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ROCHESTER INSTITUTE OF TECHNOLOGY

A Thesis Submitted to the Faculty of

The College of Fine and Applied Arts

in Candidacy for the Degree of

MASTER OF FINE ARTS

RESEARCH INTO LEAD GLASS

By

S. LEON APPLEBAUM

APRIL 1981

APPROVALS

Advisor: Andrew Magclay

Date: 5/19/81

Associate Advisor: D.W. Dickinson

Date: 5/19/81

Associate Advisor: ______

Date: ______

Graduate Academic Council Representative: Fred Meyer

Date: 5/21/81

Dean, College of Fine & Applied Arts: Robert Johnston PhD.

Date: 5/24/1981

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Date: May 12, 1981

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PREFACE

The purpose of this project was to make a lead glass best suited to my work - a glass that melts rapidly, becomes free of bubbles, has extensive color range, and is durable.

INTRODUCTION

Lead oxide first appeared about 550 B.C. in early Chinese glass. The modern employment of lead oxide in glass was contained in English "flint" or lead crystal of the 1670's and 1680's. Early interest was centered in the lowered fusion temperature and increased brilliance of the resulting glass. As more became known about the properties of glass, an ever expanding list of desirable characteristics was attributed to the use of lead oxide in glass. Still, the most apparent property was the easily noticed brilliance caused by a high index of refraction.

The properties of low fusion range, wide softening and working range, resistance to devitrification, adaptable coefficient of expansion, good durability, and freedom from unwanted tints in color are in lead glass.

I. PRE-TEST

Before experimenting with lead glass systems, it was determined that a specially constructed furnace, made to give excellent thermal efficiency, would be of great importance for the correct control of the furnace atmosphere.

Since lead burns off readily when in direct contact with the flame and also has a great tendency to reduce, it is necessary to control the atmosphere as much as possible. A neutral atmosphere is a must for melting lead glass. This is difficult to obtain using the Rochester Institute of Technology furnaces. Also, the ventilation is inadequate: no flues exist to remove harmful gases. For the above reason it was important to construct a pot furnace to suit the writer's needs.

In melting lead glass, the furnace performs an absolute and important part. A pot furnace was designed and constructed to melt the lead glass. The furnace has an oval-shaped interior which contains five test crucibles.

There were several criteria which this furnace had to meet. The guidelines were as follows: economy of operation, durability of furnace, adequate exhaust, and easy-to-replace crucibles.

Economy of fuel was a main consideration. The use of less fuel depends upon the construction of the furnace and the amount

of insulation used.

The durability of the furnace depends upon the stability of materials and construction. The interior of the pot furnace is exposed to a high degree of corrosion from the gaseous melts, especially in the furnace top.

Furnace Description

The furnace was built on an angle iron stand, forty-six inches by thirty-six inches, with a one-half inch sheet of transite between the stand and the first layer of castable. This stand was built to hold a weight of approximately 2,000 pounds.

The furnace bottom has two different layers. The first layer (exterior) was five inches of 2800° insulating castable followed by two inches of mono-T9 raming mix.

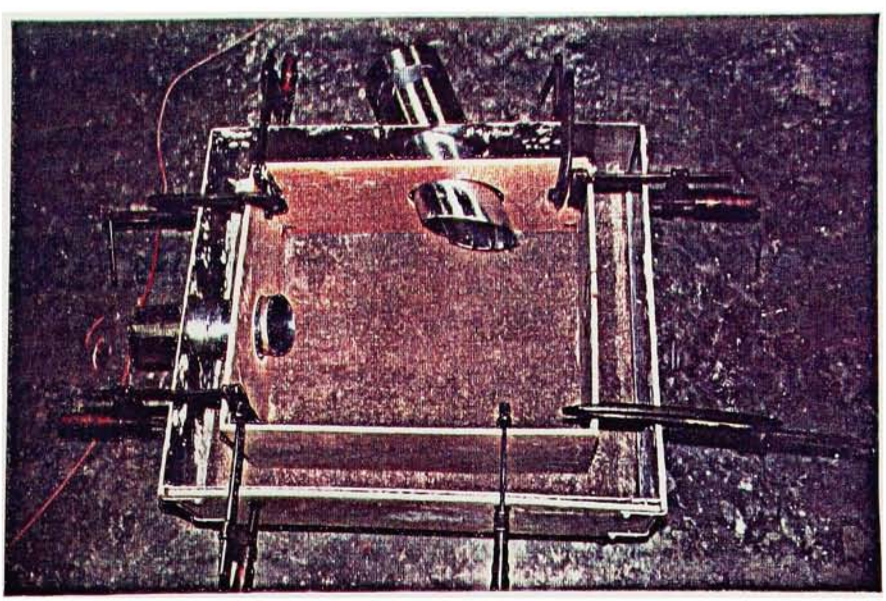
The furnace interior walls were made from four inches of 2800° insulating castable, and the outside walls were three inches of 1600° insulating castable. The arch-shaped door was made from 3100° castable.

