

THE TECHNIQUE OF OPTICAL GLASS MELTING.

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Without going into a full account of the circumstances which led to the coöperation of the Geophysical Laboratory with the manufacturers of optical glass of the country it will be desirable, as an introduction to this article, to summarize our activities in brief form.

Our coöperation began about the end of April, 1917, when certain members of the staff of the Laboratory were detailed to the plant of the Bausch & Lomb Optical Company at Rochester, New York. In December, 1917, the coöperation was extended to the Spencer Lens Company's plant at Hamburg, N. Y., and to the Pittsburgh Plate Glass Company's plant at Charleroi, Pa. At all these plants active coöperation continued for many months, and, with the last two, until the close of the war.

At the Bausch & Lomb plant the men from the Geophysical Laboratory had from the beginning the benefit of the many years' experience in glass-making of Mr. Victor Martin, chief glass-maker there, and the advantage of entering a works in which many of the difficulties attendant upon the first stages of starting up a new technical process had been surmounted. These facts were of the greatest assistance to us in becoming familiar with many details of practical glass-making, and further advances were thereby much facilitated. Although descriptions of ordinary glass-making operations were to be found in the literature, almost nothing had been published regarding the numerous important details in which the making of optical glass differs from that of other glasses.

At about the time that the work of the Laboratory was extended to the other plants, arrangements with the companies assumed a somewhat different form. At Rochester a more direct supervision of furnace operations was exercised; at Hamburg the Spencer Lens Company placed the entire operation and super-

intendence of its plant unreservedly in the hands of the Laboratory men; at Charleroi the supervision of the furnace-floor operations, in so far as the production and treatment of optical glass were concerned, was likewise placed in their charge.

The problems with which we had to deal were very different in many respects from problems of scientific research. Our task was essentially this: To produce as a matter of daily routine, glass in large quantities and free from serious defects; to seek constantly to eliminate defects and increase percentage of yield per pot; and to add to furnace capacity as rapidly as possible in order to meet the insistent demands for quantity production of good glass. The last requirement was always before us and practically everything else had to be subordinated to it. Problems of scientific importance, no matter how interesting, had to give way if they did not lead to the main object in view.

Because of the fact that the Laboratory men were at work at three different plants, among which conditions were, in some respects, quite dissimilar, experiences varied. By interchange of ideas this fact worked to the benefit of all. During the whole period under consideration the technique of the making of optical glass was in a state of change and development. New ideas which occurred to one or another were tested, and either rejected or, if found to be an improvement, were adopted as part of the routine of operation. From a consideration of this process of evolution it will not be a matter of surprise to anyone that the stage which has been reached at the present moment is not to be looked upon as the final stage of evolution, or that it is expected that no further progress will be made. It is fully realized that many problems of importance still remain for solution, but it is a source of great gratification to us that we have assisted in some measure in the production of thousands of pounds of optical glass of a quality equal to the demands imposed by military requirements, and much of it, as rigid tests show, not surpassed by the product of the more famous foreign works.

It would be beside the mark to describe the stages by which the present technique of optical glass melting has been evolved. It is rather the purpose to describe it at the stage which it has reached at present in its course toward more perfect development.

The description will be based not alone on individual experience but on the experience of all the men of the Geophysical Laboratory who took active part in this phase of the work. Those who were connected most directly with the operations which form the subject of this article were L. H. Adams, N. L. Bowen, C. N. Fenner, J. C. Hostetter, G. W. Morey, and F. E. Wright.

This article will deal with the melting process and closely allied operations. Particular attention will be given to those details of practice in which the melting of optical glass differs from that of other glasses, but in order to present matters in connected form it will be necessary to give an account of operations in the sequence in which they occur, even though this may involve some description of processes with which all glass-makers are familiar. It is not the purpose to emphasize any matters with whose development the members of the Geophysical Laboratory were especially concerned, but rather to present, for general information, a plain description of processes which have been found satisfactory in the making of optical glass. Other phases of the work connected with the preparation of optical glass will be treated by other writers in separate articles. Some of these have already appeared and others are being prepared at the present time.

Preliminary Operations.

An essential need in making good optical glass is pure raw materials. Especially important is freedom from those metallic oxides which impart color, such as iron, nickel, and manganese, and freedom from such impurities as sulphates and chlorides, which tend to produce milkiness or opalescence in glass. A full consideration of the requirements which the raw materials must satisfy will be given in detail in another article. It is sufficient at this point to say that the glass-maker must know beyond doubt what goes into his batch, and this can be done only by frequent chemical analyses.

It must be realized from the beginning and borne in mind constantly that, from the standpoint of the purposes for which optical glass is to be used, it has little in common with other kinds of glass. In order to serve its purpose an essential requirement is

that its optical constants should be definitely fixed and maintained. Other requirements of a similarly exacting nature must also be met, and it is possible to do this only by the most careful control throughout the process of manufacture. It would not be amiss to compare the precautions required in the making of a pot of glass to those which must be exercised in making an exact quantitative analysis.

The batch is mixed in a long, open box of such capacity that the whole may be shoveled from a pile at one end to a pile at the other in the process of mixing. It is best to use broad, flat wooden paddles or grain-scoops for this purpose, rather than iron shovels. The amount of iron which would be added to the batch by the wear of iron shovels is probably extremely small, but wooden paddles or scoops are as easy to use for the purpose of mixing, and it is better to avoid iron tools where possible if only to impress the workmen with a proper appreciation of the dangerous qualities of iron.

The batch must be so well mixed that any portion which is left over after filling a pot will not differ appreciably in composition from that which has been used. This will be secured by shoveling the material at least three times from one end of the box to the other with a turning and spreading motion. At some stage during this mixing, preferably after the first transfer from end to end, the whole should be passed through a sieve of four to six meshes per inch, which rests in a frame at one end of the batch-box.¹ This will remove nails, chips, and so forth, and will insure that no batch-material is left in a lumpy condition. If the scale of operations is large enough to warrant it, some form of mechanical mixer may be used. In any case care should be taken to see that the mixing of the batch is so thorough that any appreciable fraction does not differ in composition from the whole. After the batch has been mixed it may be left in the batch-box until it is used, if operations are conducted in such a manner that only a short time will elapse, or it may be stored in a bin. A discussion of questions of this kind, however, is rather apart from the purpose of this paper. They are matters of considerable

¹ It would really be better to put all materials through sieves before adding them to the batch, as well as to make a sieving at a later stage.

importance in works-management, but are not peculiar to optical glass-making.

Attention should be directed to one matter at this point—the care which should be exercised to keep different batches separate. Any confusion in this matter is likely to lead to a chain of serious consequences which will not be broken until all stock on hand of possibly contaminated batch has been thrown away, and all glass produced from it (which is not usable even as cullet) likewise disposed of.

In order to carry out completely the idea of avoiding contamination we should have at least three batch-boxes, one to be used for crown glasses, a second for flints, and a third for dense barium crowns. Moreover, it is well to sweep out the batch-box each time before use. It may seem somewhat trivial to emphasize apparently unimportant matters like these, but it is by paying attention to details of this kind and establishing a standard of careful procedure throughout all steps of manufacture that the qualities essential to optical glass can be maintained.

Considerable leeway is permitted to us in the matter of the form of combination in which a given ingredient of the glass is added to the batch, but in some cases compounds which, at first sight, might appear unobjectionable are found to be limited in usability by certain qualities which they possess. As a source of K_2O we have the carbonate, bicarbonate, and nitrate. The sulphate is out of the question because of its tendency to segregate as a layer of "salt water" on top of the melt and because it has the effect, even in small quantities, of inducing milkiness in some glasses.¹ KCl is objectionable for similar reasons, and also because of its volatility. Commonly, most of the K_2O is added in the form of carbonate with a very appreciable percentage of nitrate (say 25 to 33 per cent of the alkalis in the latter form). The nitrate produces oxidizing conditions during the thermal dissociation and recombination of the batch ingredients and this is

¹ J. D. Cauwood and W. E. S. Turner, "The Influence of Small Quantities of Chlorides and Sulphate in Producing Opalescence in Glass," *Jour. Soc. Glass Tech.*, 1, 187 (1917). C. N. Fenner and J. B. Ferguson, "The Effect of Certain Impurities in Causing Milkiness in Optical Glass," *J. Am. Ceram. Soc.*, 1, 7, 468 (1918).

a highly desirable function. If it be used in large quantities, however, there is danger on this score: that at a temperature which is considerably below that at which there is active combination of the basic oxides with silica the nitrate will be decomposed into a highly caustic liquid which is likely to segregate from the rest of the batch and attack the pot. For this reason it should not be used ordinarily in quantities greater than those given. At Charleroi, however, the Pittsburgh Plate Glass Company use a pot of their own manufacture which seems especially resistant to this corrosive action. This, combined with the fact that large quantities of cullet are added to the batch, enables them to replace even the whole of the carbonate with nitrate. They are thus able to avoid the several somewhat objectionable features of the carbonate. The bicarbonate has been said by some to cause difficulty in fining, but we have used a considerable quantity of it in pots of medium flint and baryta flint without any observable deleterious effects.

In most glasses the replacement of K_2O by an equal weight of Na_2O has not a great effect on refractive index or dispersion. As the price of potash compounds is ordinarily greater than that of soda compounds and has recently been very much higher, the total substitution of soda for potash would offer decided advantages from that standpoint. Unfortunately it does not seem that this may be done without evil effects ensuing. The use of a certain amount of soda seems to be desirable, as it probably increases fluidity, but according to general opinion (for which there seems to be some basis) the use of large quantities tends to increase the color. The amount to which Na_2O may be used without injurious consequences varies with the composition of the glass. Frequently in the common glasses it may be used in amounts equal to those of K_2O , but if the glass has a tendency to show more depth of color than is desirable it is better to keep the Na_2O down. Such glasses include those high in lead or high in barium. In a baryta flint which was made regularly at Hamburg (a glass containing about 38 per cent PbO , 6.5 per cent BaO , and 3 per cent ZnO) the alkali used was wholly K_2O . When we tried a batch containing Na_2O to K_2O in the ratio 1 : 1.18 the color was distinctly increased. Other evidence of the color-

inducing effect of Na_2O has also been obtained. For this we have not been able to find a wholly satisfactory explanation. It does not seem likely that the soda itself gives color, but that the effect is secondary. Possibly a large quantity of soda causes greater corrosion of the pot and leads in that way to a larger amount of iron in the glass, or the same amount of iron may show up more in a soda glass, or the soda used may contain a small amount of sulphide or other reducing material which causes more of the iron to assume the ferrous form and therefore exert a more powerful coloring effect. It would be of considerable interest to settle this question, although the present commercial incentive arising from the abnormally high price of potash may partly disappear. A great deal of information on the relative quantities of K_2O and Na_2O used in the Schott works at Jena may be found in Zschimmer's tables.¹ However, a study of the syntheses appearing there gives very little insight as to the principles on which the relative amounts of K_2O and Na_2O used were based. They seem to be almost haphazard. A little later in this article batches for a number of typical glasses made in this country will be given, and these will show the amounts of Na_2O which we considered safe to use.

