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RESEARCH AND DEVELOPMENT OF
HIGH QUALITY LASER GLASS

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NUMBER 2

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Prepared by

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ABSTRACT

The use of Nd doped glass systems for high brightness or high intensity applications requires that the laser material must be free of metallic inclusions, of good optical quality, free of Fe^{2+} ion impurities which absorb strongly at 1.06 μm and in many cases must possess these properties over large volumes of glass. This report describes progress over the second six month period toward achieving this end. Laser glass durability studies are delineated. Model homogenization experiments were performed and results are presented. Finally, conclusions drawn from these studies are given.

FOREWORD

This report has been prepared under Contract No. N00014-68-C-0192 entitled "Platinum-free Laser Glass" under the direction of Head, Physics Branch, Office of Naval Research, Washington, D. C. by the Central Research Laboratory, American Optical Corporation, Southbridge, Massachusetts. The contract was received 1 March 1968, effective as of 1 September 1967.

The project scientist was Dr. Richard F. Woodcock and project engineer, Carl G. Silverberg. The research efforts are under the over-all cognizance of Dr. Elias Snitzer, Director of Basic Research.

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RESEARCH AND DEVELOPMENT OF HIGH QUALITY LASER GLASS

Semiannual Technical Report No. 2

Richard F. Woodcock

1. INTRODUCTION

The goal of this contract was to determine the feasibility of producing high optical quality laser glass in an all-ceramic melting system. Such a system should eliminate the presence of small platinum particles, found in the glasses melted in platinum crucibles, which serve as laser damage sites. The availability of high quality inclusion-free laser glass will enable further work to be done on damage threshold studies of laser materials.

Previous work in high purity all-ceramic melting systems indicated that the high purity crucibles used in this study were not a source of Fe^{2+} ion impurities which absorb strongly at 1.06 μm. The main problem at the present time is that of obtaining good optical quality glass in large volumes. The present contract has been devoted mainly to this problem.

The second generation of furnace design which was put into operation earlier in the year is operating well mechanically. The optical quality of glass produced from this furnace although much improved, was not as good as one would like from a production point of view. In order to examine the optical quality problem more thoroughly, a study of the stirring process was initiated. Studying this process in the actual melting system is not feasible because of the high temperatures involved and the fact that radiation from the melt tends to mask the phenomena being studied. For this reason a simulated melting system was set up in which the stirring action in cooled glycerin is studied as a function of stirrer design, viscosity of medium being stirred and stirring cycles.

During this period work was performed in two general areas: Namely, (1) studies with and improvements in the cooled glycerin system used for investigating stirring action in the "melt," and (2) analysis of damage sites produced in glass made from the all-ceramic melting system in an attempt to determine their origin.

2. LASER GLASS DURABILITY

Laser damage has been observed under conditions of high power densities in some laser rods fabricated from glass produced in the all-ceramic system. This occurence of damage is less frequent than for platinum melted glasses, i.e., about once per 1000 cm^3 in ceramic melted glass versus about once per 10 cm^3 in platinum melted glass. The fact that it occurs below the bulk damage threshold of the material and is localized in nature, however, suggests the existence of localized damage sites. Mechanisms considered as possible sources of damage sites include: (1) areas of local reduction (including complete reduction) which result in ions in valent states which are absorbing, (2) inclusions of impurities, such as high refractory materials, which remain as small particles in the glass, and (3) devitrification of the glass either in its manufacture or subsequent thermal treatment.

In order to investigate the possibilities of devitrification, samples of a standard laser glass were soaked for a long period of time in a temperature gradient furnace. No evidence of devitrification was found. Electron microscope examination of these samples indicates that some phase separation occurred in the sample which was held at 715°C but not in one held at 1090°C. This indicates that the immiscibility phase boundary lies at some temperature between these two values. This temperature region lies above the Littleton softening point of the glass but below the temperature at which the glass is melted and cast. The glass would normally spend very little time in this temperature region. Phase separation per se should not serve as a damage site. It is, however, closely linked to crystal formation and is considered by some to be a necessary although not sufficient condition for crystallization. Taking these factors into consideration, it is not felt that devitrification is a major source of damage in these glasses.

