of aluminum and placed between heavy iron plates, as shown in Figure 3. The weight of the top plate did not rest on the glass, but was supported at three points by small iron spacers. The lower plate, resting on a thin layer of sand which covered the bottom of the furnace, was placed symmetrically with respect to the furnace walls.

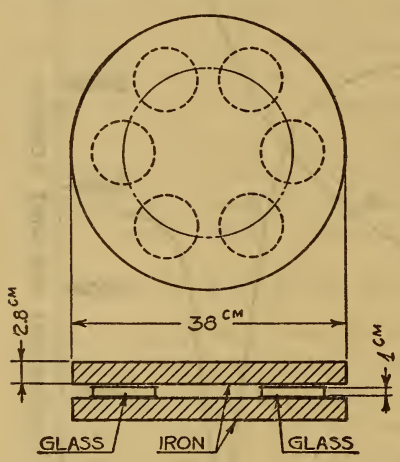

Fig. 3.—*Use of iron disks during the first reannealing*

Index measurements made after this reannealing show that an average horizontal temperature gradient of 0.4° C. per 15 cm existed in the region between the iron disks while the space was occupied by the glass during this treatment.

The schedule followed in heating and cooling is shown in Figure 4, and it is thought that large factors of safety were allowed. The preheating indicated by the curve was especially advisable in view of a desire for a complete removal of all differential effects of the previous heat history which might have included pressing and the attendant sudden cooling. Temperature readings were taken once every half hour, at least, and current adjustments made as often as necessary from the time the temperature of the furnace reached 515° C. in the initial heating until it dropped to 372° C. in the final cooling. During the holding period of 13 days at 486° C.[22] the variation in temperature was less than ±1.5° C.

VI. DISCUSSION AND ANALYSIS OF DATA ON THE FIRST REANNEALING

Subsequent to the reannealing the blanks were again examined for birefringence and their condition in this respect found to be substantially the same as that previously observed. The surfaces were considerably tarnished and no longer sufficiently plane for prism

[21] Originally 12 equally spaced couples were used, but the indicated temperature differences were so small that the continued use of so many couples was not justified for routine annealing.

[22] The results of a check on the performance of the thermocouples indicated a temperature during holding of 1° more than the 485° C. which had been intended.

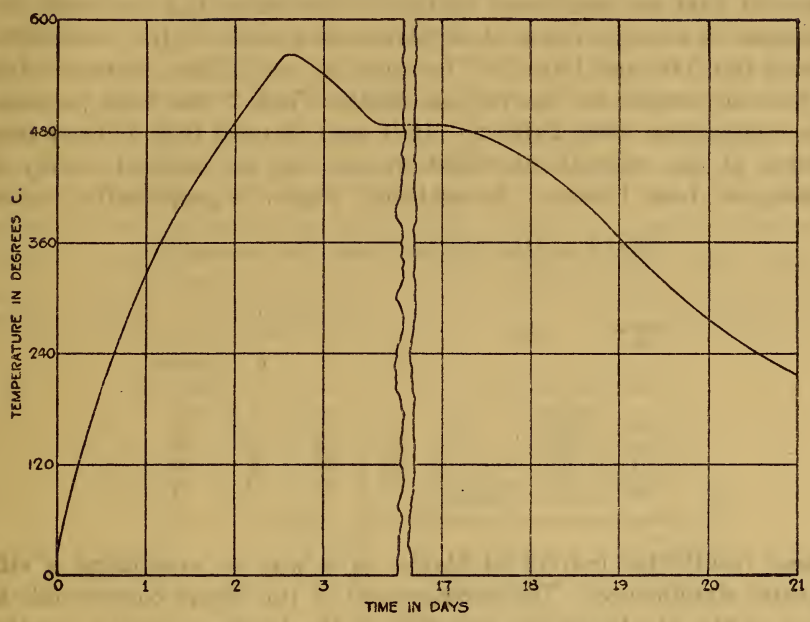

FIG. 4.—*Schedule for the first reannealing*

During the holding period of 13 days at 486° C. the variation in temperature was less than ±1.5° C.