As a source of lead for flint batches either red lead (Pb_3O_4) or litharge (PbO) may be used. Red lead contains a little excess oxygen and might for that reason be considered preferable. Practically there seems to be no difference. After observing the results obtained from a great number of batches, some made with red lead and some with litharge, subjected to the same furnace conditions, we have not been able to see that there is any choice between them. It will simply be a question of purity of material and of price (calculated on the basis of lead content).

With most of the raw materials the size of grain has little effect on melting, and as long as the material is not lumpy the size of grain gives us little concern. With sand, however, the processes of combination and solution during melting are slow, and if unduly prolonged (as when the sand is coarse) the consequences are bad in several respects. The length of time which a run

¹ E. Zschimmer, in "Handbuch der Mineralchemie, herausgegeben von C. Doelter," article "Glas." Bd. I, p. 855.

takes is increased; there is more opportunity for liquation of the easily fusible materials, leaving the quartz floating on top; and slow melting is likely to mean poor fining. Therefore, quartz sand of coarse grain is undesirable. A very satisfactory sand which has been used largely at all three glass plants was of a size to pass through a 35-mesh Tyler standard screen.

The Use of Cullet.

In all optical glass making a large proportion of the glass in a pot is rejected because of defects of one kind or another. Thus a large quantity of glass which is not of optical quality but which represents considerable monetary value simply from the materials used in making it is likely to accumulate. The defects which have caused rejection are likely to be bubbles and striae. By putting this glass through the melting process a second time under proper conditions the percentage of saving in good glass from this cullet will probably be as high as in glass made from a new batch. We should, therefore, consider the manner in which the cullet may be used.

A first and very obvious requirement is that each type of cullet should be kept separate. Moreover, glass which is very stony or contains other defects which will probably not be removed in remelting should be rejected entirely. Milky or opalescent glass, however, which is otherwise suitable, may be used without fear. On the other hand, it must be remembered that certain properties of the glass will be changed each time it is remelted. It will take up more and more iron and other material from the pot, which will increase the color and change the index. Selective volatilization likewise will affect the index. These last-mentioned factors are likely to be the effective ones restricting the amount of cullet which it will be wise to add to a batch. It is quite feasible to make melts of cullet only, and indeed this has frequently been done, but there is likely to be some deterioration of the glass from standard quality under such conditions.

The changes consequent upon remelting will be different with the different types of glass so that no exact figures can be given as to percentages of cullet which we may add. Probably in heavy lead glasses the effects will be more marked than in other

common types. The standard of quality which is aimed at and the general care with which operations are conducted will likewise affect the question. If to a batch which is supposed to give a glass having $n_D = 1.605$ and $\nu = 37.7$ there is added 30 per cent of cullet which is supposed to be of the same type but which in reality has $n_D = 1.603$ and $\nu = 37.9$ we cannot expect to get exactly what we want. The essence of the matter is that there is no special trouble of operation arising from the use of almost any amount of cullet, but as for the amount that the manager will use, that will be decided by the way in which the properties of the cullet which he has on hand correspond to those of the glass he is trying to get.

For ease of handling the cullet should be broken up. This may be done simply with a hammer, but labor is saved and a better job is made by passing it through a jaw crusher. The jaws need not be set to crush very finely. We merely wish to get a shaly mass which can be shoveled without trouble. After this crushing the material should by all means be passed over a magnetic separator. A surprising amount of iron gets into the glass from the jaws of the crusher, but most of it is easily removed magnetically. In using the cullet it may either be mixed with the batch or filled in with it in alternating layers.

Setting the Pot and Filling in the Batch.

We will suppose that a pot of glass has just been removed from the furnace and we are about to start a new run. We will suppose also that the furnace we use is a reverberatory furnace operated on the regenerative principle. This is the type used by the Bausch & Lomb Optical Company and by the Spencer Lens Company. At the Charleroi plant of the Pittsburgh Plate Glass Company some of the optical glass is made in non-regenerative stackless furnaces of approximately cubical shape, heated by a blast, and some in large regenerative furnaces of twenty pots capacity each, such as are used for making plate glass. In all these types of furnaces the glass-making operations proper are essentially the same. The chief point of difference lies in the ability to control the conditions to which each pot is subjected, and in that respect the single-pot regenerative furnace seems to

offer considerable advantages. The description which follows will be based upon the operation of such a furnace. In many cases the portions of the description which are not applicable to the other types will be readily eliminated by the reader who is familiar with furnace operations, but where it seems desirable the description will be supplemented by an account of the modifications of procedure which are necessary in other furnaces. However, the endeavor will be to point out and emphasize the salient features in furnace conditions and operation which are desirable in making optical glass in distinction from other kinds of glass rather than to consider in detail the design and construction of furnaces which are necessary for the attainment of these results.

The first operation is to get the "siege" or floor of the furnace in good condition for the next run. This operation, however, is common to other kinds of glass-making and a description will be omitted. Likewise we shall pass over the transfer of the new pot from the arch in which it has been heating to the furnace, merely remarking that it is important to see that when the pot has been placed in the furnace it rests level on the siege. When these preparations have been finished the fire which, several hours before, had been shut off, is started again, and the furnace is brought up to melting temperature.

We will suppose that the previous pot was taken out of the furnace about the middle of the afternoon and that the operations referred to have been finished about four P.M. As will appear immediately, working conditions will often make it desirable to run on about this schedule, although this will not of necessity be the case. The furnace has become fairly cold, as no fire has been burning for several hours, and until the temperature is brought up again there is a hiatus in operations. Therefore the temperature is raised as rapidly as possible. Under the best conditions this will take considerable time, and if the gas pressure is not satisfactory seven or eight hours may be required to reach 1400° C. In some cases this may be more of a loss than is evident at first sight. Unless the plant be a very large one, employing great numbers of men at all hours of the day and night, the working arrangements will probably be such that pots will

be finished and taken out at about the same time each day. This will probably render it impracticable to base operations on anything but a twenty-four or a forty-eight hour schedule. Until recently forty-eight hours has been considered the normal length of time for completing a run. It was evident that the time could be shortened considerably, but unless it could be brought down to twenty-four hours there was not much incentive to curtail operations. Recent operations at Hamburg, however, have shown that in most cases it is perfectly feasible to work on a twenty-four hour schedule and produce just as good glass. To accomplish this it is essential that there should be no long delays anywhere. Therefore, the importance of having a good supply of gas and bringing the temperature up rapidly is evident. In doing this the beneficial effects of exposing the pot to a prolonged baking and sintering have to be sacrificed in some measure, but if by making this sacrifice the run is shortened to twenty-four hours the advantages are in favor of this procedure. At Charleroi the conditions are such that there has been no necessity of choosing between twenty-four and forty-eight hours. The optical glass plant is run in conjunction with an establishment having a very large output of plate-glass, and a large number of men are available on all shifts throughout the twenty-four hours. Other considerations exert their influence here, and the result is that the schedule aimed at has been twenty-seven to thirty hours in length. A description of the practical details of the twenty-four-hour schedule and the conditions under which it is applicable are given in the article by G. W. Morey in this number.

After the temperature has reached 1400°C , it is held there for about one hour in order to complete the baking of the pot and cause it to assume the dense condition which it must have to resist the corrosive action of the glass.¹

A word may be said here about the means of determining temperatures in glass-furnaces. Proper temperature regulation is a matter of the very greatest importance in making optical glass, and an exact and reliable method of measurement is essen-

¹ Even higher temperatures (1430° – 1440°) have been used with good results.

tial. The old method of regulating temperatures by the eye is hopeless. Undoubtedly some men who have had years of experience become remarkably proficient in this respect, but even the best have their off-days. Thermoelements are now much in use, but as shown in a previous article,¹ they are not very reliable for this work. An optical pyrometer meets the requirements much better, and is probably the most satisfactory instrument for glass-furnaces that we have. A detailed discussion of this matter and a description of the use of such instruments will appear later as one of the articles of the present series.

Although thermoelements are unreliable as standards, it is nevertheless very convenient to have each furnace equipped with one. Their changes of calibration are likely to be slow, and if the readings are controlled occasionally by an optical pyrometer, they may be used for ready reference.

The furnace having reached the condition described, the pot is glazed with cullet. The object is to have the pores filled with material of the same composition as the glass which will be made in the pot. If this be not done, but batch-mixture be the first material put in, the most fusible and at the same time most corrosive elements of the batch will enter the pores and possibly effect a disaggregation of the pot-material, which will subsequently lead to leakage or stones.

At least three or four scoopfuls of cullet are used, and it is best to pour it around the inside of the pot and allow it to run down to the bottom. The quantity should be sufficient to form a pool at the bottom, and if a large amount of cullet is on hand and is to be disposed of, it may be added in much larger amount than mentioned. The pot is then allowed to stand one hour longer. By holding the furnace for two hours at 1400° C before starting to fill in the batch proper we have made sure that all parts of the furnace and regenerative chambers are well heated and that the heat has penetrated the furnace lining to such a depth as to make available a certain store of heat for aiding in

¹ C. N. Fenner, "Methods of Temperature-Control in Glass-Melting Furnaces," *Phys. Rev.*, 2nd series, 11, 2, 141. Abstract of a paper presented at the Rochester meeting of the American Physical Society, October, 1917.

a quick melting of the batch. The quicker the batch melts down the more satisfactory is the fining likely to be.

The normal quantity of batch to put in in the first fill is that which will about half fill the pot with unmelted batch. If the glass is one which is apt to give trouble in fining it is well to use a less quantity in order to give quicker melting, and fill in oftener.