There is one type of damage that might be explained by this mechanism, namely, a fatigue phenomenon whereby a piece of glass will survive tens of laser shots without damage but will fail catastrophically on a subsequent shot with an inclusion-type damage pattern. It is conceivable that progressive localized devitrification can occur or that incompletely dissolved foreign matter can grow due to the heat generated on successive laser shots until the aggregate is large enough to create a fracture center. It was felt that the effort necessary to establish the role of devitrification in the fatigue phenomena was beyond the scope of this contract, and the subject was not pursued further.

In order to investigate proposed mechanisms (1) and (2) above, the whole manufacturing process was analyzed for possible sources of contamination. A few controlled experiments were performed to further investigate some of the suspect sources of contamination. In addition, an attempt was made to analyze some of the damaged areas in the glass. The latter were performed by spectrographic and electron probe techniques by outside concerns.

One possible source of local reduction in the melt is the globar heating elements which could serve as a source of silicon carbide particles. Experimental melts showed that when silicon carbide particles were deliberately added to the melt, local reduction took place resulting in dark spots in the glass. These areas appeared to be phase separated when examined with an electron microscope. To reduce this potential source of contamination, the top row of heating elements was removed from the furnace. This required an increase in insulation in the top of the furnace to compensate for the decrease in heat source.

Another possible source of local reduction arises from the fact that the raw glass ingredients come in contact with a variety of plastic materials during the manufacturing process. It was reasoned that small pieces of plastic could serve as carbon-rich regions in the glass which would result in local reduction of the glass ingredients. Experimental glass melts to which pieces of various plastics were added indicate that the carbon content of the plastics appears to burn off completely and that this is not a potential source of damage by mechanism (1) above.

One source of inclusions in the glass is the high refractory material from which the crucible and the furnaces are made. These materials tend to act more as scattering agents than absorbing agents and thus are not as deleterious as an absorbing particle would be. They do serve as damage sites, however, when power densities are high enough. Changes in the design of the roof of the new furnaces to a cast monolithic piece of alumina have appreciably reduced the possibility of getting ceramic particles into the melt.

The examination of damage sites and/or damage areas which have been resealed by heating has been initiated using electron microprobe and laser probe-equipped spectrometer techniques as well as conventional microscope observation and wet chemistry analysis. Samples are prepared by grinding and polishing down to the plane containing the damage site. Although sample preparation is quite time consuming and the location of the plane containing the damage site is not always successful, particularly on resealed samples, this has been a fruitful method of determining the source of damage.

On one occasion in which the resealed damage area showed no visible inclusion, the spectrometer data indicated an aluminum rich area with enhanced amounts of copper, magnesium and iron. This suggested the possibility of contamination by a particle of aluminum alloy in the melt. Aluminum had been considered a safe material to use since it forms an oxide easily and the glass composition contains Al_2O_3 as one of its constituents. It now appears that particles of the metal do oxidize but form a small volume of highly viscous material which does not disperse in the rest of the glass. The alloys are particularly bad because of the above elements used in alloying such as copper and iron which are highly absorbing at 1.06 μm. Among the steps being taken to eliminate aluminum contamination from the system is the construction of a new all-ceramic feeder to load glass batch into the furnace.

3. HOMOGENEITY STUDIES

In order to study the problem of glass homogeneization in the all-ceramic system a full scale analogue of the stirring system was set up using cooled glycerin to stimulate the behavior of molten glass.* The glycerin contains phenolphthalein and thus may be turned red by the addition of a basic solution of glycerin plus sodium hydroxide and subsequently made colorless again by

*Research and Development of High Quality Laser Glass Semi-annual Technical Report No. 1, Contract No. N00014-68-C-0192, American Optical Corporation, January 1969.

