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PRELIMINARY STUDIES ON THE DEVELOPMENT OF BOROSILICATE GLASSES IN PAKISTAN

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Four borosilicate glass compositions containing B_2O_3 2.5–6.5% have been melted on laboratory as well as on pilot plant scale. It was observed that glasses containing B_2O_3 upto 5% were almost free of cords and seeds. With the exception of borax and boric acid, indigenous raw materials were used in these investigations. Thermal expansion co-efficients of these glasses varied between 70–60 x 10^{-7} per °C (20 - 300°C). Laboratory articles such as beakers, flasks, funnels, petridishes etc. have been fabricated and tested. Glass No. 3 containing 5.0% B_2O_3 has been found reasonably good to be used in schools and colleges.

Key words: Glass, Borosilicate, Technical glass.

Introduction

The modern laboratory glassware is essentially a borosilicate glass which is resistant to corrosive chemicals and has low co- efficient of thermal expansion and can withstand sudden changes of temperature. It has also good mechanical endurance. The early laboratory glasswares were prepared from lime based glasses, high in silica and lime with slightly lower alkali content, because such compositions were reasonably resistant to chemical attack [1]. Resistance to temperature changes was obtained by making the articles very thin.

This process, however, made the laboratory glassware too fragile, increasing the breakage during transportation and handling. The high mechanical strength laboratory glassware was manufactured for the first time by Sullivan and Taylor [2] in 1919 by replacing a part of soda with boric acid, in order to lower the alkali content, without producing drastic changes in the melting behaviour. Since then a number of laboratory glassware compositions containing varied contents of boric oxide have been developed and exploited on commercial scale [3].

The current yearly imports of scientific glassware in Pakistan is around Rs. 35.0 million and according to the projected demand, its import will increase with the potential expansion of education, industry and research centres [4]. The indigenous production of this glass is thus highly desirable, firstly to impart self-reliance to our chemical process industry and secondly to meet vital requirement of research and educational institutions.

Literature dealing with the actual manufacture of laboratory glassware of borosilicate type is very scare. Some studies done on the volatilization of alkali borate and borosilicate glasses are not of much use for the present work [5–8]. In view of this a reasearch scheme was made to suit our circumstances.

A few laboratory meltings were made in clay-grog crucibles in a small fired furnace. A sufficient quantity of batch to give 1 kg glass was melted. In the light of previous experience and keeping in view the iron content of sand, 0.064g Se and 0.0025 g Co per 1 kg sand were found suitable amount to decolourise the glass 3g AS_2O_3 per 1 kg sand was also used as refining agent. Almost same quantities of the minor ingredients were used in pilot plant meltings. Specimens were fabricated to study refining and quality of glass. Glass compositions and results of laboratory meltings are given in Table 7. In the light of above results four compositions after minor adjustments were selected for pilot plant trials Table 9.

After laboratory experiments a regenerative end-fired glass furnace to melt one ton of glass/24 hr. was designed and erected for pilot plant production. Imported AZS (Alumino Zircon Silica), sillaminite and silica refractories were used for the construction of furnace. With the exception of soda ash, borax and boric acid, indigenous raw materials were used in this work. The glass articles like beakers, flasks, petri dishes, funnels and desiccators were fabricated and their properties studied. The product was evaluated by the users and found satisfactory for general use in schools and colleges. Further work to improve the quality of the glass is in progress and encouraging results are expected.

Experimental

Designing of the Furnace

Furnace dimensions. The melting area of glass was taken as 15 ft^2/ton/24 hr. [9]. Assuming 60% breakage during fabrication, annealing cutting and printing, the effective area for melting one ton of finished glass was 24 ft^2/24 hr. The depth is limited by the requirements that glass workers be able to reach the glass with their gathering tools as it is worked out. Since the furnace is rectangular in shape and therefore, its dimension is taken 6' x 4' with 3 ft. as depth. The throat

dimension for this type of furnace is 6"x12" (Table 1). The furnace breast wall is 1.25 ft. The drawings of the furnace, tuck stone and skew back are given in Fig. 1–3 respectively.

Fuel requirements of the furnace. The holding heat/sq. ft. of the furnace area as calculated from the extra plotted graph of the furnace [9] is 720000 B.T.U./sq.ft. Other calculations and amount of natural gas are given in Table 2.