When the first fill has melted down to a level surface, or in about three hours, a second fill of the same quantity is put in,

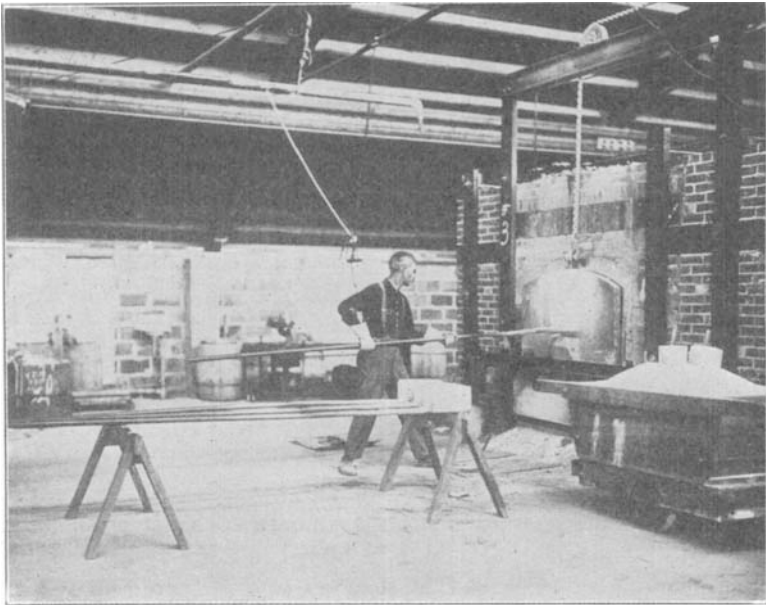


FIG. 1.—Filling in the batch.

and three hours later a third fill. Then one after another smaller fills are added, and finally the melt is topped off by a few scoops of batch. The level at which filling ceases is that at which the melt is an inch or an inch and a half below the rim of the pot. The operation of filling is illustrated in Fig. 1.

Melting and Fining.

During melting such volatile substances as water, carbon dioxide, and oxides of nitrogen, likewise the excess oxygen in red lead, are driven off and the bases unite with silica (and with boric oxide, if that is present). A few moments after a fill is put in we may see little eruptions of gas, given off here and there from the batch, breaking through the liquefied surface. On the whole, however, the melting process is rather quiet. The presence of niter insures that the conditions shall be oxidizing, and gives the melt a fair start in the right direction in that respect. It is our business to see that the subsequent history does not involve reduction. That is a matter of keeping the furnace atmosphere in proper condition, and will be discussed later. Most of the volatile gases given off in melting escape entirely, but a relatively small amount is entrapped as bubbles, and another portion, there is reason to believe, is dissolved by the molten glass. The combination of the basic oxides with silica is likely to be slow, and as the silica is of relatively low specific gravity, this gives an opportunity for gravitative differentiation. In flint glasses especially a surface layer containing large quantities of grains of undissolved silica is likely to persist for a long time. In very dense flints a bottom layer of excessive lead content is also formed.¹ In one striking case which came under observation a pot of glass, which was supposed to have an index of 1.648, showed, because of improper stirring, the following phenomena: At the bottom a distinct layer, of about a foot in thickness, of glass of a pale greenish-yellow color, having an index of about 1.690; above this a mass of glass in which the index varied from 1.630 in the lower portions to 1.610 in the upper. During the melting of this glass samples from the top had shown quantities of silica grains embedded in a glass having an index of about 1.545. Probably in most cases a glass of this kind has undergone a similar segregation, but in this example the subsequent procedure was faulty and the segregation was not destroyed by stirring. Possibly, also, in this case the fills were not given time to melt down

¹ Liqutation is naturally less pronounced when a large amount of cullet has been added before the batch is filled in.

sufficiently before others were added. In a paper by N. L. Bowen¹ phenomena of this nature are discussed in some detail.

It has been held by some who have made observations on gravity-separation effects in glasses that the evidence points to liquid immiscibility, but to anyone who has studied the phenomena of glass-making for a long period and who has been able to make observations at all stages of the process this explanation appears entirely unwarranted. Nothing seems more certain than that, if the mixing is sufficiently thorough, a homogeneous solution is formed, and that it is only by subsidiary processes, such as volatilization from the surface and solution of the pot walls, that there is a tendency for the glass to become inhomogeneous later. It is necessary, however, that such compounds as chlorides and sulphates be excepted, for the solubility of these in the melt is undoubtedly rather small. Instead of forming a homogeneous solution they rise to the top and form immiscible layers.²

The filling and melting will probably take eight to ten hours. Ordinarily this will be followed by a period of several hours during which the melt is allowed to stand and fine. However, according to the twenty-four-hour schedule it has been found possible in most cases to dispense altogether with fining as a separate process. The glass is given a hand-stirring before the melting is really complete. Then, a short time after the last fill, the machine-stirrer is set in operation and stirring continued until the pot is ready to come out.

During most of the fining period the glass is allowed to rest quietly. Filling has taken, we will say, from 10 P.M. to 8 A.M. Two or three hours later most of the surface of the glass should appear smooth and mirror-like, but if a proof or sample be taken the glass will be found to contain numerous large and small bubbles. Gradually the quantity will diminish. The large ones will disappear first. There is usually a period during which the evolution of large bubbles is quite active and this effect is termed the "boil." The fine bubbles ("seed") will continue rather longer

¹ N. L. Bowen, "The Significance of Glass-Making Processes to the Petrologist," *J. Wash. Acad. Sci.*, **8**, No. 4, p. 88 (Feb. 19, 1918).

² See F. Gelstharp, *Trans. Am. Ceram. Soc.*, **14**, 665 (1912).

than the larger ones but, if matters go properly, they should disappear almost entirely within a few hours. Occasionally a pot of glass will, for some reason, show a persistent layer of froth on top. One dislikes to see this, but nevertheless, such a pot will frequently come out all right in the end.

During fining the direction of flow of the air and burnt gases through the regenerative chambers should be reversed often enough so that one side does not become chilled and the other overheated. Reversal at intervals of twenty minutes answers very well for this.

For most of the common types of glasses a temperature of about 1400° C during melting and fining is required. If the batch materials contain sulphate or chloride in any but very small amounts and the glass is one which is likely to turn milky because of these impurities,¹ the danger may be avoided by keeping the temperature at 1420 – 1430° C during these operations.² This temperature is somewhat severe on the pot and the danger of the pot leaking or casting stones is increased, but pots are now manufactured in this country of such quality that, with proper care in previous treatment, the risk of disastrous consequences from running at this temperature is not so great that it need cause us to hesitate. It is essential, however, to see that, through carelessness, the temperature does not rise 15 or 20 degrees higher than the point established. Excessive temperatures are not only hard on the pot but increase the amount of selective volatilization from the surface and thus tend to alter the index of the glass.

Under ordinary circumstances (that is, when there is no danger of milkiness) a temperature of 1400° for a light flint or a boro-silicate crown answers very well. An ordinary light crown forms a more viscous melt and may be run at 1410° . Dense flints are very liquid, and need not be heated to more than 1370° .

Zschimmer³ gives the following as the melting temperatures used at the Jena works:

¹ Light flints seem especially susceptible.

² C. N. Fenner and J. B. Ferguson, *Op. cit.*

³ E. Zschimmer, *Op. cit.*, p. 865.

- 1000° C Phosphate glass (3B₂O₃, 70.5P₂O₅, 12K₂O, 4MgO, 9Al₂O₃, 1.5As₂O₃, according to synthesis).
- 1100° Dense lead silicate glass (20.8SiO₂, 79PbO, 0.2As₂O₃—Syn.).
- 1130° Borate glass (52.5B₂O₃, 1SiO₂, 1.5Na₂O, 1.5K₂O, 6ZnO, 12BaO, 16PbO, 9Al₂O₃, 0.5As₂O₃—Syn.).
- 1320° Dense barium borosilicate glass (14.5B₂O₃, 39SiO₂, 41BaO, 5Al₂O₃, 0.5As₂O₃—Syn.).
- 1370° Ordinary flint glass (45.7SiO₂, 1.5Na₂O, 7.1K₂O, 45.4PbO, 0.3As₂O₃—Syn.).
- 1410° Ordinary crown glass (2B₂O₃, 69.2SiO₂, 8Na₂O, 11K₂O, 4CaO, 3.5ZnO, 2PbO, 0.3As₂O₃—Syn.).

Where a covered pot is used, having only a comparatively small opening in front through which there is any possibility of furnace gases reaching the melt, the atmospheric conditions in the furnace around the pot are not of very great importance. Volatile materials, such as lead oxide, alkalis, and boric acid, are evolved and supply a protective covering within the hood of the pot, and through this protective atmosphere the furnace gases seldom penetrate. On the other hand, if open pots be used, it is important to keep reducing gases away from the glass. If the conditions within the furnace are kept anywhere near right the reducing action will never be sufficient to precipitate metallic lead, but at a considerably less intensity of reducing conditions the ferric oxide will be partly changed to ferrous oxide, and the same amount of iron in this lower state of oxidation has a much more intense coloring effect. In order to avoid this the gas should be burned with a rather short flame. A criterion which may be used is to see that the visible flames do not extend much beyond the top of the crown. Slowly moving flames, curling down over the pot, should be avoided if possible. In a multiple-pot furnace it may be difficult at times to avoid contact of the flames with the surface of the melt, but in single-pot furnaces, especially of the regenerative type, matters are under control to a greater degree, and here we may quite easily keep the temperature at the desired point and at the same time have the proper kind of flame by making correct adjustment between amount of gas, width of opening of air-inlet, and pull of stack, and a good furnace-man will soon learn to keep things very steady after having been shown what conditions are required. Some difficulty may be ex-

perienced at first in getting him to understand that economy in combustion may occasionally have to give way to other requirements.

Different types of glasses show considerable differences in the facility with which they free themselves of bubbles. For those glasses which give difficulty in this respect an old practice, which has been applied commonly not only to optical glasses but to other kinds, is "blocking." This consists in introducing some substances below the surface of the metal which will quickly evolve vapor. The large bubbles which are given off and rise through the metal tend to sweep out smaller bubbles with them. For this purpose various substances have been used—a block of wood, a potato, arsenic, etc. The Pittsburgh Plate Glass Company has developed the use of a substance which is especially applicable to optical glasses. A small amount of ammonium nitrate, sufficient to give rise to a number of large bubbles when it is inserted below the surface of the metal, is wrapped in paper so as to form a package. This is fastened to an iron rod which has been bent at almost a right angle, and plunged quickly into the metal and down to the bottom of the pot.¹ The ammonium nitrate is rapidly volatilized and the vapor rises in several great bubbles.² The blocking is begun when the metal has reached an open boil, at which time the operation is carried out three times in rapid succession, and fifteen minutes later three times more. This is continued until the metal is "plain" or free from bubbles. The fact that the vaporization of this substance is complete and without residue, and that the gas is oxidizing in character makes this material almost ideal for the purpose. Besides its effect upon enclosed bubbles it probably aids mixing somewhat by throwing up any heavy layer that has settled to the bottom.³

¹ We need have no hesitation in inserting iron tools temporarily in the melt if we see to it that their surfaces are kept free from scale.