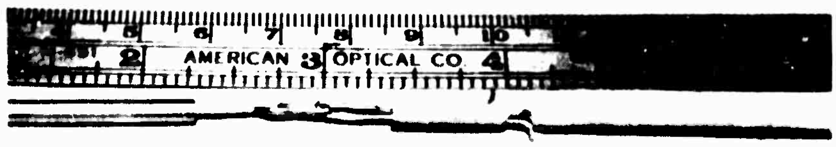
the addition of an acidic solution of glycerin plus boric acid. Stirring act on is visualized by the addition of the basic solution to .e colorless glycerin while the latter is being stirred in a transparent container or by adding the acidic solution to glycerin colored uniformly red by the previous reaction. This system was of great aid in studying the effectiveness of various stirrer designs and establishing stirring cycles.

3.1 VISCOSITY MEASUREMENTS

Problems with glass homogeneity were encountered when changes were made in the composition of the glass being melted. This indicated that more accurate data was needed for the relationship between temperature and viscosity in the molten glass temperature range in order to set up proper stirring cycles. High accuracy is needed in the determination of the temperature of the glycerin bath because the viscosity range of 10^2 to 10^4 poises, which corresponds to a temperature range of about 1000°C to 1500°C in molten glass, represents a temperature difference of only 30°C in the cooled glycerin bath. For this reason temperature controls of the glycerin bath were improved to provide an accuracy of 0.01°C.

To establish an accurate relationship between temperature and viscosity for both glass and cooled glycerin over the viscosity range of interest, requires a viscometer capable of reading viscosities down to 10-100 poises in the temperature range from 1000° to 1400°C. Since a high temperature viscometer of this nature was not available a commercial Brookfield instrument was adapted for this purpose. This was accomplished by the construction of a new spindle made from platinum as shown in Fig. 1. This spindle was calibrated using viscosity standards in the 300 to 1000 poise range. The latter were also measured with the standard spindles from the Brookfield Instrument for comparison. The apparatus used in the determination of the viscosity of glass at high temperature is shown schematically in Fig. 2.

Accurate temperature-viscosity curves of each of the glasses to be melted in the all-ceramic system will be determined using this equipment. With this data and the temperature vs viscosity curves of glycerin it is now possible to translate the information obtained in the cooled glycerin bath to a temperature stirring cycle to be used in the actual glass furnace.



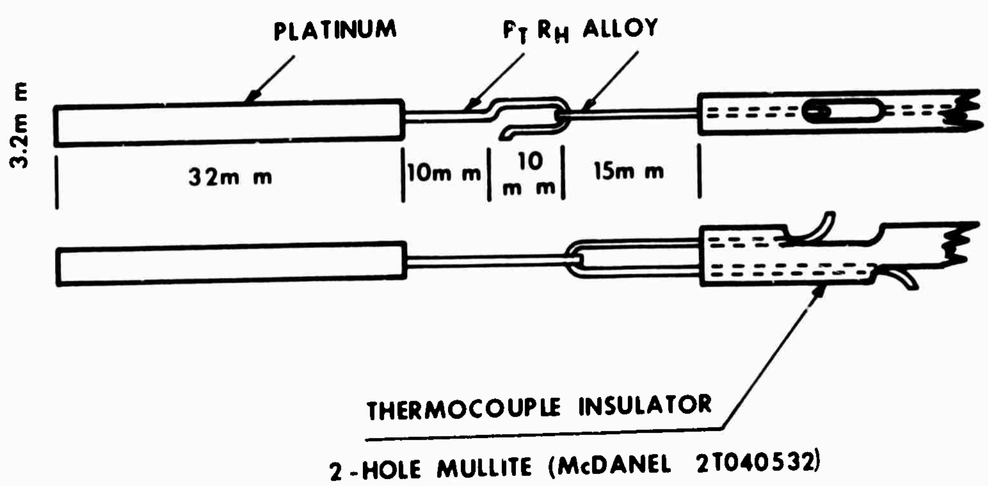


Figure 1. Platinum spindle for high temperature Viscometer.