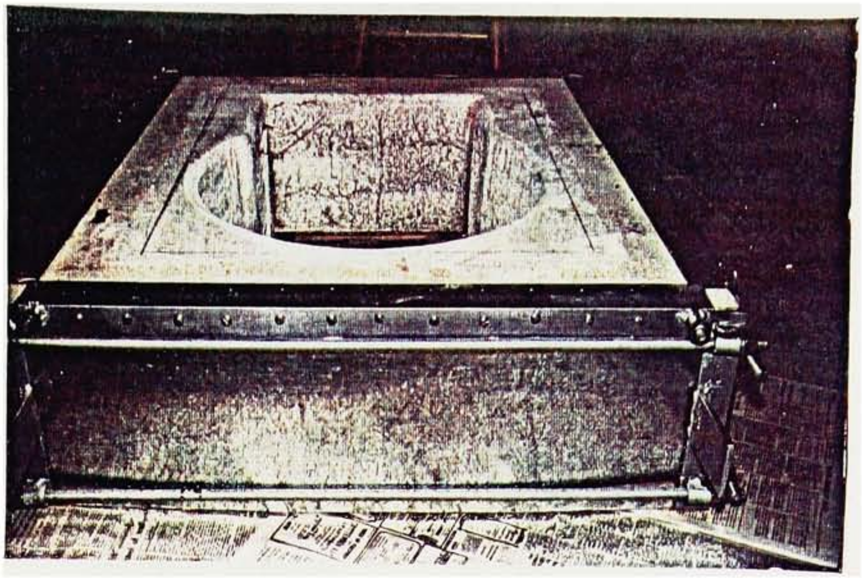
The upper half of the furnace was constructed so that it could be taken apart from the bottom. This was to insure mobility because the furnace had to be transported from the construction site at Rochester Institute of Technology to its home in Naples, New York.

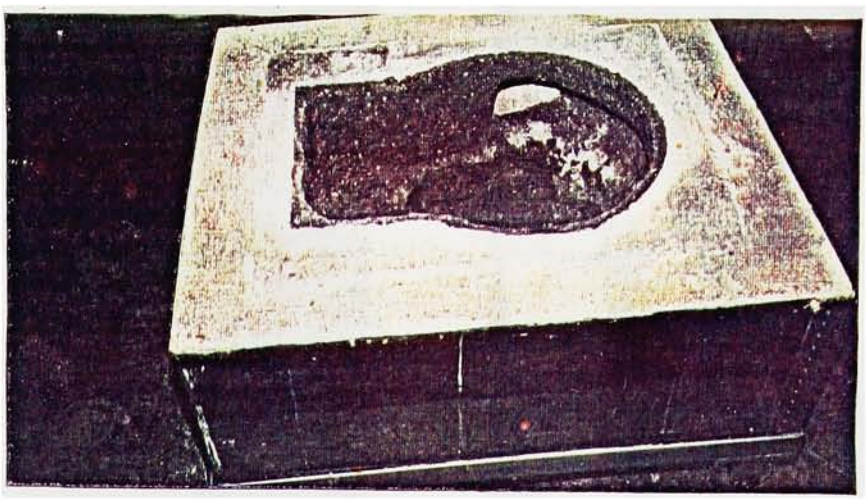
The burner system for this furnace is a B1½ venture type burner by Randsom Burner Company. The orifice size was number

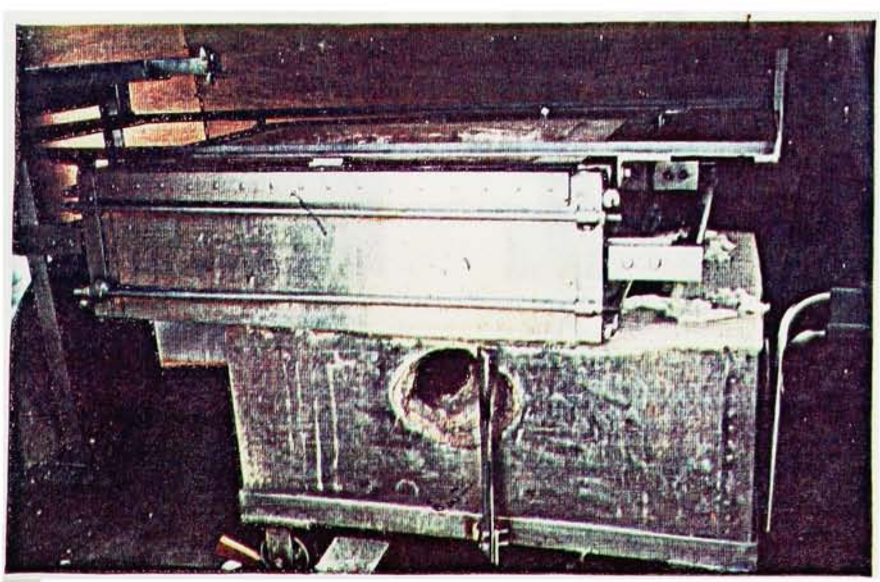
sixty-two. The burner was positioned in the back of the furnace coming in clockwise on a forty-five degree angle. The entire structure was encased in a galvanized metal shell.