² Instead of enclosing the ammonium nitrate in a paper wrapper it is sometimes melted over a low flame and cast in "pencils" in a mold. A section of one of these "pencils" is fitted into a cylindrical receptacle on the end of the rod and used as before. This method is rather neater and seems preferable, but it necessitates a little previous preparation.

³ At Hamburg, in running on the twenty-four-hour schedule, it has been found effective in some cases, when the fine bubbles will not clean up, to stop stirring, turn off the gas, and drop the temperature from 1400 to 1250°, then turn on the gas, heat to 1400°, and resume operations.

The period of quiet during fining gives opportunity not only for the bubbles to rise but for pot-stones also to come to the surface. With a good pot the amount of stones cast should be small and often is negligible. If they appear they will be removed later by skimming.

Bubbles and Their Origin.

One of the chief purposes served in fining is the elimination of bubbles. It seems opportune, therefore, to discuss at this point the origin of bubbles, although such discussion will involve to some extent a reference to subsequent processes.

There are several obvious methods by which bubbles and seeds are formed, and others which are more obscure. Likewise the removal of some kinds of bubbles (or the bubbles in some glasses) gives no special difficulty, while in other cases the difficulties are very great. There are phases of this problem which have given us much concern and some questions regarding which we do not feel that we can give a definite and satisfactory answer. There are one or two types of glass which still give an occasional pot with many "seeds" (small bubbles) in spite of all precautions.

The great majority of the bubbles are doubtless entrapped mechanically, but others appear to be set free from solution in the glass. Of those entrapped mechanically many are to be referred to the first melting of the batch. With these the best possible opportunity for escape is offered during the period of fining, when the temperature is high and the glass is in its most liquid condition, and most of them should escape at this time, especially if assistance be given by blocking. We find, however, that often with the rather viscous melts, such as light crown, and less frequently with other melts, quantities of bubbles collect on the walls of the pot and adhere tenaciously. A proof taken after the first hand-stirring will often show many bubbles which have been set free by the agitation and have arisen to the surface, though prior to the stirring the glass may have seemed free of bubbles. These are probably to be attributed in part to gas which has been clinging to the walls and in part to gas which has been dissolved in the melt beyond the point of saturation and has

been set free by the mechanical agitation. In general, bubbles which have been entrapped during melting are not likely to be so troublesome as to cause us much anxiety. Certainly that is true with the more fluid glasses and probably with even the more viscous.

A second kind of mechanically entrapped bubbles are those which are stirred into the glass. During the last stages of stirring the viscosity of all glasses increases very greatly, and unless considerable care be used to adjust the speed of stirring to the viscosity the wave of glass which accompanies the stirring-tube is likely to fold over and entrap air. That this happens is not a matter of conjecture; such entrapped bubbles have been actually observed as they were swept downward into the melt. The remedy is to see that the stirring-tube does not travel so fast as to push a high ridge of glass in front of it. Further on in this article the stirring process will be described and data on the speed of movement for different types of glasses will be given. By using care bubbles of this kind may be avoided. Before the danger of entrapping air in this manner had been fully realized, a pot of borosilicate crown had, in one rather striking instance, been carried to a lower temperature (and greater viscosity) than usual. As a result the glass contained innumerable bubbles, whereas ordinarily this type of glass was almost perfectly free of them.

A third source of mechanical bubbles is a leaky stirring-rod. The stirring-rod is a water-cooled contrivance, at whose furnace end a reducing, right-angled elbow receives a hollow iron pin, which fits into the orifice left for the purpose in the upper end of the clay stirring-tubes (see Fig. 2). We have found that the joint made by screwing the pin into the elbow may appear water-tight when tested in the cold, but that during use in the furnace there may be a slow leak, probably due to unequal expansion. The evidence of this is twofold. First, we had the very direct evidence that when the pin was lifted out of the tube at the end of stirring a little dampness or even a drop or two of water has been observed on it. Second, while the stirring of the metal was being watched, a rather large bubble had been observed to rise to the surface of the melt occasionally, very close to the

stirring-tube. This had apparently been formed in the following manner: A drop of water had collected on the pin and had finally dropped down into the tube. There it had been vaporized so suddenly that some of the vapor had been forced out through the pores of the tube into the melt. If the melt were at a high temperature and of an intrinsically fluid nature the vapor rose to the surface, but if not it was distributed through the melt. An effective remedy for this is to set the pin in the elbow with a litharge-glycerine cement.¹

In addition to the bubbles entrapped by the various methods which have been described it appears that there are bubbles of quite different origin. They seem to consist of gas which has been in solution in the melt at a high temperature and has been evolved on cooling. We have found that in some cases, after care had been taken to eliminate all the possibilities mentioned and the glass had become free from bubbles during fining, nevertheless, in the subsequent cooling during stirring, bubbles had reappeared and had persisted to the end. Such a phenomenon of greater solubility at higher temperatures is rather exceptional and is not, strictly speaking, one in which we have a simple solution of gas in a liquid. There is probably of necessity a chemical reaction between the gas and the constituents of the liquid. This reaction must be endothermic, for it is only under this condition that the solubility of a gas is increased on heating and decreased on cooling.

Our experience indicates that not all types of glass are affected by bubbles of this kind, and not any type under all conditions, but we are not able to state definitely what the conditions are which cause them to appear. We suspect rather strongly that those crown glasses which contain barium in small to moderate amounts are especially prone to dissolve gas and later evolve it as bubbles. Therefore, until more certain evidence is obtained,

¹ Made by adding litharge to glycerine and working it to a paste with a spatula. A very little water may be added to the glycerine. The time required for setting depends upon the fineness of grain of the litharge, amount of water, and proportion of litharge to glycerine. See a paper by H. E. Merwin in *Jour. Ind. Eng. Chem.*, **9**, 390 (1917).

we would look upon barium as a trouble-maker in such glasses and avoid its use where possible.

Still another class of bubbles, which may be termed vacuum bubbles, appear under certain exceptional circumstances. If a pot of glass be cooled quickly a rigid crust forms over the surface while the interior is still hot. Then when the interior cools and endeavors to contract it is held by the rigidity of the crust. If the glass contain bubbles of even the most minute dimensions (and probably they are always present), they act as points of weakness, and the glass contracts in every direction from them. Such a glass may, after cooling, appear full of large bubbles, especially in the last-cooled portions, but if it be carefully heated to a softening temperature the bubbles collapse until they are invisible or nearly so. If the proper procedure is followed, bubbles of this kind should never appear in our regular melts. They may be expected, however, in small experimental melts, where no special effort is made to have the glass cool properly.

The Function of Arsenic.

Closely associated with questions of the origin and elimination of bubbles is the matter of the use of arsenic in glass-making.

Arsenic in small quantities in the form of As_2O_3 is almost universally used in optical glass and very commonly used in other glasses. It is said to cause the melt to fine better and to make the glass more brilliant. The manner in which it accomplishes these results is rather uncertain. Allen and Zies,¹ in a recent article, have discussed the matter in the light of the latest information and have indicated the manner in which the oxides of arsenic may function in causing a boil and sweeping out the small bubbles, whose rate of ascent when unaided may be almost negligible.² We may amplify their idea slightly and add the suggestion that bubbles of arsenic vapors may not only gather up gases which have already been set free as bubbles, but that they may collect *potential* bubbles; that is, in the relation of these

¹ E. T. Allen and E. G. Zies, "The Condition of Arsenic in Glass and Its Rôle in Glass-making," *J. Am. Ceram. Soc.*, **1**, 787 (1918).

² Raymond M. Howe, "Principles Controlling the Formation and Removal of Bubbles in Molten Glass," *Trans. Am. Ceram. Soc.*, **19**, 201 (1917).

vapors to other substances which tend to be evolved slowly because of the hydrostatic pressure and surface tension¹ to which they are subjected; they may act as vacuum chambers into which these substances may evaporate at a much more rapid rate.² Although our knowledge of the manner in which arsenic acts upon the melt is rather deficient, the addition of arsenic is generally looked upon as being beneficial, and we may well continue its use. The amount added is always small. If an excess be used it has a tendency to produce a milky or opalescent glass. Zschimmer's tables show that at the Jena works the amount of As_2O_3 ordinarily put into the batch is about 0.3 per cent of the weight of the glass. In our own practice we generally used about the same amount or a little more.³

Leakage.—During the whole period of making a pot of glass a watch should be kept to see that the pot has not begun to leak. On account of the relatively corrosive properties of many optical glasses the danger is much greater with them than with plate glass, tableware, window glass, and batches of similar nature. The means which we found most effective in reducing leakage losses was to see that the temperature was kept uniform and not allowed to rise thirty or forty degrees beyond the established point as might happen through carelessness. The inauguration of a reliable system of temperature-control was attended by a remarkable difference in respect to losses of that kind. Inasmuch as the likelihood of leakage is greater with optical glasses,

¹ Raymond M. Howe, *Op. cit.* Howe shows that surface tension is probably a very effective force in restraining the growth of bubbles.

² According to the laws of gases a bubble filled with one gas represents, to all intents and purposes, a vacuum for a second gas. This is closely related to what is known as Dalton's law. See E. W. Washburn, "Principles of Physical Chemistry" (1915), p. 26, or W. Nernst, "Theoretical Chemistry," Fourth English Edition (1916), p. 39.

³ The question of the use and function of arsenic requires further investigation. At Charleroi the preference was given to the use of considerably larger quantities of arsenic than 0.3 per cent, especially in the crown glasses. This practice was based on that of plate-glass making and the greater quantity was supposed to help fining. On the other hand, arsenic has been left out altogether in some instances at Hamburg, and the metal appeared to fine equally well.

precautions against it must be more strictly observed. In addition to keeping the temperature uniform other measures which should be carried out may be summarized as follows:

We must see that only best-quality pots are used; that they do not become damp or subjected to extremely cold temperatures while in storage; that they are handled gently while in the unburned condition; that the preliminary heating in the arch is done slowly and evenly and is carried to a bright cherry-red; that they are examined in the transfer from arch to furnace; that they are heated in the furnace to fining temperature or higher before filling is begun; that cullet is charged and allowed to soak into the pores before raw batch is added; and that for especially corrosive glasses the pot used be of a special clay mixture designed to withstand corrosion. With these precautions regularly enforced the number of pots that will fail will be extremely small.