Checker free area and stack dimension. The checker-free area and stack dimensions calculated from the temperature gradients and flue requirements of the furnace are given in Table 3.

Refractory requirements. Due to the corrosive nature of the glass, sillaminite vacuum cast and alumino-zircon-silica (AZS) fused cast refracotries were used for the various parts of the frunace depending upon the severity of corrosion by glass. AZS refractories were used in the construction of side walls, breast walls, ports and crown of the working and melting end while bottom of the furnace and side walls of the working end were made from sillaminite blocks. The checkers attached to

TABLE 1.FURNACE DIMENSIONS.

1.	Area for melting one ton of glass/24 hours of the borosilicate glass 15 ft.
2*.	Assuming 60% loss due to breakage, cutting, annealing and printing, the effective area for melting one ton of glass would be 24 ft².
3.	Since the furnace is rectangular in shape, the dimensions are: Length 6 ft.; Breadth 4 ft.; Depth 3 ft. Size of throat for one ton 0.5'x1 output of glass/day.

* In practice breakage is normally 25 to 30%, therefore finished glass product would be one ton at least.

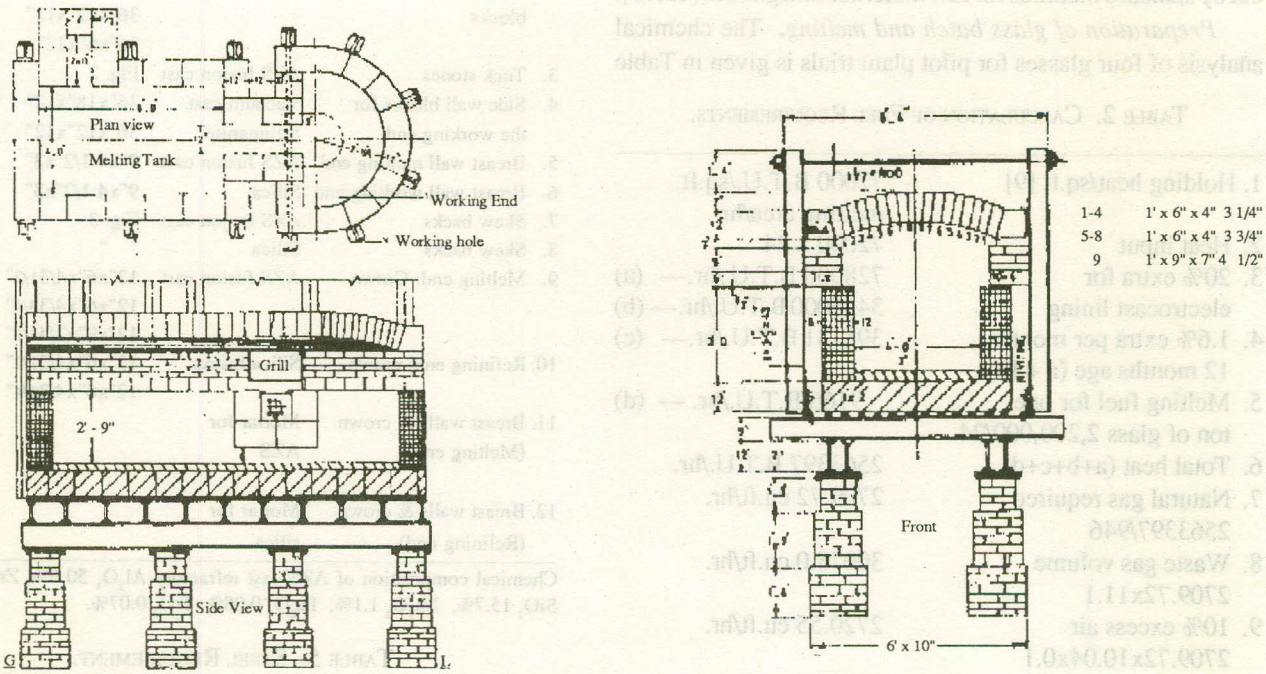

Fig. 1. Laboratory Glass ware furnace

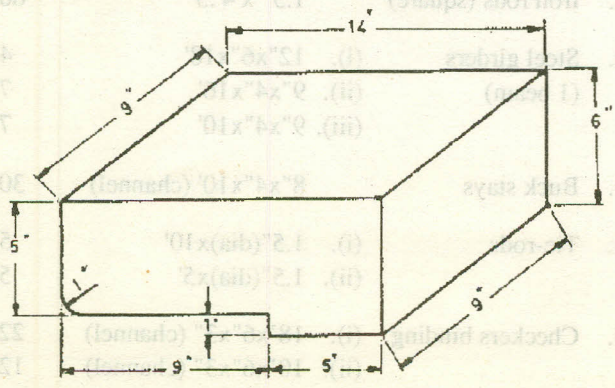

Fig. 2. Tuck stone

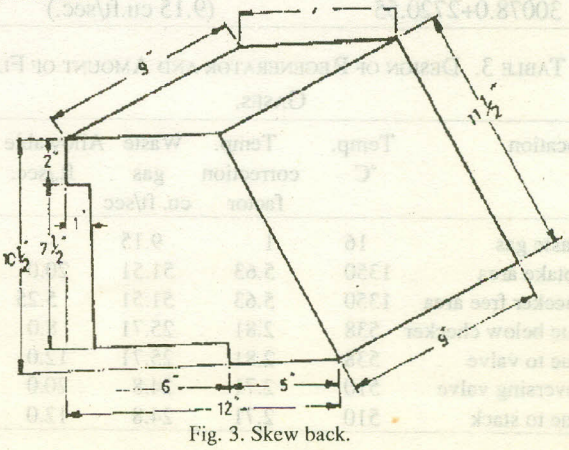

Fig. 3. Skew back.

one end of the furnace were of dimension 7'x15'x3.5'. Local high alumina bricks were used in the erection of checkers. The total refractory requirement is given in Table 4.

Steel requirements. This is a raised furnace and is usually 5 ft. above the ground level. The total steel requirements including buck stays are given in Table 5.

Raw materials. The main raw materials are silica sand, borax, boric acid, soda ash, potash, feldspar, calcite and dolomite. With the exception of borax, boric acid and potash, all other materials are indigenous materials. Pakistan have very good deposits of silica sand, feldspar, calcite and dolomite