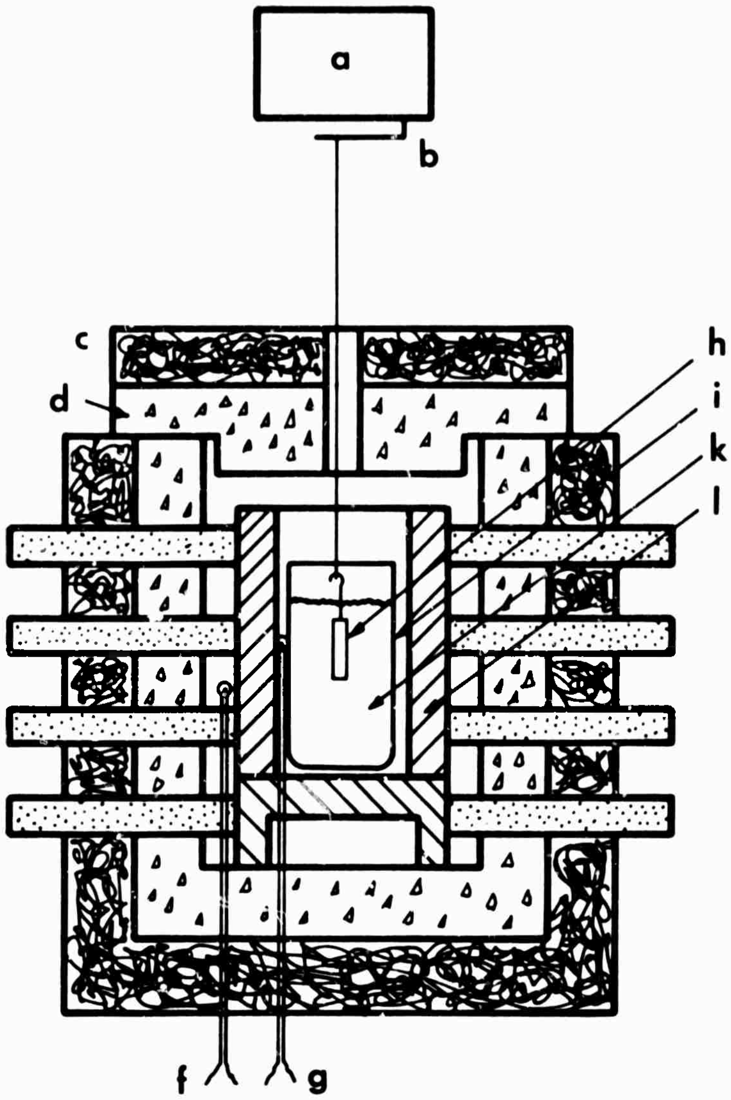


Figure 2. High temperature viscometer. (a) constant speed motor, (b) torque register, (c) ceramic fiber board, (d) K28 brick, (e) silicon carbide heaters, (f) thermocouple for furnace control, (g) thermocouple for glass temperature, (h) platinum spindle, (i) platinum crucible, (k) molten glass and (l) alumina sleeve.

3.2 IMPROVEMENTS IN GLYCERIN APPARATUS

Homogenization studies using the cooled glycerin apparatus during this period pointed out several shortcomings in the apparatus itself which stem primarily from insufficient thermal insulation of the freezer cabinet. Heat generated by the stirring motors made it impossible to maintain viscosities of 10^3 to 10^4 poises for stirring cycles up to forty-eight hours duration. Present results indicate that this is the direction which should be taken for improved stirring. This problem is accentuated in general by the fact that a large size window is required in one side of the freezer cabinet in order to observe stirring action taking place in the glycerin. Moisture condensing on the windows made it difficult to observe the stirring action in the glycerin and, in addition, some moisture was getting inside the cabinet where it was absorbed by the glycerin thus changing its viscosity. For these reasons, it was felt that some rebuilding on the freezer cabinet was required, and a time extension of the contract was requested and received for this purpose. Work in this direction is now in progress which should alleviate the above problems.