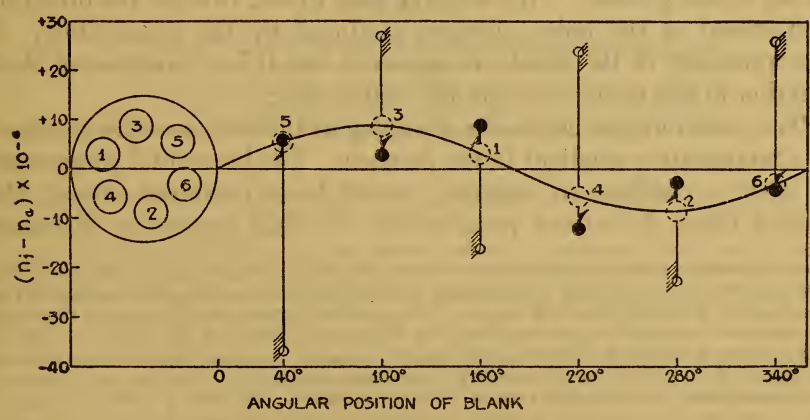

FIG. 5.—*Index changes effected by the first reannealing*

The deviations of individual blanks are shown, with sine curve for reference, the abscissas being the relative angular distributions of the blanks on the iron disk in the furnace. The small circles, ○, indicate values before reannealing, and the circular dots, ●, the corresponding values after the first reannealing, the radii giving the probable errors in measurements. The arrows show the direction and extent of the changes produced. Concerning the dotted circles, see text. (After the second reannealing the largest deviations in index did not exceed the smallest shown on this graph.)

angle measurements.[23] After resurfacing, precision measurements showed that no significant change in dispersion had occurred, the increase in average index of all blanks as a result of the reannealing being 149, 149, and 150×10^{-6} for the C, e, and F lines, respectively.[24] From the results for the various blanks Table 3 has been prepared for comparison with Table 2. It is seen at once that at least two-thirds of the original interblank spread can be ascribed wholly to dissimilar heat history. In addition, Figure 5 graphically depicts

TABLE 3.—*Index deviation after first reannealing*

Blank No.	Path	$(n_i - n_a) \times 10^{-6}$			
		C	e	F	Average
1	Primary	+6	+11	+11	+9
2	do	−2	−3	−3	−3
3	do	+5	+2	+3	+3
4	do	−12	−13	−10	−12
5	do	+6	+8	+4	+6
6	do	−3	−5	−5	−4

these results for individual blanks in a way to emphasize a still greater significance. The arrangement in this figure corresponds to that of the blanks on the iron disk in the furnace, relative angular separation being given in degrees of arc. The small circles represent the data in Table 2 and the circular dots those in Table 3, their radii being in each case indicative of the estimated probable errors in the values plotted. Arrows have been drawn to show the direction and extent of the index changes produced by the reannealing. A new grouping of the blanks is apparent and it is a function of their location in the furnace during the reannealing.

The most obvious cause of a grouping of this sort was the existence of a temperature gradient in the furnace. The horizontal component of such a gradient, if uniform, would have produced among the blanks index deviations proportional to their respective distances

[23] It was known in advance from the curves of Figure 2 and from previous experience in the heat treating of prisms with optical surfaces that the reannealing would not completely mar the optical surfaces and that determinations of deviation could still be made. This was done, for the C line only, on all six blanks and the indices were computed on the assumption that the refracting angles had not changed. In spite of relatively large deviations of individual results from the means, the averaging of indices for the groups A and B, as in Table 4, p. 732, yielded values which were later found to be in surprisingly good agreement with measurements on the resurfaced prisms. This is an indication that errors in index measurements on individual prisms whose surfaces have been distorted in this way are as likely to be positive as negative, provided no appreciable amounts of strain are removed or introduced and that no material change in density gradient occurs.

[24] This increase in index corresponds to a combined error of −5° C. in the estimation and reproduction of the effective annealing temperature which had been used by the manufacturer; that is, the temperature in the furnace during reannealing should have been adjusted so that the thermocouples indicated a corrected temperature of 491° C. rather than 485° C. as estimated. This agreement is all that could be expected in view of possible inaccuracies in the various temperature measurements involved. Furthermore, the discrepancy is in the direction expected since the rate of cooling in the large annealing furnace was much less than that employed in the preliminary tests with the small prism.

from the isotherm [25] through the center of the system which they formed; that is, the results should fall on a sine curve of proper amplitude. But in this particular case there are two known reasons why the points should not fall exactly on such a curve. In the first place the blanks were not radially equidistant from the center of the system which they formed, but varied in this respect by about ± 1 cm. Secondly, the glass paths used were not centered with respect to the individual blanks and when they were placed in the furnace no attention was given to their orientation. On this account a further effective displacement of ± 1.3 cm from a truly circular distribution of the centers of the paths was possible. To aid in this analysis the dotted circles along the reference sine curve, plotted in Figure 5,