available in different parts of the country [10,11]. The sand from Daud Khel (Mianwali, Punjab) was sieved through 30 mesh sieve before water washing. Afterwards, it was treated with conc. HCl. The chemical analysis of raw materials is given in Table 6 and 7. Chemical analysis was carried out by standard methods for raw materials and glasses [12,13].

Preparation of glass batch and melting. The chemical analysis of four glasses for pilot plant trials is given in Table 9. The raw materials and chemicals alongwith 20% crushed cullet of the same glass were weighed on an Avery balance while minor ingredients like selenium and cobalt oxide were weighed on an analytical balance (Table 9). Twenty percent excess boron oxide was added to compensate its loss due to volatilization. The batch was mixed in a mixer for 30 mins. In order to minimize dusting during charging 5% water was added during mixing. It was found that if the batch was mixed

TABLE 2. CALCULATION OF FUEL REQUIREMENTS.

1. Holding heat/sq.ft [9]	72000 B.T.U./sq.ft. melting area/hr.
2. Heat input	72000 x 24
3. 20% extra for	728000 B.T.U./hr.— (a)
electrocast lining	3456000 B.T.U./hr.— (b)
4. 1.6% extra per month 12 months age (a + b)	398131 B.T.U./hr.— (c)
5. Melting fuel for one ton of glass 2,200,000/24	9166 B.T.U./hr. — (d)
6. Total heat (a+b+c+d)	2563397 B.T.U./hr.
7. Natural gas required 2563397/946	2709.72 cu.ft/hr.
8. Waste gas volume 2709.72x11.1	30078.0 cu.ft/hr.
9. 10% excess air 2709.72x10.04x0.1	2720.55 cu.ft/hr.
10.Total waste gas 30078.0+2720.55	32798.55 cu.ft/hr. (9.15 cu.ft/sec.)

TABLE 3. DESIGN OF REGENERATOR AND AMOUNT OF FLUE GASES.

Location	Temp. °C	Temp. correction factor	Waste gas cu. ft/sec	Allowable ft./sec.	Area sq.ft.
Waste gas	16	1	9.15	-	-
Uptake area	1350	5.63	51.51	20.0	2.57
Checker free area	1350	5.63	51.51	5.25	9.81
Flue below checker	538	2.81	25.71	8.0	3.21
Flue to valve	538	2.81	25.71	12.0	2.14
Reversing valve	510	2.71	24.8	20.0	1.23
Flue to stack	510	2.71	24.8	12.0	2.06

TABLE 4. QUANTITY OF IMPORTED REFRACTORIES.