Skimming and Stirring.—In running on a 48-hour schedule the melt or metal should be fine or plain by the evening of the day following that on which filling began. In fact, the fining may have reached a satisfactory stage before this, but unless we are endeavoring to hurry the process the melt may be allowed to stand quietly until about 7 P.M. Then, if it seems necessary, the surface should be skimmed. The indications are the presence of a scum of froth or stones on the surface. The stopper of the hole in the tuille is taken down and the skimmer inserted. This is a long-handled iron tool at whose further end a skimming blade is joined at right angles to the handle. The operation must be performed in such a fashion that the blade passes over the surface of the melt with a smooth, even stroke without bringing about such swirls or other disturbances as would cause surface material to be carried down into the melt, and at the end of the stroke the material must be gathered up on the tool and brought out. Some knack is required to perform these operations properly. If they are improperly performed surface material is forced down into the metal and does not soon rise again.

Care should be taken not to remove more glass than necessary. There has been gravitative segregation or liquation dur-

ing melting, and the composition of the surface layer does not represent the average composition of the melt. Therefore the greater the quantity of glass that is removed the more the average composition of the whole is changed. It would be better if we could avoid skimming altogether, but where it is necessary to skim, as is occasionally the case, we should see to it that an unnecessary quantity of glass is not removed. Some workmen will fall into this error through carelessness and some from excess of zeal.

After the metal has been skimmed it is allowed to rest for an hour and then the first hand-stirring is performed. Prior to this, however, certain preparations must have been made in the way of getting stirring-tubes ready. The stirring-tube is a thick-walled tube of clay whose length is about equal to the depth of the pot. For a pot 27 inches in depth we should have the tube about 26 inches long when dried and burned, keeping in mind that an appreciable shrinkage results from the latter operations. The outside diameter at top should be about 4 inches for a tube of this length, and should decrease to 3 or $3\frac{1}{2}$ inches at the lower end.¹ At the upper end there is a circular flange about an inch thick, which projects about an inch from the main body of the tube, and is used for holding the tube when the stirring-rod is withdrawn. After a tube has been fashioned it is set aside to dry for a week or two. Then while still soft (though firm) the central hole is modified in shape a little at the upper end. By means of a coarse file the circular section is changed to that of a square which is tangent to the circle, for a length of about four inches. The purpose is to have the shape of the hole conform to the shape of the iron holding-pin of the stirring-rod which enters it. This pin is square in section for about this distance at its upper part (where it joins the main rod) and is circular below this for a length of, say, three inches. The exact value of these dimensions is not important, except that the dimensions of the hole in the clay tube must conform to those of the pin. The purpose of the pin is to hold the tube in proper

¹ The thickness of tube used varies somewhat at different plants, and some latitude is allowable. The requirements are that the tube should be large enough to be an effective stirrer without being unwieldy.

position, and the square section of a portion of it prevents rotation during stirring.¹

After the tube has been dried and the central hole shaped in the manner described, the tube must be burned. About an hour before one is to be used it is transferred from the salamander or from the arch in which it has been heating to the furnace and laid on the fire-wall to receive its final heating. A few minutes before stirring begins the tube is lifted off the fire-wall with an iron hook and gradually and carefully lowered into the melt and left floating there for a few minutes in an inclined position, with the flange at the upper end hooked over the lip of the pot. In a short time any bubbles that may have been given off will have risen to the surface. Then the water-cooled iron stirring-rod is introduced into the furnace, its pin is inserted into the hole in the tube, and stirring begins.

Just outside of the furnace the stirring-rod rests on a small grooved wheel² which turns on a horizontal axis primarily and whose shank is revolvable in a vertical socket secondarily. This permits the farther end of the rod to move continuously around a circle. Near the handles which the workman grasps the principal weight of the rod may conveniently be taken up by an iron hook attached to a cord, which passes around overhead pulleys to a counterweight. The hose connections are made near the handle and a constant stream of water is kept running through. As the water emerges from the outlet hose it should be appreciably warm but not hot.

The hand-stirring is carried on for 15 minutes at a time, at the rate of 24-28 revolutions per minute. The movement is a

¹ This description applies to the practice at two of the plants. At the third the construction of the stirring-rod is such that the pin which enters the tube is simply the terminal part of the main rod bent at a right angle and drawn down to a smaller diameter. Its cross-section is circular throughout. This construction is simpler, but unless very careful blacksmithing work is done the pin is likely not to fit closely in the tube and the tube may wobble during stirring.

² This wheel is supported on a length of channel-iron which passes horizontally across the front of the tuille and is, in turn, bolted rigidly (though temporarily) to the buck-staves of the furnace frame. The device is kept in position only during the period of hand-stirring.

combination of a circular and a vertical motion. At one portion of the circle the end of the tube is brought as near to the bottom of the pot as can conveniently be done without scraping, and at another portion it is lifted several inches. The chief purpose is to produce a thorough mixture of the metal; therefore in medium and heavy flints the stirring should be especially vigorous.

A proof taken after the stirring is over will often show that a quantity of bubbles have been detached from the pot-walls or set free from solution in the glass and brought to the surface. They should be of rather large size and should escape easily from the melt.

After the 15-minute stirring is finished the water-cooled stirring-rod is withdrawn from the furnace. The tube is left floating in the melt in the same position as when it was first introduced. Hand-stirring is repeated during the night at two-hour intervals. At about seven o'clock the next morning stirring by machine is begun. The stirring-machine (shown in Fig. 2) is an electric motor-driven device so constructed as to reproduce the circular and up-and-down motions described under hand-stirring, but to perform the operations in a smooth, even manner while rigidly following a prescribed course, and to continue it for hours. At one time or another several types of machines have been tried at the different plants, and from a comparison of their performances it becomes quite evident what requirements such a machine should possess.

The machine should be easily movable from place to place and should be capable of being quickly removed when stirring is over; therefore, it is provided with traveling wheels with off-set sockets on the plan of the castors of a chair. When the machine is in position in front of the furnace the weight is taken off the wheels by elevating screw-posts. By means of these posts one may also adjust the height a trifle, but the principal adjustments for height should be elsewhere. It is essential to be able to change the speed of operation, and for this purpose we may either use a constant-speed motor in connection with step pulleys, or we may vary the speed of the motor by a rheostat and running-box. The latter arrangement is more expensive but considerably better. In any case we should be able to vary

the speed of stirring from about 28 to 4 or 5 revolutions per minute, the variation being either continuous or in not less than four steps. The horizontal rotating arm to which the outer end of the stirring-rod is attached and by which a circular motion is given to both the outer and the inner (or furnace) ends of the rod, is mounted on a vertical axle driven by bevel-gears from the pulley-shaft. In order to attach the stirring-rod to the arm the

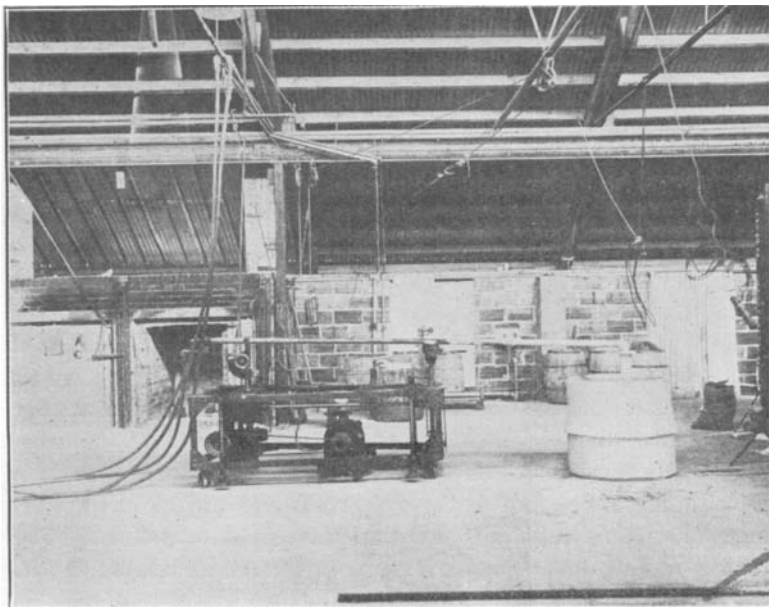


FIG. 2.—Stirring machine set up to show its position with relation to the pot.

latter is provided with a slot which receives a corresponding lug on the stirring-rod. A stout pin passes through the two and is held by a split cotter. This arrangement permits the rod to be mounted or dismounted in a moment. The height of the arm should be adjustable, and to effect this its attachment to the vertical axle which turns it is by means of a movable collar which may be slipped along the axle and held at the desired height by a set-screw.

The stirring-rod is supported at the middle on a grooved wheel similar to that used for the same purpose in hand-stirring, but here the shank (pedestal) of the wheel is extended to form a long rod or post, which passes through bearing-boxes on the framework of the stirring-machine and is attached to the mechanism in such a manner that an up-and-down motion may be imparted to the post and wheel by a crank-drive. The result of these various mechanisms is that the outer end of the stirring-rod is carried around a horizontal circle, the median portion is given a vertical motion, and the inner end combines the two. Strictly speaking, the horizontal component of the motion of the inner end is not circular. The curve described is an oval, which, however, does not differ greatly from a circle. The height of the wheel-post may be varied in a fashion similar to that described for the rotating arm. Likewise the length of stroke of the post may be varied, although this is hardly necessary. Some machines which we used were provided with means for varying the vertical stroke, but in practice they were left set at a stroke of about $2\frac{1}{4}$ inches. By all means, however, it should be possible to take off the vertical motion altogether with little trouble or delay. It is essential also that the effective radius of sweep of the horizontally rotating arm may be changed easily by a screw-feed. During most of the period of stirring the radius of the stirring-circle is left without change, but as the glass cools and stiffens in the final stages of stirring the radius of the stirring circle is cut down. The vertical motion of the supporting post should be related to the horizontal motion of the rotating arm in such a way that they do not synchronize but that the uppermost (or lowermost) part of the stroke advances a certain amount each time on the horizontal circle. A satisfactory arrangement is to have one complete stroke (from upper limit to lower limit and back) in about $1\frac{1}{4}$ revolutions. The whole machine should be rigid in construction and not likely to get out of order, and the settings and changes required for proper stirring should be easily effected.