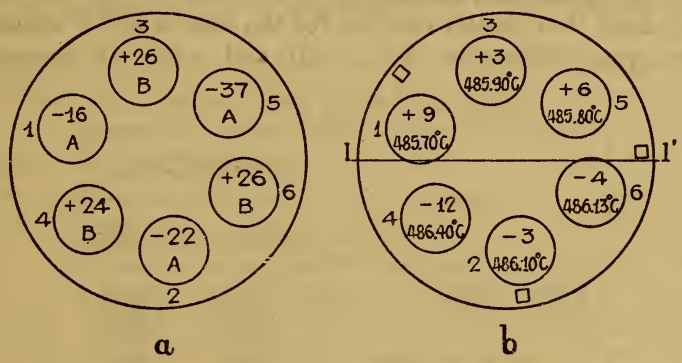

FIG. 6.—*Regrouping and temperature distribution, first reannealing*

(*a*) Group arrangement of blanks as placed in the furnace for the first reannealing, with index deviations in units of the sixth decimal place.

(*b*) Regrouping, with new deviations, and the annealing temperatures which would have caused them in glass of uniform chemical composition. The temperature gradient was nonuniform, but the isotherms ran in the general direction of the line II′.

have radii such that they show the maximum extent of both of these limits of uncertainty.

It seems fairly certain, from this test of the data, not only that an appreciable temperature gradient existed but that some other disturbing factor was present. This suggests that nonuniformities in the temperature gradient existed and produced measurable effects on the index of refraction of these blanks during the reannealing. Locally, cooler areas could, for example, have been caused by a flow of heat from the lower to the upper plate through the spacers which were located near blanks 1, 2, and 6, as will be shown in Figure 6*b*. This supposition is substantiated by the fact that the top of the fur-

[25] In drawing Figure 5 no particular care was taken in locating this isotherm. Apparently it should run between blanks 1 and 5 on one side and 4 and 6 on the other, but somewhat nearer to 1 and 6 because of their smaller deviations from the mean index. The amplitude used for the sine curve was determined by a more direct method of group averages to be mentioned later.

nace was about 1.5° C. cooler than the bottom. Furthermore, the plotted points for two of the three blanks mentioned are found to be above the sine curve; that is, in the direction to be expected on this assumption.

In studies of this kind group averages are often more satisfactory than individual results, and Table 4 has been arranged to show that the groupings indicated in Table 2 are merely a matter of more or less accidental differences in treating temperatures rather than the result of variations in chemical composition. Only two groups have been formed, A, consisting of the three blanks which originally had indices below the general average, and B, of those whose indices were above the average. The reversal in sign of the group difference (B–A) is significant and not caused by accidental errors in data. It may be added that similar exhibits for the lines e and F would show for these group differences, +51, −10, and +53, −9, respectively.

TABLE 4.—*Data by group averages*

Group	Average index, n_C (25.0° C., 760 mm, 0 mm)	
	Before reannealing	After (first) reannealing
A (Nos. 1, 2, and 5)	1.565345	1.565522
B (Nos. 3, 4, and 6)	1.565394	1.565516
(B–A)	+.000049	−.000006
Average for all blanks	1.565370	1.565519

The probable cause of this reversal in sign of the intergroup difference is apparent (see fig. 6) when attention is again directed to relative location in the furnace during the reannealing. The three blanks of group B, originally almost identical, had been placed 120° apart, as appears on *a* of Figure 6, which shows the relative position and index deviation of all blanks when placed in the furnace. On *b* of Figure 6 there have been placed, in addition to individual blank deviations in index after reannealing, the relative effective reannealing temperatures which would satisfactorily account for their indices. These were computed on the assumptions that 486° C. was the average effective reannealing temperature and that complete chemical uniformity of the glass existed, using, of course, the equilibrium coefficient of −0.00003. It is quite evident that the area occupied by blanks 1, 3, and 5 was cooler than that in which Nos. 4, 2, and 6 were placed. The temperature averages for these new groups are 485.80 and 486.21° C., respectively, the isotherms running in the general direction of the line *II′*. It is thus due to the fortunate inclusion of two of the three blanks of group B within the hotter area of the plate that the reversal in sign of the group difference was obtained.