3.3 RESULTS

Typical results obtained with the equipment prior to its redesign are shown in Fig. 3. These experiments were carried out at a glycerin viscosity of 15 to 25 poises. The stirring rod is turning in a counterclockwise direction and the coloring solution is added at the top of a clear "melt." In Figs. 3b, 3c, 3d and 3e, one sees that the initial stirring action is one of wrapping a corkscrew of stria around the stirring rod. In Fig. 3e, this is still visible around the stirring rod although coloration in the rest of the melt is starting to obscure the action at the stirring rod. In Fig. 3f, the coloration of the rest of the melt completely masks any stirring action or lack thereof occurring at the stirring rod. For this reason the technique of adding a clearing agent to a "melt" which had previously been uniformly colored was adopted. As indicated by the clock, the first five pictures represent the initial twenty minutes of stirring in this experiment. The final picture was taken about two hours after the stirring experiment had been started.

While an experiment of the type shown in Fig. 3 is very useful in studying the type of stirring action which occurs, it does not show up dead zones which may exist in the stirring

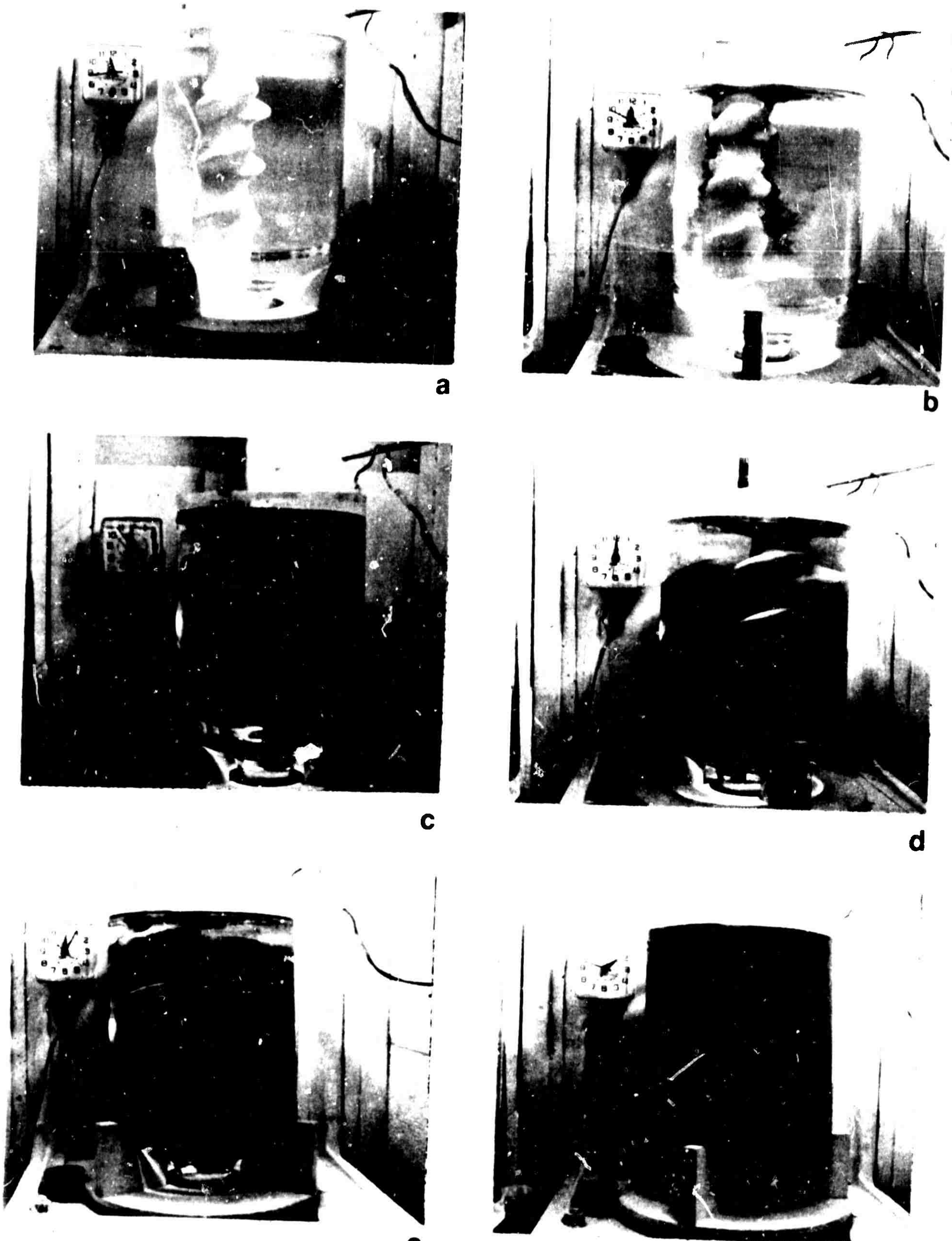


Figure 3. Stirring action with 3-tiered stirrer.

process. In order to show this, one starts with a uniformly colored solution and adds a clearing agent to the top of the "melt." An experiment of this type, shown in Fig. 4, was carried out under the same conditions of viscosity and stirring as were used in Fig. 3. As may be seen in Fig. 4b, stirring action is complete enough after fifty minutes to make the stirring rod visible although some stria is still present in the glycerin. At the end of one hour and twenty minutes of stirring, the main body