When the machine is first set in motion the radius of the stirring-circle is cut down to the lowest limit so that the clay tube makes only a very small circle around the center of the pot. Then the circle is increased in size until it approaches the outer cir-

cumference. Care should be taken, however, to see that the clay tube does not approach the pot-walls so closely that it touches at any point or does not pull off the skin of glass adhering to the walls. For a pot whose diameter at bottom equals 25 inches we have found that a stirring-circle of 7 inches radius is a quite satisfactory maximum. As the stirring-tube has a radius of about two inches the circle passed through by the outer portions of the tube has a diameter of 18 inches under such conditions. At the speed with which the machine is driven all the glass in the pot is effectively agitated and mixed when the tube describes such a circle.

In setting the tube for height the endeavor is made to have the bottom of the tube come near enough to the bottom of the pot so that no layer of glass is left unstirred, but to avoid the danger of letting the tube touch the bottom. To accomplish this a clearance of about two inches between the end of the tube and the bottom of the pot should be allowed.

It is only with glasses which have a strong tendency to form a heavy bottom layer that a vertical motion is given to the tube in machine-stirring. Therefore, in general, the vertical motion is used only with medium and heavy flints. For these the vertical stroke of the supporting post may be made $2-2\frac{1}{4}$ inches. As this motion is imparted to the stirring-rod at midway of its length, the far end of the rod with its attached tube is given a vertical motion of $4-4\frac{1}{2}$ inches. It has been found in some cases that even with dense flints ($n_b = 1.650$) the vertical motion may be dispensed with. In these cases large quantities of cullet (40 to 50 per cent) were used, and under such circumstances there is much less likelihood of the settling of a heavy layer to the bottom.

The viscosity of different glasses varies considerably at the stirring temperature, and the speed of stirring likewise varies to some degree. Of the common glasses dense flint stands at one extreme and light crown at the other. A speed which has been found to work well with flints is 18 revolutions per minute with a stirring circle of 7 inches radius. This gives a speed of 792 inches or 66 feet per minute as the rate of horizontal travel of the stirring-tube through the glass. In addition there is, with

flints, a vertical motion imparted to the tube, as already stated. In the case of light crown and similar glasses the danger of stirring bubbles into the melt makes it desirable to run more slowly. Therefore a speed of about 45 feet per minute has been used. For borosilicate crown the speed has been about the same as for flints.

Up to the time that stirring by machine has been begun the temperature has been kept up to 1400°C or thereabouts (varying somewhat with the type of glass). During the progress of machine-stirring the stopper is out continuously and the furnace naturally cools somewhat. This is quite allowable at this stage, but the drop should not exceed $75\text{--}80^{\circ}\text{C}$.

Machine-stirring is continued without change for four or five hours. Then the gas is shut off, the air-inlet to the regenerative chambers is closed, the stack-damper lowered, and the butterfly-valve swung to the intermediate position. The metal has been thoroughly mixed and now it is allowed to cool and stiffen. Stirring must be continued, however, for the sources of inhomogeneity are still active. The principal source is doubtless the bottom and walls of the pot, by whose solution foreign material is constantly supplied; but another source is the upper surface of the metal, from which selective volatilization has been going on. The actual change in mass composition due to these gains and losses is probably so small that when mixture is complete and uniform the optical properties are not greatly affected thereby. It is not, indeed, the change in total composition which gives us concern, but the likelihood that material of different composition will be only imperfectly distributed through the mass. It is astonishing to find what slight differences in refractive index are exhibited by cords or striae which are so pronounced as to stand out in plain relief. When the difference is only in the third place of decimals a cord is quite perceptible. This means that the difference in composition is so small that diffusion is not a very effective factor and must be mechanically aided. The principle on which stirring effects its results is that these heterogeneous portions of the melt are mechanically spread out to such a degree that they present great surfaces of contact per unit of volume and only a short time is required for diffusion to overcome all

differences that exist. From the time that the gas is turned off the procedure followed is directed chiefly toward eliminating the conditions which permit striae to form. To effect this the heterogeneous material must be thoroughly distributed through the mass almost at the source from which it proceeds; at the same time conditions must be so changed that the tendency toward solution of the pot and volatilization from the surface is decreased, while the mechanical obstacles presented by viscosity to the movement of convection-currents are gradually becoming greater. These objects are attained more or less perfectly by continuing stirring as vigorously as may be without running the risk of causing air to be entrapped, while cooling the melt to a temperature which has been found by experience to be suitable. This temperature varies widely with different glasses, and the time required for cooling varies accordingly.

If one watches the stirring while the temperature is dropping one sees that the ridge of glass pushed ahead of the stirring-tube gradually becomes more prominent and if no change in the speed of stirring were made the ridge would, before long, reach a height of several inches. Obviously it is necessary to decrease the speed as the glass thickens. The vertical motion of the tube is unnecessary after the fire has been turned off and may be dispensed with at that time, and soon it is advisable to lessen the speed of angular rotation and to diminish the size of the stirring-circle. The proper amount of diminution is judged by the appearance that the passage of the tube through the glass presents, and is a matter that can hardly be described but must be learned by experience. However, temperature charts and records of operations during some typical runs are here presented, which may serve as a basis of comparison. The information is taken without modification from records made during actual operations. Where it is believed that the procedure might have been improved at some point a memorandum is introduced. The radii of stirring circles given are those measured at the outer end of the stirring-rod, but as the point of support or pivot of angular movement of the rod is about midway of its length the same figures apply without much modification to the inner end.

EXAMPLES OF PROCEDURE IN STIRRING.

(See also Charts 1-4.)

No. 1. Medium Flint. ($n_D = 1.605$, $\nu = 37.6$)

Pot 25 inches in inside diameter at bottom, 27 inches deep.

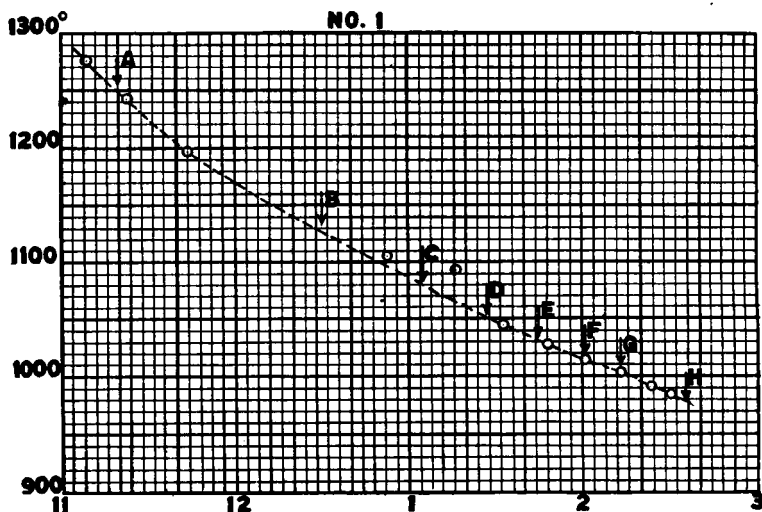
8 : 03 A.M. Started stirring machine at 13 rev. per min. Radius of stirring circle = $6\frac{1}{8}$ inches. Vertical motion = $4\frac{1}{4}$ inches. (Mem.: A stirring circle of greater radius would have been preferable.)

8 : 07 A.M. Changed speed to 18 rev. per min.

11 : 00 A.M. Shut off gas, air, etc.

11 : 09 A.M. Temp. (sighting on surface of glass) = 1276°C .

11 : 20 A.M. (A) Took off vertical motion.

11 : 23 A.M. Temp. = 1241°C .11 : 44 A.M. Temp. = 1197°C .12 : 30 P.M. (B) Radius of stirring circle reduced to $5\frac{1}{8}$ inches. (Mem.: It might well have been kept a little larger.)12 : 53 P.M. Temp. = 1104°C .

1 : 05 P.M. (C) Changed speed from 18 to 13 rev. per min.

1 : 17 P.M. Temp. = 1092°C .

1 : 27 P.M. (D) Radius of stirring circle reduced to 4 inches.

1 : 33 P.M. Temp. = 1044°C .1 : 45 P.M. (E) Reduced radius of stirring circle to $3\frac{1}{4}$ inches.1 : 48 P.M. Temp. = 1028°C .2 : 01 P.M. (F) Temp. = 1013°C . Reduced radius of stirring circle lightly.

2 : 13 P.M. (G) Temp. = 1003° C. Radius of stirring circle now about 1½ inches.

2 : 23 P.M. Temp. = 990° C.

2 : 30 P.M. Temp. = 984° C.

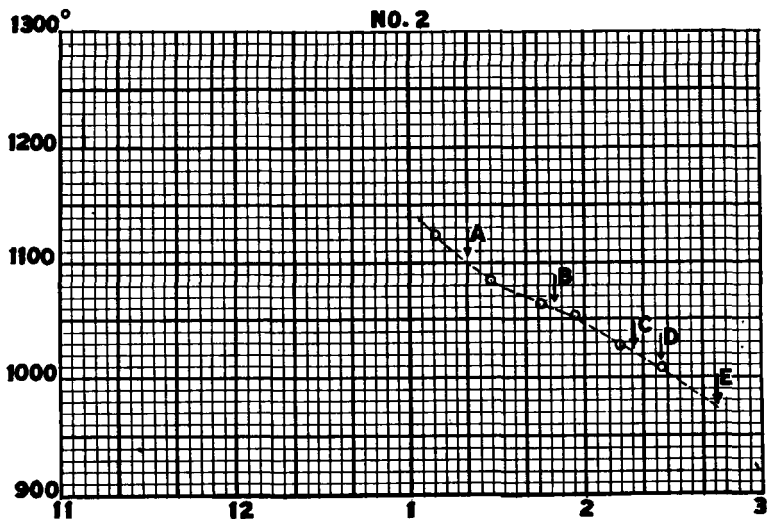
2 : 35 P.M. (H) Stirring stopped. Extrapolation gives temperature of 975° C.

2 : 40 P.M. Pot out.

(Mem.: A temperature of 950° C at time of stoppage of stirring would have been preferable for this type of glass.)

No. 2. *Baryta Flint*. ($n_D = 1.619$, $\nu = 37.6$.)

Pot 20 inches in inside diameter at bottom, 25 inches deep.



8 : 15 A.M. Started stirring machine at 13 rev. per min.; soon afterward changed to 26 rev. per min. Vertical motion 4½ inches. Radius of stirring circle = 5 inches.

11 : 50 A.M. Shut off gas, air, etc. Changed speed to 18 rev. per min. Took off vertical motion.

1 : 09 P.M. Temp. = 1122° C.

1 : 20 P.M. (A) Changed speed to 13 rev. per min.