This grouping permits a determination of the average temperature gradient which is thought to be more reliable than one made graphically by adjusting the amplitude of the sine curve of Figure 5. The result is a value of approximately 0.4° C. over a distance of 15 cm, which is the average linear separation involved between members of the new groups. When considered from the standpoint of requisite intrablank homogeneity, a gradient reduced to this value may be objectionable even when uniform, and it will be especially so whenever local temperature inequalities are superimposed. In the present instance this average value of the gradient is equivalent to intrablank deviations from the mean of $\pm 4 \times 10^{-6}$ at the extremes of the 9 cm. diameters of the blanks.[26]

VII. SECOND OR CONFIRMATORY REANNEALING

Although the average value of intrablank heterogeneity after the first reannealing was only one-half the tolerance tentatively considered as permissible, some doubt did remain about the condition of individual blanks, particularly Nos. 1 and 4, in the locality of which the asymmetries mentioned conspired to produce maximum local furnace gradients. It also appeared desirable to ascertain whether or not added care in packing would reduce the furnace gradients, and whether a different arrangement of the blanks would cause a regrouping which would conform to the vestige of this gradient.

Accordingly, it was decided to reanneal the blanks a second time using greater precautions to reduce furnace gradients. For this reason the blanks were placed in a specially prepared aluminum box which was insulated from the previously used iron plates by asbestos. Also a heavy iron ring was substituted for the three spacers in supporting the upper plate and the rest of the furnace was filled with sand. Figure 7 shows most of the details, and the symmetrical location of the glass with respect to the whole furnace.

In three respects the schedule followed differed essentially from that previously used. The preheating temperature was only 501° C. for five hours because there was no necessity for repeating the previous treatment at 561° C. A treating temperature of 491° C. was used instead of 486° C. which in the first reannealing had failed to compensate sufficiently for the lowering of the effective annealing temperature resulting from the slow cooling necessary. A reduction was made in the holding period, viz, from 13 to 8 days, this decrease being

[26] It is realized that the reduction of the interblank spread in index to one-third its initial value argues little or nothing about the average change produced in the degree of the physicochemical intrablank heterogeneity, or about the relative furnace gradients in the two annealings, unless some assumptions are made concerning the relative linear separations existing in the different furnaces concerned. For example, these linear separations during the original annealing at the glass plant in Europe might well have been approximately three times those in the reannealing; and it is then evident, if the linear gradients in the two furnaces were nearly identical, that the concomitant contributions to the optical density gradients within the individual blanks could be the same in both cases.