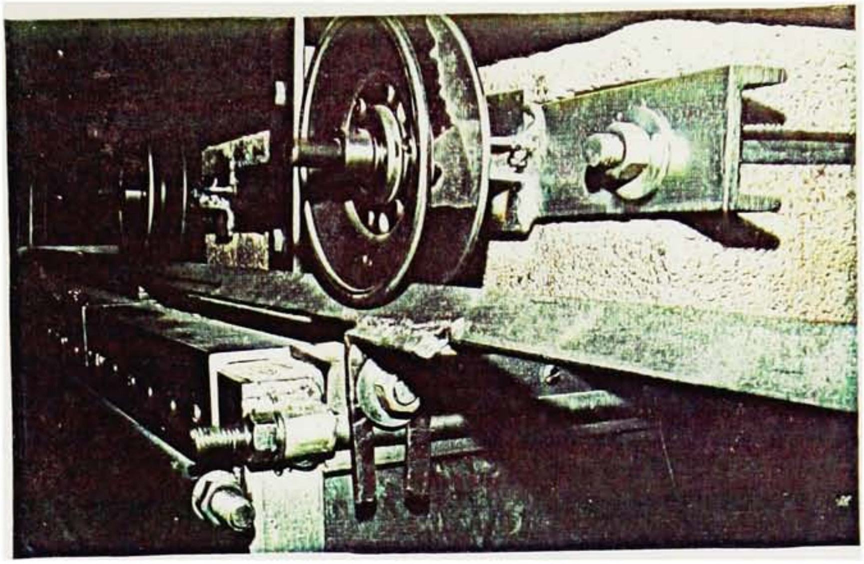
Photographs of Furnace Construction

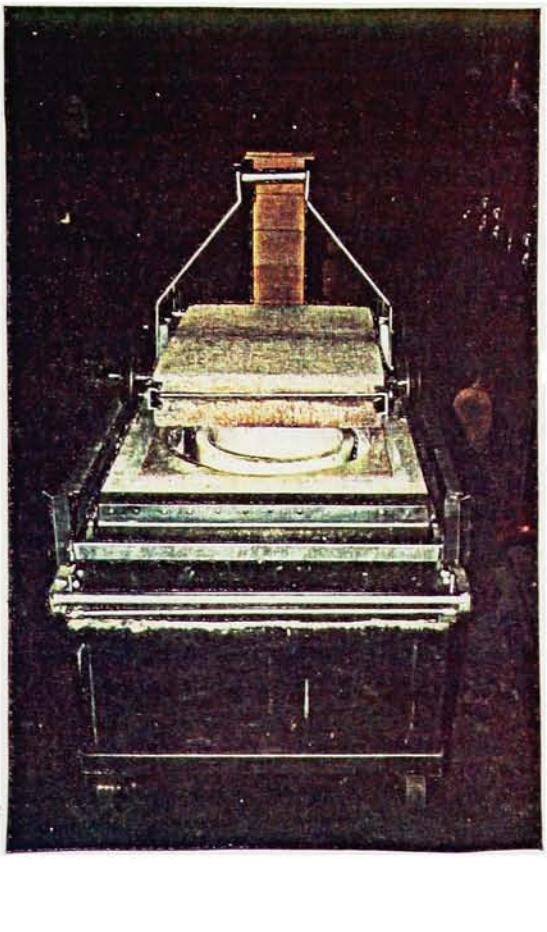


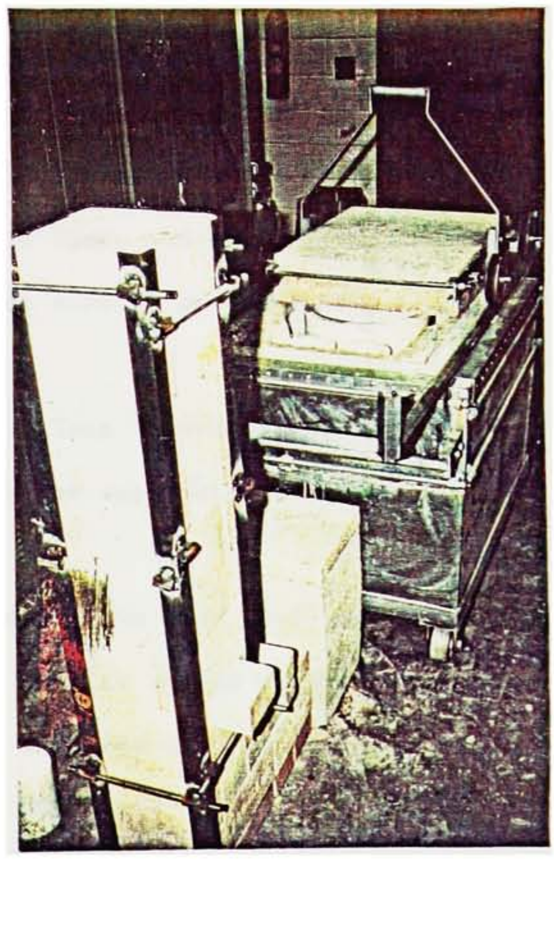












II. BASE GLASS

Lead oxide can be added to glasses in virtually any quantity up to ninety percent without contributing properties other than those desired. Lead oxide is a very powerful flux in itself, but too expensive for the ordinary fluxing of silicates. From an economic standpoint it then becomes necessary to employ secondary fluxing ingredients such as alkaline earth oxides. For lead glass systems it is the practice to use potash instead of soda as the main alkaline. Potash glasses are more brilliant, more resistant to water attack, have a lower coefficient of expansion, lower fluidity, and greater scratch hardness than comparable soda glasses.

This research is concerned with glass in which lead is the primary fluxing ingredient and potash the secondary fluxing ingredient.

A great number of papers and books have been published concerning the use of lead in glass. Pellot in his Curiosities of Glassmaking recommends the following for good lead glass:

Sand	300 parts
Potash	100 parts
Lead	200 parts
Sodium Nitrate	14 to 28 parts

Giller and Bunting of the National Bureau of Standards studied the system of silica-lead-potash (SiO_2 - PbO - K_2O) from

a phase equilibrium standpoint. Among other things, they determined the area of stability for lead glasses. The area of compositions resulting in clear stable glasses as being bounded by a line extending from 30 percent K_2O, 70% SiO_2 to 90 percent PbO, 10% SiO_2 on the SiO_2 - PbO - K_2 triaxial. In addition, they determined the refractive index of lead glass. The refractive index increases with increasing lead content and to a lesser extent with increasing potash content.[1] The first attempts at limiting the glass composition for the writer's work was based on their data.