of the glycerin appears to be fairly free of stria. On the lower portion of the stirring rod, however, there is still a thin layer of uncleared glycerin next to the stirring rod. This is most noticeable near the bottom of the stirring rod at the junction between the straight cylindrical portion and the spherical bottom. This ring at the bottom of the stirrer is still noticeable after three hours of stirring. The final photograph after ten hours of stirring shows the glycerin to be completely clear.

An unexpected observation made with the cooled glycerin unit is that material from the top of the orifice tube is continuously drawn up into the crucible in the form of a thread-like stria which wraps around the stirring rod where it appears to remain without further homogenization. Action of this type is shown in Fig. 5. This could account for the striae observed in the cast billets of laser glass which were found to correlate with the position of the stirring rod during casting, and therefore, were assumed to be coming from the stirring rod itself. Further investigation of this effect and methods of preventing it will be attempted when the freezer cabinet has been rebuilt.

Improving the insulating properties of the cabinet should make it possible to investigate stirring cycles at higher viscosities and for longer periods of time. Present indications are that better stirring action occurs as the viscosity is increased. This has the added advantage that the lower temperatures used to get higher viscosities will also result in less crucible attack by the molten glass.

3.4 FURNACE FACILITIES

Because of the better quality of the glass produced in the new all-ceramic furnace (No. 14) compared with the old furnace (No, 12), furnace was shut down and dismantled and a new furnace, to be designated No. 15, is being constructed.