S. No.	Location in the furnace	Material	Size	Quantity/ Number
1.	Tank bottom blocks	Vaccum cast sillimanite	36"x18"x12"	5
			24"x24"x12"	18
			24"x18"x12"	3
			24"x12"x12"	4
2.	Melting end: Side wall blocks	AZS Fusion cast	36"x18"x12"	30
			36"x12"x12"	4
			36"x6"x12"	3
3.	Tuck stones	AZS fusion cast	Fig. 2	30
4.	Side wall blocks for the working end	Vacuum cast Sillimanite	36"x18"x12"	8
			36"x12"x12"	4
5.	Breast wall melting end	AZS fusion cast	9"x4 1/2"x3"	325
6.	Breast wall working end	Silica	9"x4 1/2"x3"	190
7.	Skew backs	AZS fusion cast	Fig. 3	35
8.	Skew backs	Silica	" "	25
9.	Melting end: Crown	AZS fusion cast	12"x6"x4/31/2"	192
			12"x6"x4/33/4"	192
			12"x9"x7/41/2"	18
10.	Refining end: crown	Silica bricks	12"x6"x4/31/2"	60
			12"x6"x4/33/4"	60
11.	Breast walls & crown (Melting end)	Mortar for AZS		3 Cwt
12.	Breast walls & crown (Refining end)	Mortar for silica		3 Cwt

Chemical composition of AZS cast refractory Al_2O_3 50.6%, ZrO_2 32.5%, SiO_2 15.7%, Na_2O_3 1.1%, Fe_2O_3 0.08%, TiO_2 0.07%.

TABLE 5. STEEL REQUIREMENT.

	Item	Size	No.
1.	Iron rods (square)	1.5" x 4'.5'	60
2.	Steel girders (1 beam)	(i). 12"x6"x18'	4
		(ii). 9"x4"x16'	7
		(iii). 9"x4"x10'	7
3.	Buck stays	8"x4"x10' (channel)	30
4.	Tie-rods	(i). 1.5"(dia)x10'	5
		(ii). 1.5"(dia)x5'	5
5.	Checkers binding	(i). 18'x6"x3" (channel)	22
		(ii). 10'x6"x3" (channel)	12

in a ball mill for about 20 hr. it had very beneficial effects on the finished product by reducing the cords. The effect of milling the batch on the quality of glass is being studied and results will be published soon. The mixed batch was charged manually to the furnace after every 20 min. or when the first filling had melted. The melting was carried out at 1550±10°

TABLE 6. CHEMICAL ANALYSIS OF SAND (DAUD KHEL).

	Original (%)	Water washed and graded (%)	HCl treated (%)
I/L	0.45	0.30	0.25
SiO_2	98.45	99.04	99.56
Al_2O_3	0.67	0.56	0.31
Fe_2O_3	0.12	0.06	0.025
CaO	0.21	0.05	—
%Useful fraction (-30+100)	—	78-80	—

TABLE-7. CHEMICAL ANALYSIS OF RAW MATERIALS..

	Dolomite (Swabi) %	Calcite (Pampokha) %	Feldspar (Mansehra) %
I/L	46.60	43.80	0.26
SiO_2	1.50	0.6	68.35
Al_2O_3	0.83	0.5	19.27
Fe_2O_3	0.02	0.05	0.045
CaO	30.83	55.1	0.6
MgO	19.78	0.36	0.41
Na_2O	—	—	10.46
K_2O	—	—	0.15

TABLE 8. GLASS COMPOSITION MELTED ON LABORATORY SCALE (WEIGHT PERCENT).

SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	CaO	MgO	Remarks
68.77	3.48	2.50	9.78	6.19	8.43	0.85	Colourless, seed free
69.0	2.0	3.00	12.66	3.10	8.36	1.88	Colourless, no cords
71.5	2.5	5.5	8.5	2.0	7.5	2.5	Colourless, seed free, transparent, thin surface cords
72.0	2.0	6.0	8.5	2.5	7.5	1.5	Colourless, bubble free, very thin surface cords
74.0	2.0	6.5	8.0	2.5	7.0	–	A few seeds, considerable thin and thick cords on the surface
75.5	2.0	10.0	9.5	–	3.0	–	Colourless, bubbles, seed and full of cords
77.0	2.0	10.5	7.5	–	3.0	–	Unmelted sand grains, and band of thick cords
75.0	2.5	8.0	7.8	1.2	4.5	1.0	Unmelted sand grains, and band of thick cords

depending upon the glass composition. After the required level has reached in the furnace, 8–10 hr. were found sufficient for complete melting and refining. The temperature was measured by an optical pyrometer and record was maintained for future reference.