Peddle also investigated lead glasses. He found that glasses with more than 65% by weight of sand (SiO_2) tended to devitrify by crystallization, but even with the highest proportions of lead there was no crystallization. Increasing the potash content of the glasses decreased the durability to water attack, but not as much as soda (Na_2O). He found that the addition of lead increased the density of the glass, and that the role of density increase was greater with lower percentages of potash in the glass. A similar tendency was noted for the index of refraction. As a rule, the greater the amount of lead in the glass, the lesser the effect of potash addition.

The durability of these glasses was increased by the addition of more lead or sand. The most durable, least devitrificable compositions were found to be those with:

Potash (K_2O)	20 molecules
Lead (PbO)	30-40 molecules
Sand (SiO_2)	100 molecules[2]

Preston and Turner studied the effect of alkaline additions and of substitutions of borax and calcium for lead in glass. In general, glasses containing soda devitrified at a lower temperature than those containing potash; "the colorlessness and brilliance of the substituted glass up to $6Na_2O$ $6K_2O$ were comparable with the full potash glass, but there was a noticeable deterioration when the soda content was increased beyond eight percent." They did find, on the other hand, that substitution of borax and calcium for some of the lead resulted in better melting.[3] This study led the writer to believe that the addition of borax and calcium (dolomite) might be helpful in attaining good results.