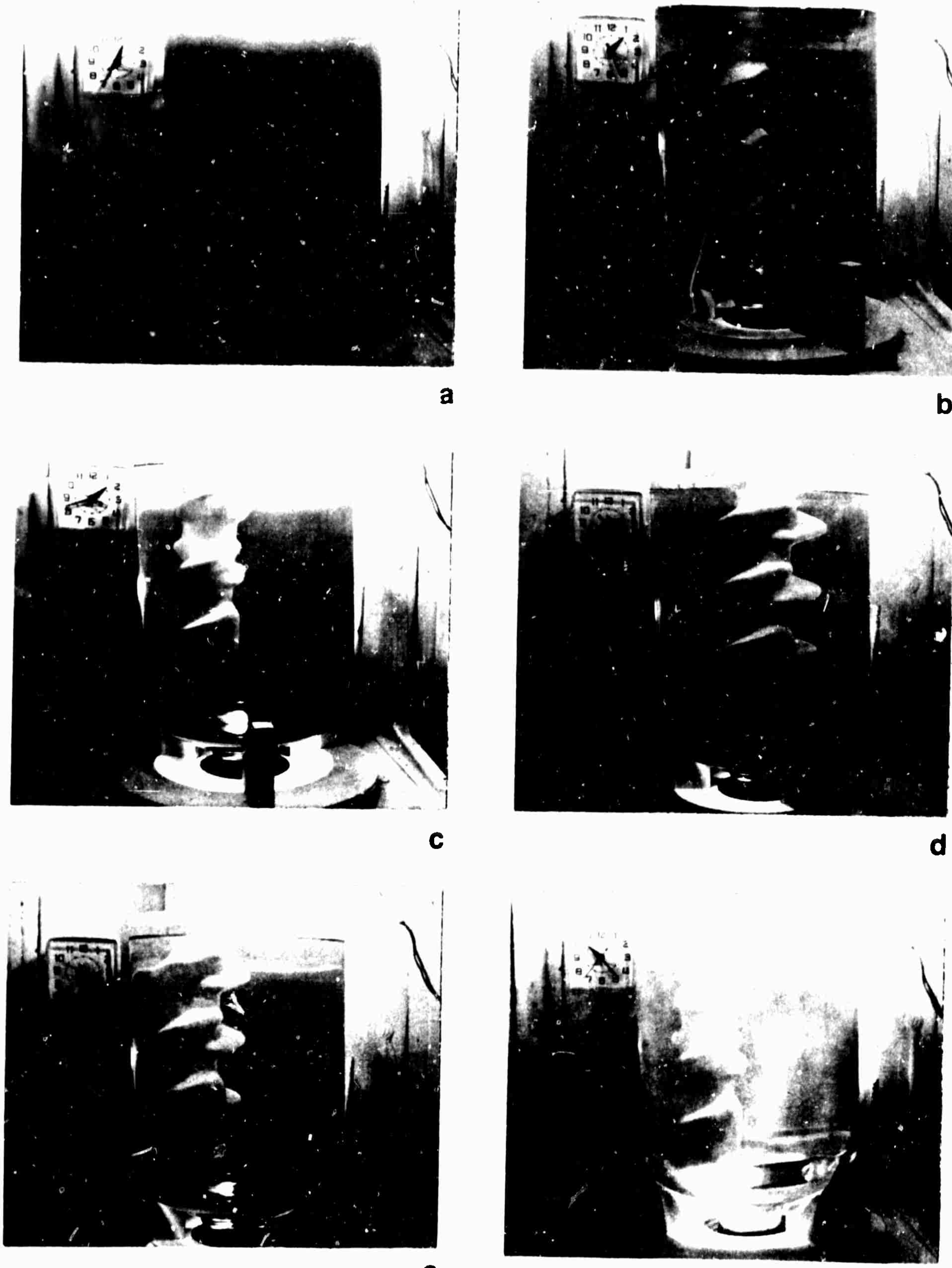


Figure 4. Dead zones with 3-tiered stirrer.