1 : 28 P.M. Temp. = 1084° C.

1 : 45 P.M. Temp. = 1061° C.

1 : 50 P.M. (B) Reduced radius of stirring circle to 4 inches.

1 : 57 P.M. Temp. = 1053° C.

2 : 12 P.M. Temp. = 1028° C.

2 : 17 P.M. (C) Radius of stirring circle reduced to 3 inches.

2 : 26 P.M. (D) Temp. = 1007° C. Radius of stirring circle reduced again.

2 : 45 P.M. (E) Stirring stopped. Extrapolated temperature = 975° C.

2 : 50 P.M. Pot out.

No. 3. Light Crown. ($n_D = 1.516, \nu = 60.0.$)

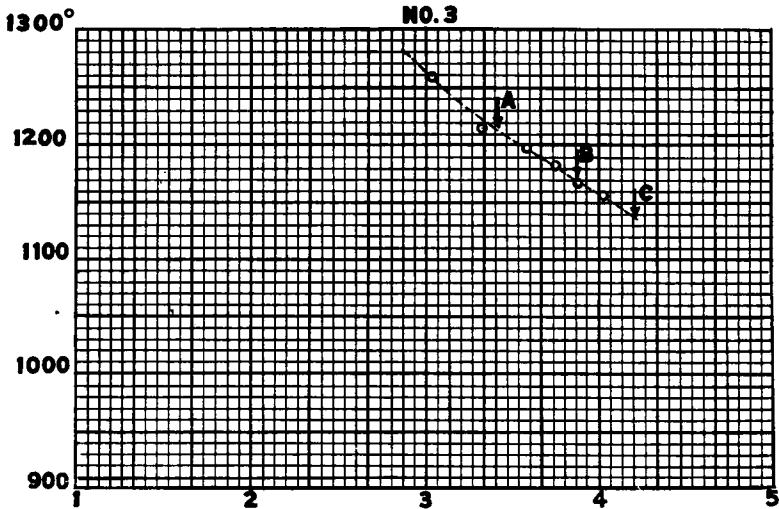
Pot 25 inches in inside diameter at bottom, 27 inches deep.

8 : 03 A.M. Started stirring machine at 13 rev. per min. No vertical motion. Radius of stirring circle = 6½ inches.

8 : 25 A.M. Changed speed from 13 to 18 rev. per min.

8 : 55 A.M. Changed speed from 18 to 13 rev. per min.

9 : 50 A.M. Reduced radius of stirring circle to about 5 inches. (Mem.: A proof taken just before this had shown quite numerous bubbles; therefore,



the speed of travel was reduced to avoid the danger of stirring air into the metal.)

2 : 35 P.M. Shut off gas, air, etc.

3 : 02 P.M. Temp. = 1259° C.

3 : 19 P.M. Temp. = 1214° C.

3 : 25 P.M. (A) Radius of stirring-circle reduced to 4 inches.

3 : 35 P.M. Temp. = 1197° C.

3 : 45 P.M. Temp. = 1182° C.

3 : 53 P.M. (B) Temp. = 1168° C. Radius of stirring-circle = 2½ inches.

4 : 02 P.M. Temp. = 1156° C.

4 : 13 P.M. (C) Stirring stopped. Extrapolated temp. = 1138° C.

4 : 18 P.M. Pot out.

No. 4. Borosilicate Crown. ($n_D = 1.511$, $\nu = 64.1$.)

Pot 25 inches in inside diameter at bottom, 27 inches deep.

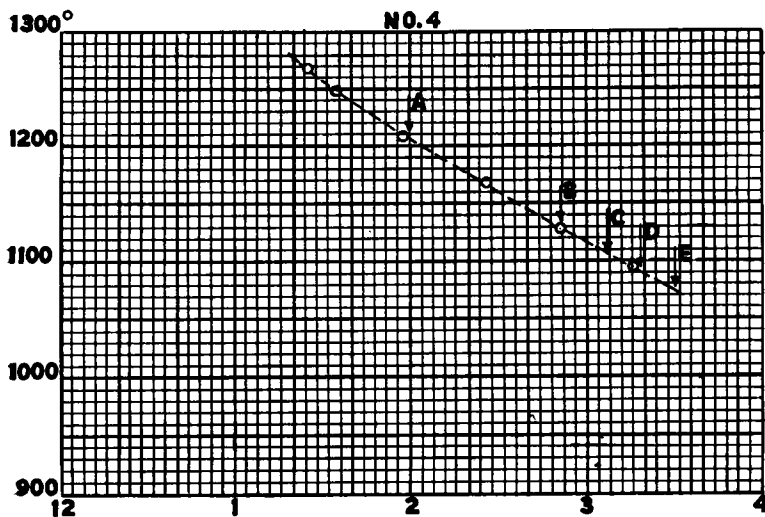
8 : 10 A.M. Started stirring-machine at 13 rev. per min. No vertical motion. Radius of stirring circle = $6\frac{1}{2}$ inches. Changed in a few minutes to 18 rev. per min.

1 : 15 P.M. Shut off gas, air, etc.

1 : 25 P.M. Temp. = 1266°C .

1 : 35 P.M. Temp. = 1247°C .

1 : 58 P.M. Temp. = 1208°C .



2 : 00 P.M. (A) Changed speed of stirring to 13 rev. per min.

2 : 26 P.M. Temp. = 1166°C .

2 : 51 P.M. (B) Temp. = 1127°C . Reduced radius of stirring-circle to 5 inches.

3 : 07 P.M. (C) Reduced radius of stirring-circle to 4 inches.

3 : 16 P.M. Temp. = 1095°C .

3 : 18 P.M. (D) Reduced radius of stirring-circle.

3 : 30 P.M. (E) Stirring stopped. Extrapolated temperature = 1075°C

C. (Mem.: This is rather high. 1050°C would have been preferable.)

3 : 35 P.M. Pot out.

Probably the examples given may be taken as fairly representative of the procedure to be followed during cooling and stiffening, but in making application to other cases caution must be used because of the fact that a type of glass having certain optical

properties may vary in chemical composition, and the treatment necessary will be closely related to the latter. For instance, it was found at Hamburg that the light flint made there should be cooled to 925° C before stirring was stopped. A glass of very similar optical properties but of somewhat different chemical composition (lower in alkalis), made at Charleroi, was removed from the furnace at a temperature higher by 100° .

There is much room for the personal equation to enter as an important factor in making measurements with the optical pyrometer on a pot of cooling glass. Different observers differ considerably in their ability to match the luminosity of the filament with that of the object sighted upon. Moreover, the angle at which the pyrometer is directed upon the surface of the glass is probably of some importance (because of surface reflections); and also, in the later stages of cooling, there actually are marked differences of temperature at different parts of the surface. At high temperatures the conditions of temperature-measurement are probably almost ideal for the employment of an optical pyrometer, as the light emanates from a self-luminous, transparent source within the mass, and the agreement with black-body conditions should be practically perfect¹. Moreover, at this stage the temperature-differences in different regions are small. At a later stage, however, it is easy to perceive that the swirls of liquid brought to the surface by the passage of the stirring-tube are hotter than the surrounding material. Then the measurement of temperature becomes, to a certain degree, an empirical opera-

¹ This is true unless glass at a high temperature possesses the property of luminescence; that is, that it emits light whose intensity does not correspond to that which a black body would emit at the same temperature. This is a possibility which must be taken into account until our data on the matter are more complete. At present the probabilities seem to be against it.

If one tries to look into a pot of glass which has just been removed from the furnace and has a temperature somewhere between 950° and 1100° , the impression produced is not that of looking deeply into a transparent mass but of looking into something which has the appearance of a milky, luminous haze. The explanation is probably this: that a body whose luminosity is due to its temperature tends to cut off light of any wave-length which it itself is sending out. Therefore, in such a pot of glass, the cool crust is transparent to the light proceeding from the glowing mass below, but the latter is (within a certain distance) opaque to its own radiations.

tion, and one must decide where he shall sight the pyrometer. The temperatures which have been given and others which will appear in a similar connection later refer to the hottest parts of the melt, close to the stirring-tube.

The temperature at which stirring is stopped and the pot set out is a matter of the greatest importance. Upon this principally will depend whether the glass is badly affected by striae or not. There are probably other factors to which, at times, striae are due. One of these is failure to break up and diffuse by vigorous stirring the layer of heavy glass which has segregated and sunk to the bottom of the pot, especially in dense flints. The formation of this layer has been referred to a number of times, and attention has been called to the procedure to be followed to eliminate it. Striae may be caused also by setting the pot, after removal from the furnace, into an arch that is too hot, thus causing convection-currents to be set in motion. This also may be quite easily avoided by proper attention. It is a somewhat more delicate and difficult matter to have stirring stopped at just the right moment and have the pot brought out promptly.

On a previous page the principal source of striae has been traced to dissolved pot material. If stirring be stopped at too high a temperature, this solvent action is still going on quite vigorously, and the viscosity of the metal has not yet become sufficient to oppose much resistance to the rise of convection-currents. The hottest part of the pot is the bottom, for during cooling the siege has been protected by the pot itself. Therefore, during the few minutes which elapse after stirring has stopped and before the pot is lifted from the siege convection-currents tend to be set in motion from this source. For this reason the metal must be cooled to a point where this tendency is small. Moreover, no unnecessary delay should be allowed to occur between the stopping of stirring and the removal of the pot. It might seem that cooling and stirring should continue to a point where the danger arising from convection-currents is obviously past, but this may not be done. There would be a probability of stirring air into the glass under such a procedure, and also a probability of dragging off into the melt the skin of glass lying next to the sides and bottom of the pot. This is a thin layer whose composition

is affected by solution of pot-material, and which, under ordinary circumstances, adheres closely to the pot, but may be pulled off if the stirring be continued until the glass is very stiff, and then gives rise to heavy cords. For these reasons the optimum temperatures for the cessation of stirring must be determined within rather narrow limits. Especially is this true with medium and heavy flints, whose compositions and optical constants differ greatly from those of the materials arising from pot-solution. With ordinary crown and borosilicate crown there is much less difference in this respect and more leeway is permissible.

In order to insure that the pot is set out at the proper temperature the fall of temperature is followed with the optical pyrometer during the later stages of stirring, and a few minutes before the end an extrapolation of the course of the temperature-time curve is made to the desired point. Following is given a list of temperatures for the cessation of stirring which have been found applicable to a number of common types of glass. In making use of this table the caution must be kept in mind that each figure applies to a glass of a certain chemical composition and not to a glass of a certain optical type. Moreover, it is not unlikely that furnace construction affects the rate of cooling, and perhaps other factors of an unknown nature may change the figures slightly. They may be taken at least, as fairly definite starting-points for experiment, and it is believed that, on the whole, not much change will be found necessary.