Lewis studied the devitrification of various lead glasses in a gradient furnace. The glasses contained 54-78 percent sand, 8-20 percent lead, 2-10 percent calcium, 6-16 percent soda, and 0-69 percent potash. He concluded that glasses containing sixteen percent of total alkaline and more than eight percent lead in general have liquidus temperatures sufficiently low that can be used for the production of crystal glassware.[4]

Lead oxide is known to be volatile during the melt. Anderson found that the volatilization in fifteen minutes from an unstirred glass melt was about the same as from a stirred glass melt heated for a longer period. The rate of volatilization of the unstirred glass is greater than the stirred glass because a layer of lower lead concentration forms on the surface of the melt, and lead from

below has to diffuse through it before it can escape. Anderson also reported that volatilization does not affect the refractive index of the resulting glasses if the procedure of melting is kept reasonably constant.[5]

Hallase and Cook provided a more recent study of volatilization of lead oxide from glass. They demonstrated that volatilization may be reduced by as much as eighty percent when lead oxide is replaced by the monosilicate of lead, and by ninety-five percent if the bisilicate is used.[6] The writer chose bisilicate of lead for this research.

Thermal Expansion

English and Turner evaluated a series of factors from which the thermal expansion of a glass may be predicted.[7] But it is only approximate. Since the knowledge of glass structure is still very limited, this method is the best way of approximating the coefficient. The more complex the glass chemistry, the less accurate the coefficient calculated by means of these factors.

This thesis will not attempt to explore thermal expansion in depth. The expansions were calculated and an approximation was determined. This is important because when different glasses are combined, the glasses must expand and contract at the same rate or cracking will occur when cooling. The writer calculated the test glass to have an expansion of +85. This is the expansion range of Klaus Kugler color bars.

III. INTRODUCTION TO TEST

Different proportionate quantities were tested in a series of experiments to determine a good base lead glass.

The batches were melted in open kyonite crucibles, heated indirectly by propane. Each crucible held about 1000 grams. Temperatures ranged between 1950°F and 2600°F. A stainless steel stirrer was made so that the glass could be stirred during the melting process.

The temperature of the furnace during the melts was measured quantitatively. The temperature can be judged from the color of the inside of the furnace and the gas pressure gauge.

The melting procedures were as follows: the batch, after being mixed and stored in a lidded plastic container is charged (placed) in the crucible and melted. A second portion is added after the first charge has melted. Generally, two such refillings were sufficient and were introduced at about thirty minute intervals. It is important to allow the first filling time to reach a state of fluidity before introducing any additional raw materials. This avoids interference with the previous filling, allows the gases to escape, and facilitates fusion of the additional fillings.

Much depends upon the method of melting. The pot furnace was preheated to about 2600°F before charging. Preheating allows the immediate reduction in fusion time. This insures a good

combination of all materials tested. If the pots are cold the batch does not begin to melt until the pots get thoroughly heated because a batch is a very poor conductor of heat. If the temperature is sufficiently high, the fusion of the batch proceeds from the bottom up, from the sides inward, and to a small extent from the top downward.

As the fusion continues, moisture is evaporated, and gases and acids develop, leaving through the flue. These gases stir the melt and generate an agitation of the particles. The fluxes reduce the more refractory materials until the entire batch is fluid. If this is a continuous process, the glass will be homogenous and even-tempered.

After all the materials were charged and fluid, the next process, called fining, or purification, begins. The fining process consists of freeing the seeds and bubbles from the melt. During this period the temperature of the furnace, 2600°-2700°f, must be as high as possible so the glass may become very fluid. This process should not be too long as the glass can reboil and create new types of bubbles. If the temperature of the fining process is too low the bubbles and seeds cannot force their way out.

When the glass is entirely "fined out", it must be reduced from the fluid to the viscous state. The temperature of the furnace is lowered. This process has much bearing upon the results. By reducing the temperature gradually, the glass settles

and solidifies in a uniform way.

When the glass is cooled to about 1950°F, a punty rod is dipped into the melt and samples are pulled. As many samples as possible were pulled out of the melt.

With the above information and prudent judgement, the writer began experimenting.

PURPOSE

The purpose of the first test was to disclose the variations of sand, lead and potash in a series of glass batches in which the constituents have been varied. In this way the writer was able to learn the effects of substitutions in the batch.

The writer then varied the elementary sand-lead-potash batch by substituting borax for lead, soda ash for potash, sodium nitrate and arsenic for sand, and lithium for soda.

The information was then evaluated and studied. It is hoped that this investigation will lead to work which will permit the calculation of a batch which will be brilliant, have a low softening temperature, and consequently a long working range.

For this reason, it is important to have information on the effect of various substitutions on the softening temperature.