Fabrication. As soon as the melt was free of bubbles and

TABLE 9. GLASS COMPOSITION MELTED ON PILOT PLANT (WEIGHT PERCENT).

SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	CaO	MgO	Remarks
69.0	2.5	2.5	9.70	6.20	8.5	1.60	Colourless, seed free
72.5	3.0	3.5	10.5	1.0	8.0	1.5	Colourless seed free, very rare cords
73.5	2.5	5.0	9.5	1.0	7.0	1.5	Colourless, seed free, transparent, one or two thin cords at the surface
74.5	2.0	6.5	9.0	1.0	6.0	1.0	Colourless, a few seeds, thick cords at the surface, not suitable for blowing, suitable for pressing
Glass-3 after melting							
74.27	2.57	4.5	9.42	0.97	7.12	1.53	
Minor ingredients for 100 kg sand	Se = 6.4-7.0 gm COO = 0.25-0.27 gm AS_2O_3 = 300 gm						

TABLE 10. PHYSICAL PROPERTIES OF GLASSES MELTED IN THE PILOT PLANT.

Properties	G-1	G-2	G-3	Pyrex
Linear coefficient of thermal expansion (20-300°)	$72x10^{-7}$/°C	$71.0x10^{-7}$/°C	$60.5x10^{-7}$/°C	$31-33x10^{-7}$/°C
Annealing point	540°	540°	550°	565°
Strain point	500°	505°	510°	520°
Softening point	740°	745°	752°	820°
Working point	1160°	1160°	1175°	1225°
Density	2.412	2.405	2.391	2.23
Refractive index	1.513	1.51	1.495	1.474
Thermal endurance	115°	120°	135°	200°

TABLE 11. CHEMICAL DURABILITY.

Glass type	Weight loss in 24 hr at 90° Cmg/cm²		Action in water in autoclave at 121°C for 24 hr Volume of 0.02N H_2SO_4 consumed
	NaOH 5%	HCl 5%	
Pyrex	5.4	0.006	0.51 ml
G-3	3.1	0.018	6.5 ml
Soda lime glass	2.5	0.025	10.5 ml

seeds, the temperature of the furnace was lowered to about 1250° i.e., working temperature. It was observed that glass melts containing B_2O_3 upto 5% were almost free of cords and visible defects. The glass became full of cords as the boron content was increased more than 5%. In view of this, glass articles were mainly made from compositions containing B_2O_3 3.5% and 5.0%. All the fabrication was done either by mouth blowing or by hand press. Paste moulds made of cast iron were used. Laboratory glass articles like beaker, conical flasks, round and flat bottom flasks, petri dishes, funnels and desiccators were fabricated.

Annealing. It is very important operation to be carried out just after fabrication. Glass containers and pressed wares must be free of internal stresses large enough to weaken spontaneously. Therefore, an annealing lehr about 60 ft. long and 4.0 ft. wide was constructed. It consisted of three zones (i) heating zone (ii) annealing zone and (iii) cooling zone. After fabrication, glass wares were transferred to the lehr where temperature was raised slowly (80° min.) to annealing point (550°) and this temperature was maintained for about 10 min. to relieve all stresses. After this, temperature was decreased slowly (60°/min.) to room temperature. Finishing operations like cutting, mouth making and printing were carried out afterwards. Annealing was checked from time to time by a strain detector polariscope. Comparison was also made with standard strain disks manufactured by British Glass Industry Research Association [14]. Annealing was also done after cutting operation as stresses reappear during this operation.