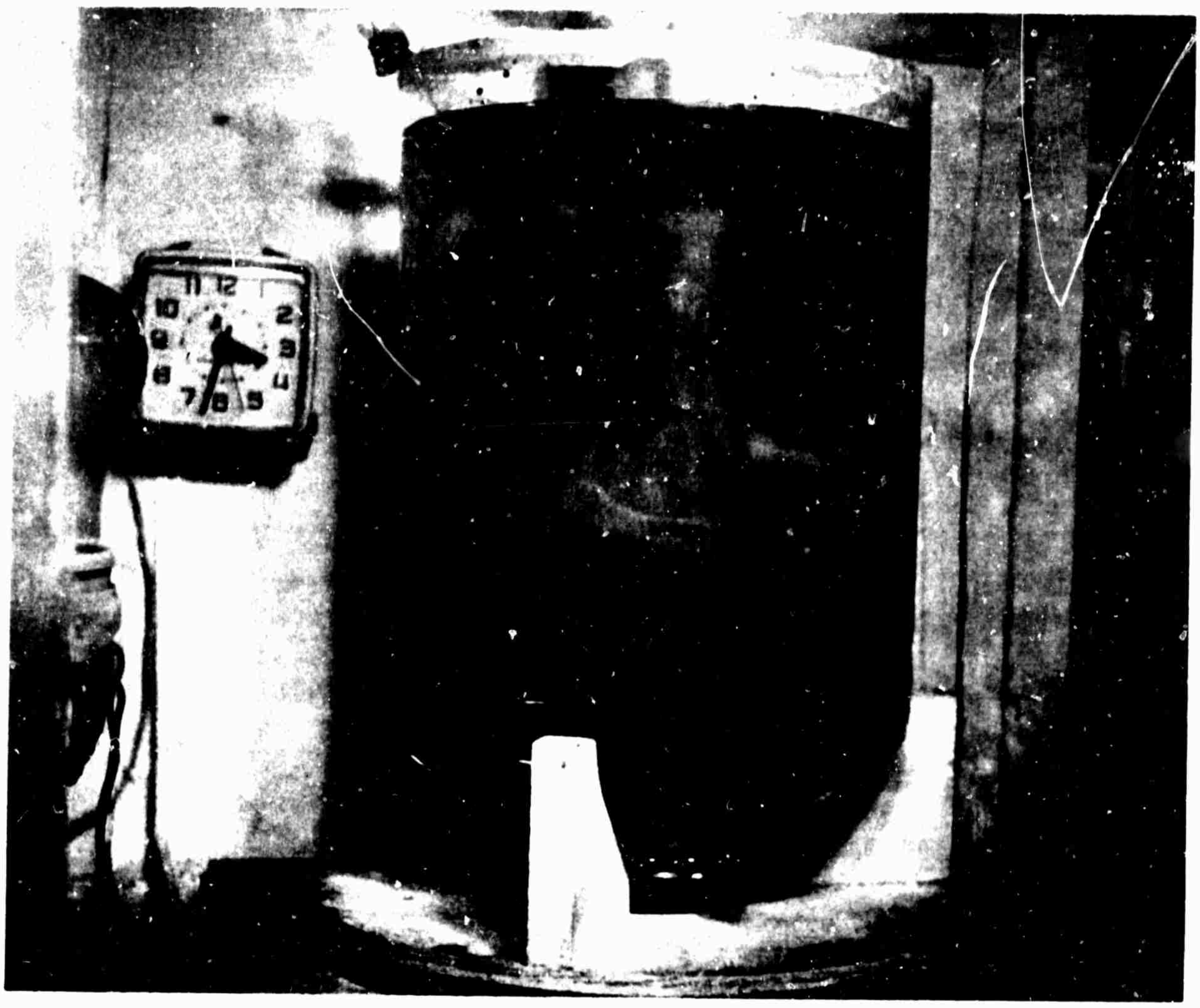


Figure 5. Stria generated at the top of the orifice tube.

This is similar in design to No. 14 and will be located adjacent to No. 14. Number 12 furnace was originally constructed under an ONR supported contract and was kept as a production facility when the first furnace of improved design (No. 14) was constructed as an experimental furnace. The operation of No. 12 as a production unit and the construction of No. 15 to replace No. 12 as a production unit were carried out under company funding.

4. CONCLUSIONS

The technique of analyzing the chemical content of sites where damage has occured has proven to be a useful method of determining the source of the damage. More samples are being prepared from damage tested glass to continue this work.

The original all-ceramic furnace (No. 12) was retired from service because the optical quality of the glass produced by it was not as good as the new furnace and because its design and physical location were not conducive to contamination-free melts.

Stirring experiments performed in cooled glycerin have been used to evaluate the effectiveness of different stirrer designs in the viscosity range up to about 10^3 poises for periods of a few hours. Results indicate that "pick-up" from the top of the orifice tube of the crucible may be a source of stria. There are also indications that further work should be done at higher viscosities for longer periods of time if optimum stirring conditions are to be attained. Changes in the cooling cabinet are now in progress to make this possible. When this is complete, further evaluation of stirring rod designs should be performed.

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13. ABSTRACT

The use of Nd doped glass systems for high brightness or high intensity applications requires that the laser material must be free of metallic inclusions, of good optical quality, free of Fe^{2+} ion impurities which absorb strongly at 1.06 μm and in many cases must possess these properties over large volumes of glass. This report describes progress over the second six month period toward achieving this end. Laser glass durability studies are delineated. Model homogenization experiments were performed and results are presented. Finally, conclusions drawn from these studies are given.

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