Procedure

The procedure which was used in this investigation is simple, and is best described by Paul Manners in Glass Art Magazine, "Custom-Made to Fit." In his article, Mr. Manners presents his method for the determination of the softening point of glasses. This served as the method for his thesis. "When the softening point is lowered, the optimum annealing temperature is lowered. When two glasses soften at the same temperature, they can be annealed at the same temperature. Pull out the straight rods of the glasses in question. Arrange them in the annealing oven so that they are fixed at one end and the other end sticks straight out. Bring the oven up to temperature slowly checking the rods every 10°F or so once you pass 800°F. Softening seems to take place all at once."[8]

IV. VARIATION OF LEAD-POTASH-SILICATE

The first test presented the properties of lead-potash-silicate glasses. The work is not intended to be quantitatively exact. The object has been to observe the effects variation in composition may produce.

The properties of silica are fairly well known. It contributes a very low expansion factor, but contributes greatly toward an increased viscosity at any given temperature.

The addition of potash to a glass causes lowering of the viscosity, but also increases the thermal expansion. In general potash adds fusion and brilliance.

Lead is a powerful flux and promotes fusion at a very low temperature. Lead adds brilliance and density. Lead also decreases the viscosity of the melt at all temperatures.

Table #1
Batch Compositions

Batch #	Silica	Lead	Potash
1	61%	34%	5%
2	58	32	10
3	55	30	15
4	50	30	20
5	48	40	12
6	55	40	5
7	55	35	10
8	55	25	20
9	55	20	25
10	55	15	30

Results from Test #1

1. As lead replaces sand the glass is softer and fuses faster.

2. As potash replaces silica, the expansion increases and the fusion is lowered. Glass becomes more workable and more soft.

3. However, as lead replaces potash (with silica being constant), very small changes in softness and workability occur.

The changes which take place with changes in composition are consistent and appear to act in a predictable manner.

From the test results, it seems that the fluxing action of lead and potash apparently change the viscosity and brilliancy of the glass as both are increased and sand decreases.

The decrease in viscosity caused by an increase in lead may make up the differency between the increase in viscosity caused by a decrease in potash.

Conclusion of Text #1

The melting of the glasses was easy when the lead content was high. The higher the concentration of silica, however, the harder it was to melt the batches.

The viscosity of the glass increased with increased silica content. Lead seemed to decrease the viscosity more than potash. These remarks on viscosity are purely qualitative and are based on observation of the behavior of the glasses.

V. TEST II. SUBSTITUTION OF BORAX FOR LEAD

The purpose of this test was to observe the addition of borax.

Table #2

Batch #	Sand	Lead	Potash	Borax
1	55%	30%	15%	%
2	55	25	15	5
3	55	20	15	10
4	55	15	15	15
5	55	10	15	20

Results of Test #2

1. In batches 1, 2, 3, and 4, the linear coefficient of expansion gradually decreases as borax replaces lead except in batch #5. Batch #5 begins to increase expansion.

2. As borax replaces lead, the glass becomes hard-to-work.

3. All batches seem to melt equally.

4.. It seems that the fluxing action of lead is almost identical with the fluxing action of borax and that the two compounds can be interchanged in small quantities without any apparent change in viscosity at a high temperature.

Conclusion of Test #2

Borax does seem to exhibit a continous contribution toward viscosity at high temperatures. An increase in borax will decrease the viscosity, but at lower temperatures a substitution of borax for lead caused an increase in viscosity.

VI. TEST III. SUBSTITUTION OF SODA FOR POTASH

The purpose of this test was to compart Batch #2, test #2 with a small addition of soda.

Table #3

Batch #	Sand	Lead	Potash	Borax	Soda
1	55%	25%	15%	5%	%
2	55	25	13	5	2
3	55	25	10	5	5
4	55	25	8	5	7
5	55	25	5	5	10

Results of Test #3

When soda ash was substituted for potash, the writer discovered that substitution results in a rising of the softening temperature. This rising, however, continued only up to the point where the potash content was eight percent. Therefore, it would appear that to obtain the lowest softening temperature, the substitution of soda ash for potash is only advisable up to the point where the soda ash is about two to five percent of the total alkaline content. Above that amount, the soda has the effect of lowering the viscosity and adding a bluish tint to the glass.

VII. TEST IV. ADDITION OF ARSENIC AND SODIUM NITRATE AS A FINING AGENT

The purpose of this test was to compare the diffusion rates of test #3, Batch #2 with no fining agent and with the addition of arsenic plus sodium nitrate.

Table #4

Batch #	Sand	Lead	Potash	Borax	Soda	Arsenic	Sodium Nitrate
1	55%	25%	13%	5%	2%	%	%
2	54	25	13	5	2	1	½
3	54	25	13	5	2	½	2
4	53	25	13	5	2	½	1½
5	52	25	13	5	2	½	2½

Results of Test #4

The addition of arsenic and sodium nitrate to this glass batch aids the fining process. No attempt was made to determine the amount of arsenic that yields the greatest rate of fining. A comparison of Batch #2 and Batches #4 and #5 indicates that the addition of sodium nitrate to a Batch containing arsenic results in a further increase in the rate of absorption of oxygen in glass fining. The reason for this increase is that the nitrate decomposes at a low temperature and forms an alkali arsenate which is less volatile than $A5_2 0_3$, and thus more of the arsenic is retained in the glass.