Measurement of properties. Important properties like density, thermal expansion co-efficient, thermal shock endurance, softening point, refractive index and annealing point were determined. The results are reported in Table 10. Chemical durability was determined by ASTM 255-68 standard methods [15]. Glass grains screened between 40 and 50 mesh sieves were cleaned from iron particles and washed with aceton. 10 Grams grains were taken in a 250 ml Erlenmeyer flask. Exactly 50 ml of high purity water was added and heated to 121± 0.5° in an autoclave for 30 min. After cooling, the water extract was decanted from the glass powder which was washed with four 15 ml portions of high purity water. The extract was titrated with 0.02N H_2SO_4, using methyl red indicator. Results are given in Table 11.

The attack by 5% NaOH and 5% HCl on glass pieces measuring 2.5 cm x 3 cm was also studied at 90° for 24 hr. and loss in weight determined. Imported pyrex, soda-lime and G-3 (PCSIR made) glasses were put to test. Results are given in Table 11.

Results and Discussion

The first prerequisite of a glass raw materials is their purity. It must be, as far as possible, free from iron and other elements that would introduce undesirable colour. Next, the material must be relatively abundant and cheap. Fortunately all the main raw materials such as sand, feldspar and lime-stone are abundantly available in Pakistan [10,11]. It is evident from the chemical analysis of the washed sand that the iron content (0.06%) is within the specified limits for making colourless glass [16] and the Fe_2O_3 has further reduced to 0.025% in the acid treated sand (Table 6). Selective batch composition of four borosilicate glasses is given in Table 9. Boron content in these glasses varies from 2.5%–6.5%. It was observed that glass No. 1,2 and 3 containing B_2O_3 2.5, 3.5 and 5.0% respectively were easy to melt and refine. The products were colourless, transparent and free of surface cords. A few cords appearing on the surface of glass 3 were controlled by careful skimming of the melt surface before starting the fabrication. The operation of skimming the melt surface was repeated after every 2 hr. to get glass free of cords. The composition No. 4 was a bit difficult to refine and the articles fabricated from this glass were full of cords. Even skimming the surface of the glass melt did not reduce the cords. It was observed that as boron content was increased beyond 5%, the quality of the product started deteriorating due to the excessive volatiliztion of boron from the glass surface. As a result of which the top surface of the melt is depleted of boron and more boron ions cannot diffuse to the surface to compensate this loss due to high viscosity of the top surface. The loss of boron is increased many times when flames play across the surface of the glass at high temperature. It has been reported that 15 to 20% boron is lost in oil and gas fired furnaces [17]. In the electric melting of borosilicate glasses only 1% loss due to volatilization has been observed [17]. 18–25% boron loss was estimated in the present studies.

The most effective way, however, to combat cords in borosilicate glasses is by eliminating free glass surfaces as far as possible by minimizing circulation of gases and by stirring the glass. When electric heat is available, much can be done to diminish or eliminate surface volatilization. Due to scarcity of electricity and high cost, electric melting of borosilicate glasses is not possible in Pakistan. However, some other methods can be adopted to minimize cords due to the volatilization of boron. One of these methods, is the use of stirrers alongwith skimming of the melt from time to time. It is being tried presently and the results are encouraging which will be published in the next paper.

It is evident from Table 9 that the physical properties are not comparable with those of pyrex glass. Thermal expansion co- efficient of glass 3 $(60 \times 10)^{-7}$ lies between that of container and pyrex glass. Durability tests (Table 11) show that alkali attack is several orders of magnitude greater than acid attack.

It seems that high silica and high boron glasses are the most durable in acid than in alkali. G-3 lies between the pyrex and soda lime glasses so far chemical durability is concerned. However, the durability of G-3 is much better than ordinary soda lime glass and therefore, it can be used in schools and colleges as laboratory glass ware where precision is not very important. Further it may also be noted that action of acid, alkali and water per hour would be very small. Glass-3 is better than glass-1 and 2 as there is reduction of (1–5%) alkali and increase of boron and silica contents as compared to glass 1 and 2.

The glass articles fabricated from glass 3 were sent to schools, colleges and other end users for evaluation. The performance has been reported satisfactory for general use in schools and colleges. It is estimated that at least 40% requirements of schools, colleges and other organizations can be met through this development and thus a considerable amount of foreign exchange can be saved very easily. The quality of this glass is far better than the quality of laboratory glassware, being manufactured in the country and supplied to schools and colleges. It is soda lime glass and therefore its use in schools and colleges should be discouraged. As mentioned earlier that the quality of the borosilicate glass can be improved by stirring the glass, the studies on these lines are being carried out and very good results are expected.

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