TABLE I.
TEMPERATURES AT WHICH TO CEASE STIRRING.

(The compositions of the glasses to which these figures apply are given in Table 2.)

Borosilicate crown.....	1050° C
Light crown.....	1150° C
Baryta flint.....	980° C
Medium flint.....	950° C
Light flint.....	925° C
Barium crown.....	1025° C

During the cooling and stiffening of the glass the speed of stirring has been reduced and the size of the stirring-circle has been diminished, until, in the last stages, the stirring-tube re-

volves slowly around a small circle in the center. Then, at a moment which has been determined some time before, the electric current is shut off from the stirring-machine and preparations are made to take the pot out. By all means this should be done quickly, in order to prevent the rise of convection-currents from the bottom, and each workman who is to take part should know what his duties are. The first operation is to move the stirring-tube from the center over to the left side of the pot. This is done, before the stirring-tube is disengaged from the rod, by swinging the rod outward from the center by means of the screw-feed. This imparts a smooth, even motion to the tube and obviates the likelihood of its digging into or otherwise disturbing the layer of glass close to the bottom of the pot. When the tube has been brought near the side it is held in place momentarily by a fork-like tool made for the purpose, while the stirring-rod is lifted out, withdrawn from the furnace, and laid aside. Then a rod of round iron, one inch in diameter, bent in the form of an inverted U, is dropped down in such a manner that one leg of the U enters the central hole in the tube and the other leg drops over the outside of the pot. The distance between the legs is such that when the hook is in this position the stirring-tube is held close to the pot-wall. One leg of the U should be about 14 inches long and the other 10 when used with a pot whose height from the shoulder to the rim equals 16 inches. The shorter leg is dropped into the tube. The weight of the hook keeps the stirring-tube in a nearly upright position.¹ The stirring-machine is now pushed to one side and the tuille is slightly lifted. By means of a heavy bar with a chisel bit a small hole is driven between the bottom of the pot and the siege (large enough to get the edge of the bar under the pot), a block of iron is laid on the siege as a fulcrum, and the pot is pried loose. The loosening should not be by sudden jolts on the outer end of the bar but by a steadily exerted force. In that way the giving-way of the gluey material which holds the pot will be gradual and will not lead to a sudden agitation of the glass. The tuille is now lifted high, the pot-wagon is run in and the pot

¹ An alternative method is to lift the tube out of the glass altogether. This seems inherently more likely to produce disturbances of a kind that will cause striae, and practical results seem to confirm this inference.

is clasped in its tongs. Counterweights nearly balancing the weight of pot and contents are lifted onto the outer pole of the wagon, the pot is raised quickly but carefully, brought out, and deposited on a tile. The time which elapses from the moment that stirring stops until the pot rests on the tile should seldom exceed five minutes, and when the working force is well organized and matters proceed without a hitch, it will probably not exceed

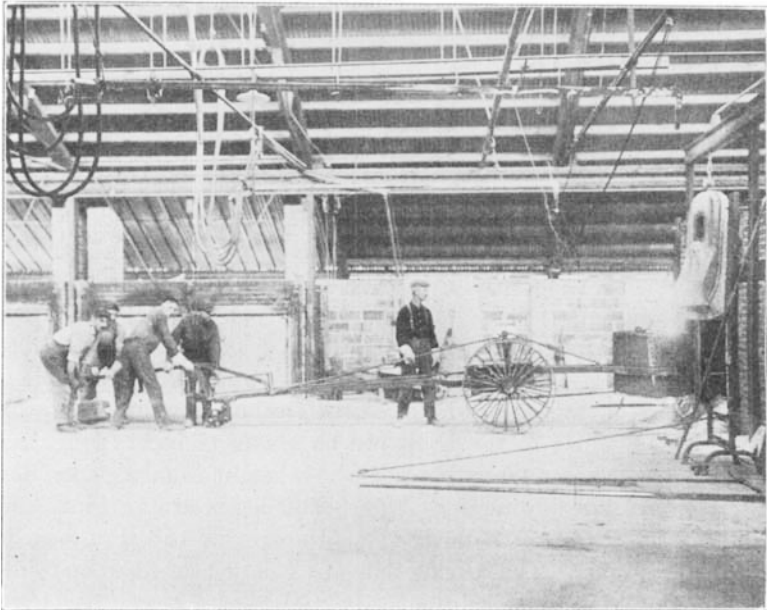


FIG. 3.—Removing pot of glass from the furnace.

three. Fig. 3 illustrates the operation at the moment that the pot is being withdrawn from the furnace.

The pot is left resting on the tile while the siege is got ready for the next run and a new pot is carried from the hot arch and set in the furnace. Then the pot just finished is placed in the arch left vacant. This procedure, however, may be modified. For instance, we found at one time that a certain lot of pots, which were very good in most respects, showed the bad feature of tending to crack while exposed to the cold air, and in one instance a

large section of pot-wall fell out and allowed nearly half the contents of the pot to escape. For these pots we adopted the practice of having an empty arch heated and ready, into which the pot of glass was carried directly from the furnace. The pot to

TABLE 2.
BATCH COMPOSITIONS.

	Medium Flint $n_D = 1.605$ $\nu = 37.6.$	Baryta Flint $n_D = 1.619$ $\nu = 37.6.$	Light Crown $n_D = 1.516$ $\nu = 60.0.$	Boro- silicate Crown $n_D = 1.511$ $\nu = 64.1.$	Light Flint $n_D = 1.580$ $\nu = 41.1.$	Barium Crown $n_D = 1.570$ $\nu = 57.0.$	Dense Flint $n_D = 1.640$ $\nu = 34.6.$
Sand	100	100	100	100	100	100	100
Pb ₃ O ₄	90.50	89.10	68.06	124.10
or	or	or			or		or
PbO	88.40	87.05	66.46	121.20
K ₂ CO ₃ (anhydr.)	10.30	21.30	10.00	15.60	9.44	5.20	5.28
KN ₃	7.81	9.63	12.39	14.00	8.77	11.30	10.30
Na ₂ CO ₃	15.40	19.30	18.15	20.51	15.09	16.40
BaCO ₃	19.00	4.69	75.28
ZnO	6.95	18.25
H ₃ BO ₃	21.00	13.60
CaCO ₃	20.00	5.00
Al ₂ O ₃	2.07
As ₂ O ₃	0.60	0.60	1.00	0.40	0.74	0.61	0.72

Percentage Equivalents.

SiO ₂	47.94	43.80	71.56	70.04	52.72	48.85	41.68
PbO	42.38	38.12	35.03	50.52
K ₂ O	5.07	8.32	9.01	12.02	5.54	4.30	3.50
Na ₂ O	4.32	8.08	7.44	6.32	4.31	4.00
ZnO	3.05	8.91
BaO	6.47	2.61	28.57
B ₂ O ₃	8.30	3.75
CaO	8.02	1.92
Al ₂ O ₃	1.01
As ₂ O ₃	0.29	0.26	0.72	0.28	0.39	0.30	0.30

be used next was heated in another arch. An alternative device for pots which showed a tendency to split open was to pass a chain around them and fasten it.

Under some circumstances it may not be necessary to place the pot in a heated arch to anneal it; instead it is allowed to cool

(with proper protection) on the floor of the furnace-room. Again some glasses may be poured on a casting-table and rolled like plate glass. These matters will be discussed in other papers.

Batch Compositions for Various Types of Glass.

The tables accompanying the article by Zschimmer, previously referred to, contain much valuable information on the compositions of many optical glasses. From these alone it is possible to reproduce almost any optical glass that is made, or we may use them to produce modifications of given types by interpolating between two or more adjacent types. In connection with the work on optical glass that the Geophysical Laboratory has done a great deal of information on the variation of optical properties with composition has been acquired and will soon be published. Thus a quantity of valuable data for producing types of glass of required constants will be available. At the present time the Laboratory is restrained by agreement from publishing any batches which the various plants have themselves developed. This restriction does not apply to batches which the men of the Laboratory introduced, and those which are given herewith in Table 2 fall in this category. Previously given data on temperatures apply to these glasses specifically.

Concluding Remarks.

During the course of this article the writer has taken occasion frequently to emphasize the necessity of attention to details. It may seem that too much stress has been laid upon this and that such matters as following closely the temperature of each pot of glass demand too much skilled labor, and are, after all, unnecessary. This view would be a great mistake. It is surprisingly easy to spoil a pot of glass by a little lack of attention, and the value of one pot will cover a great deal in the matter of wages. In order to get good results in optical glass making it is not possible to conduct operations on a routine that does not take account of variations in conditions which are constantly occurring. One must, instead, treat the process as a laboratory operation carried out on a large scale, and must provide for attention to each pot individually as its requirements demand.

The making of optical glass belongs to a class of operations which American manufacturers have shown a tendency to avoid, apparently preferring to exercise their talents in the direction of turning out great quantities of materials in which each unit may be made to follow the same routine. Products of a more highly specialized kind, such as optical glass, have been obtained from abroad. It seems hardly necessary to emphasize here the lesson which has been taught as to the mistake of a national acceptance of such a policy. It may be well to point out, moreover, that recent events in several branches of industry have demonstrated that there is no lack in this country of men of the necessary scientific and technical equipment to take charge of manufacturing operations of this class and to see that they are properly carried out. It seems that in processes of this kind the same incentives should appeal to manufacturers as in making a good job of any other piece of work in which skill, training, and intelligence are required.

Not all the problems connected with the making of optical glass of a superior quality have been solved. There is still much need of research in order to throw light on certain steps of procedure and remove them from the category of rule-of-thumb operations, and to make more certain the elimination of defects and the production of material that will exactly meet requirements. Some of the subjects for study which may be suggested as promising are a fuller investigation of the function played by arsenic in glass melts and of the amount of volatilization of different ingredients under various conditions, the viscosity of glasses through the temperatures at which stirring is carried on, and the conditions governing the solution of gases in melts. It is to be hoped that some of the manufacturers will turn their attention to having such problems investigated. It is by the inauguration of an enlightened policy of this kind that we in this country may hope to keep in the van in the manufacture of such highly specialized products as optical glass.

CARNEGIE INSTITUTION OF WASHINGTON,
GEOPHYSICAL LABORATORY,
WASHINGTON, D. C.,
February, 1919.