VIII. TEST V. ADDITION OF LITHIUM

It would appear that a small addition of lithium would greatly influence the melt. Lithium has a strong fluxing action and lowers the viscosity.

A sensible approach would be to consider the glass-forming characteristics of lithium.

Table #5

Batch #	Sand	Lead	Potash	Borax	Soda	Arsenic	Sodium Nitrate	Lithium
1	53%	25%	12%	5%	2%	½%	2%	1%
2	53	25	11	5	2	½	2	2
3	53	25	10	5	2	½	2	3
4	53	25	9	5	2	½	2	4
5	53	25	8	5	2	½	2	5

Results of Test #5

Lithium tends to lower the melting point and produce glasses that have low viscosities and high fluidities. Excessive lithium is quite likely to seriously attck the crucibles. Corrosion of the interior in crucible #5 was probably caused by the interaction of the crucible and the high percentage of lithium. This conclusion, however, was drawn from visual observation.

Conclusion of Test #5

It is the opinion of the writer that lithium should be placed in the batch.

IX. COLORS

When making colored glass one must determine color by experimentation, as no two glassblowers use precisely the same formulas or work under similar conditions. The effects are determined by such factors as materials, oxides, furnaces, fuels, and crucibles.

The writer has outlined in the preceding pages the test and results of colored melts using the base lead glass. Other colors may be produced by blending different colors, hues, and densities into new colors modified in tone and intensity. As an artist blends his pigments, so may a glassmaker blend his batches in the production of compound color.

Table #6

Violet

lead batch - 10 lbs
manganese - 30 grms
nickle - 2 grms

Green

lead batch - 10 lbs
copper - 40 grms
cobalt - ½ grms
Potassiumdichromate - 30 grms

Amber

lead batch - 10 lbs
red iron oxide - ½ oz
manganese - 1 oz

Yellow

lead batch - 10 lbs
uranium - 30 grms
boric acid - 15 grms

Black

lead batch - 10 lbs
copper oxide - 60 grms
iron oxide - 20 grms
manganese - 80 grms
cobalt - 2 grms

Blue

lead batch - 10 lbs
copper - 60 grms
cobalt - 4 grms

X. DIFFICULTIES WITH GLASS

The only immediate problem with the newly formulated glass was the appearance of cords. Cords are traceable to impure materials, improper proportions, bad mixing, or insufficient heat to properly melt or "fine" the glass.

The first remedy tried was to melt glass at a higher temperature and generate a violent agitation by stirring the molten mass with a potato. This did make a difference and fewer cords developed.

Next the writer added sodium chloride (table salt). This also helped eliminate the cord problem.

Corrosion of Crucibles

Corrosion of interior crucible walls caused by interaction of the crucible and its contained melts occurred in a number of instances. It was with the batches containing high percentages of lithium and lead that the corrosion took place. The more corrosive glasses were contaminated by their chemical action upon the crucibles.

Difficulties with Furnace

After operating the furnace for five days, there was a definite separation of the refractories used on the door. The mechanical separation of materials caused by poor design forced the writer to shut down the furnace and rebuild the door.

Difficulties were also experienced with the next door. The door was made from 2900° low iron castable. Chemical reaction from the melt was causing lumps and bleeding on the door bottom. The corrosive melts were chemically attacking the door causing fluxing of the refractories. Once again a new door was made. The next door was made from 3100° high alumina refractory and showed no signs of corrosion.