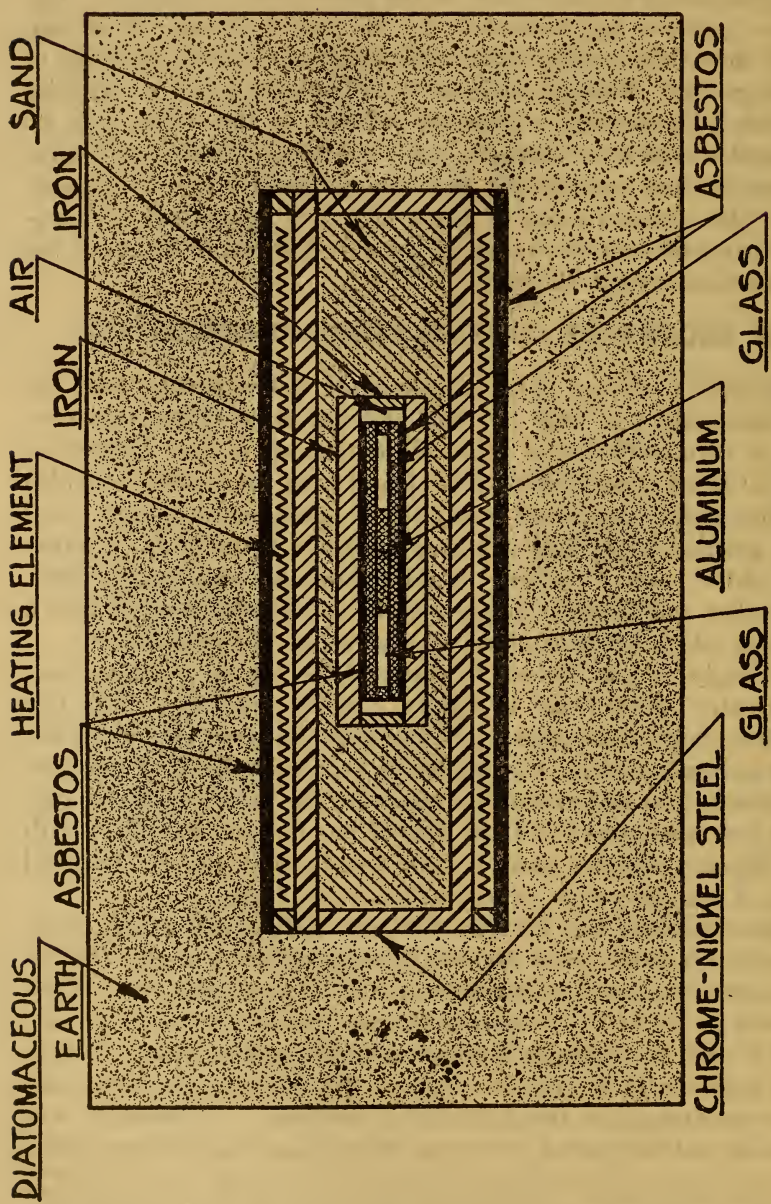

FIG. 7.—*Cross-sectional view of the annealing furnace*

This figure shows most of the details of the method of packing the disks for the second reannealing and the symmetrical location of the glass with respect to the whole furnace. Although the resulting average index deviation of the blanks was less than two units of the sixth decimal place, group averages of the data indicated the existence of a furnace temperature gradient of 0.06° C. per 15 cm. The sequence of the blanks had been changed, but it appeared that the isothermal line had approximately the same azimuth as during the first reannealing.

approximately that allowable because of the increase in treating temperature.

Some damage to the optical surfaces resulted from this second reannealing also and complete index measurements were not made until after resurfacing. The average indices found for lines C, e, and F were 1.565387, 1.571346, and 1.576466, respectively. These values exceed the initially measured indices by only 17×10^{-6} or the equivalent of approximately 0.6° C. in effective annealing temperature. The individual deviations are given in Table 5 and it is thought that neither analysis nor discussion is necessary to show the resultant confirmation of such interpretations as have been given in the foregoing discussion or to indicate their relation to the conclusions which follow. It may be stated, however, that the added precautions apparently reduced the gradient to about one-sixth of the value deduced above as that existing during the first reannealing. That a fraction did remain was indicated by the method of group averages, as previously used; the signs of the deviations, with one exception, being consistent with expectations based on the analysis of the previous data.

TABLE 5.—*Index deviation after second reannealing*

Blank No.	Path	$(n_i-n_a)\times10^{-6}$			
		C	e	F	Average
1	Primary	+1	−1	+2	+1
2	do	−4	−2	−4	−3
3	do	+2	+4	+2	+3
4	do	−3	−2	−2	−2
5	do	0	+1	+1	+1
6	do	+2	+2	0	+1

VIII. CONCLUDING DISCUSSION

The results of these experiments indicate that the variations in refractivity found in these barium flint lens blanks, both initially and after the first reannealing, were caused almost if not entirely by inadequate heat treatment. Initially the differential effects of rapid cooling, such as that which occurs in pressing, may have added materially to the effects of furnace gradients. After the first reannealing the observed index differences were certainly the result of gradients, to a great extent, and after the second, it may well be that they are still the chief factors. In this present state of the blanks, however, the deviations are so small that their significance becomes questionable.

Between the various blanks, then, there has been found no evidence of residual optical differences of such character as to make it necessary to infer that any chemical heterogeneity exists within or between any of them. The existence of such a remarkable degree of homogeneity of optical glass is quite at variance with prevalent opinion, but after all this is only what should be expected in those portions of properly made glass which are free from visible cords and strias.

This application of recent developments regarding the effects of heat treatment on the optical properties of glass shows that in addition to a consideration of actual annealing temperature and time, the necessity of which has often been discussed, the elimination of temperature gradients in annealing furnaces must also be given much more attention than it has yet received if glass of the greatest uniformity in index is to be obtained. Moreover the deleterious effects of small gradients appear to be sufficient to require their control before it will be possible even to investigate properly the effects which pressing, molding, and other operations have on the optical properties of glass. These questions are of great importance in annealing previously processed glasses whenever it is necessary to approach that true optical homogeneity of product which, in addition to mere freedom from strain, requires the highest degree of physicochemical uniformity of structure or constitution.

WASHINGTON, February-October, 1927.