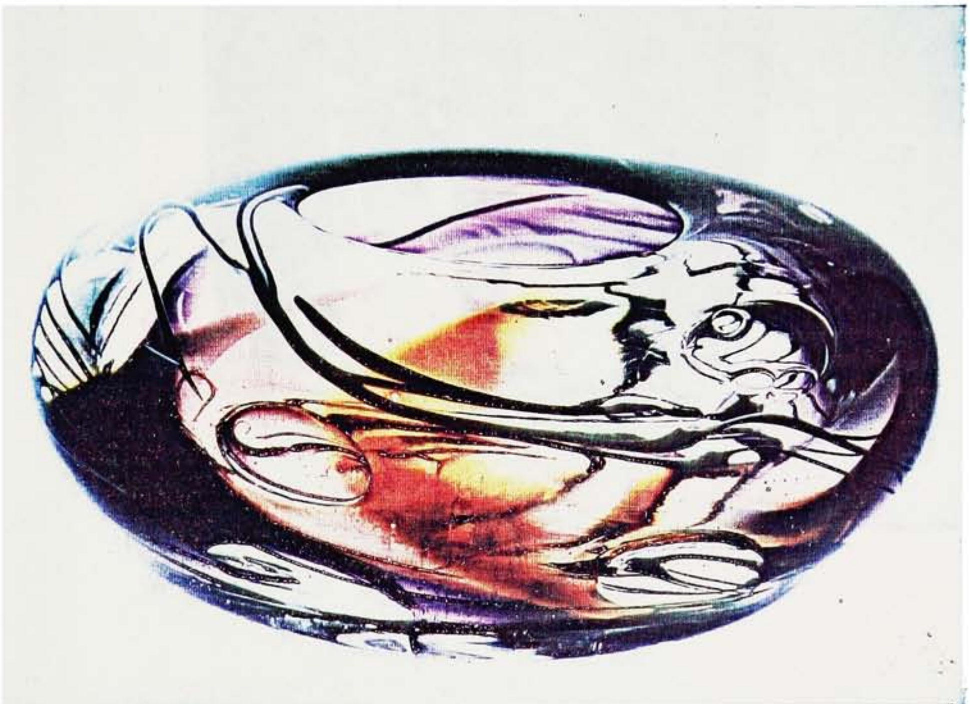
XI. CONCLUSION

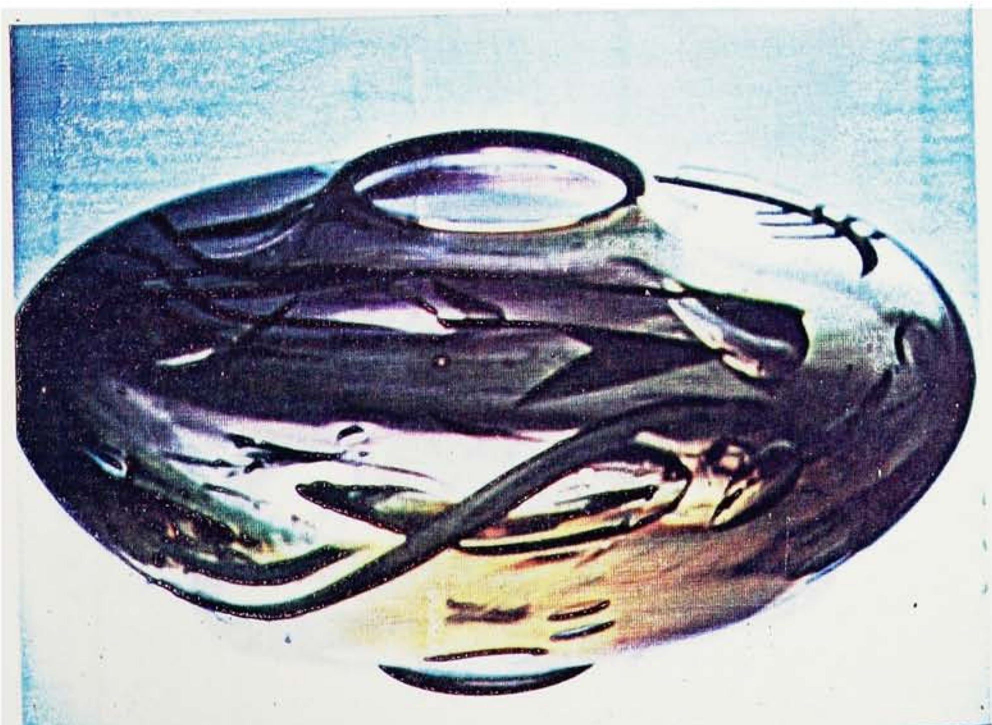
It was the writer's intention at the outset of his work to develop a glass that would have unusual brilliance and workability, melt at a low temperature, and be a good base glass for forming colors. The glass that was finally developed proved to be a good working glass, exceeding original expectations.

The formula for this glass is: sand 53%, lead 25%, potash 12%, borax 5%, soda 2%, arsenic ½%, sodium nitrate 2%, lithium 1%. From this newly formulated lead glass, sixteen pieces were made for the thesis show.

Throughout the project, the writer's intent was to explore and refine the intrinsic beauty of crystal glass. An overriding objective was to create glass that was visually rich, brilliant, and free of bubbles and cords. In this respect, the quality of the material was of crucial importance. This thesis has hopefully shown how such quality was achieved, and has provided useful information for those interested in working on projects of a similar nature.

Photographs of Blown Glass Made with Lead Base Formula





XII. FOOTNOTES

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