

## Chapter 3

### Experimental Part

#### Description of Experiments

The experimental work comprises three main parts. Firstly, the defect was traced in the production line. Secondly, the glass was analyzed by several methods. Finally, the former glass formula was re-designed and experimentally verified.

#### Scope of Experimental Work

##### 1. Tracing the defect in the production line

In order to understand the bloom occurrence, the details in the production line were investigated as follows.

The sketch of the production line is shown below

Hot end → Forming machine → Annealing Lehr → Decoration →  
Packing → Storage

The production line was investigated as mentioned below

1. the forming method
2. the type of annealing Lehr
3. packing material
4. atmosphere in warehouses.

After the investigation, interesting information was obtained. There are four annealing lehrs. All of them are gas furnaces. Among these, one is a direct furnace, i.e., the combustion atmosphere directly contacts the glass. The other furnaces are muffled.

Concerning the forming process, there is one press-press machine called MBP. The rest are press-blow Hartford machines called H-28. The mould materials are cast iron with carbon coating and stainless steel with or without hard chrome coating.

### 1.1 Packing Materials

The packing material used is paper. There are many suppliers; the sulfur content was checked. After a long storage, sulfur contained in paper will escape to the atmosphere. For comparison, sulfur content in packing material was checked by 2 laboratories. The results are summarized in the table 3.1.

Tab 3.1 Sulfur content of packing papers (%).

Suppliers	Lab.1		Lab.2	
	Inner	Outer	Inner	Outer
A	0.11	0.14*	0.14	0.18
B	0.11	0.11	0.23*	0.22
C	0.09*	0.11	0.12*	0.15
D	0.12	0.11	0.18	0.14
E	0.09	0.10	0.19	0.20

\* = rechecked samples

Unfortunately, the results of the laboratories disagreed. To select the most reliable one, the maximum and minimum sulfur contents were rechecked again (by changing sample codes). Table 3.2 shows the results.

Tab. 3.2 Rechecked sulfur content (%).

Sample	Lab.1			Lab.2		
	Old	New	Deviation	Old	New	Deviation
A-Outer	0.14	0.14	< 0.01	-	-	-
C-Inner	0.09	0.10	0.01	0.12	0.14	0.02
B-Inner	-	-	-	0.23	0.10	0.13

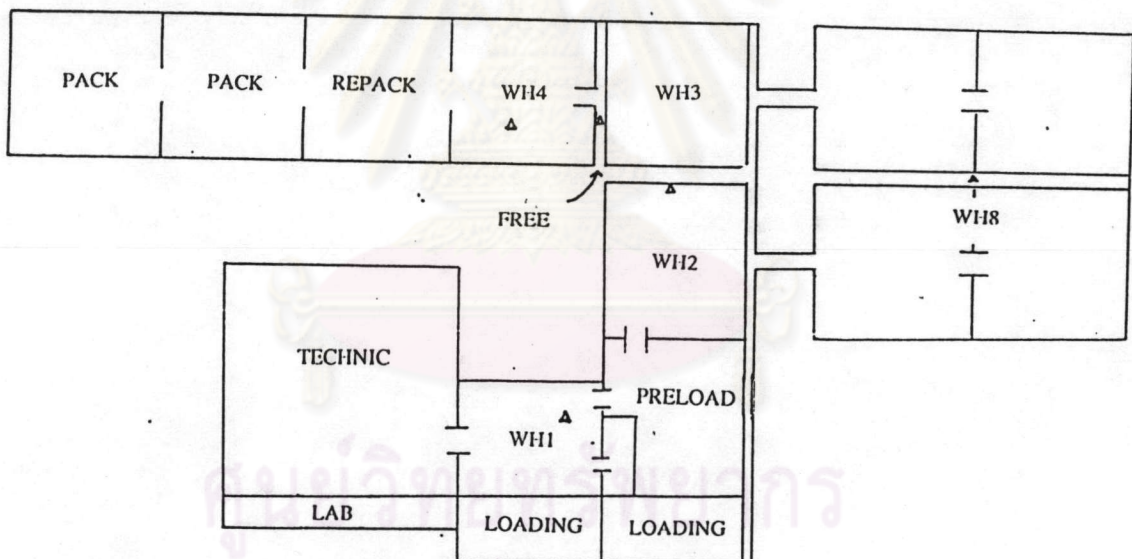
It is obvious that the results from laboratory 1 are more reliable. The latter ones from laboratory 2 were thus ignored. The table below shows the result. Sulfur contents do not differ significantly. Only the paper with high sulfur content seemed less suitable.

Tab. 3.3 Sulfur content of packing papers (%).

Suppliers	Sulfur Content	
	Inner	Outer
A	0.11	0.14
B	0.11	0.11
C	0.09	0.11
D	0.12	0.11
E	0.09	0.10

### 1.2 Atmospheric condition in the warehouses

As mentioned before, air humidity might be an important factor for bloom formation. Therefore, the atmospheric conditions in the warehouses were investigated by hygrometers. Tests were performed on a 24 h per day basis during a period of 8 months, covering the rainy, cold, and hot season of the annual weather cycle in Thailand. The hygrometer (Izuzu, 3-1126-01) measured and recorded both temperature and relative humidity. Two hygrometers were placed at selected positions. Figure 3.1 shows the outline of the warehouses. Positions of hygrometers are marked with  $\Delta$ .



$\Delta$  = positions of hygrometers

Fig. 3.1 Outline of warehouses.

The investigation was conducted stepwise in the following schedule.

Tab. 3.4 Schedule of hygrometer operation.

Date	Duration	Warehouse
29 June - 6 July 1995	1 week	WH 2 & WH 8
6 July - 13 July 1995	1 week	WH 2 & WH 8
13 July - 20 July 1995	1 week	WH 2 & WH 4
20 July - 27 July 1995	1 week	WH 2 & WH 4
28 July - 3 Aug 1995	1 week	WH 2 & free *
3 Aug - 10 Aug 1995	1 week	WH 2 & WH 1
10 Aug - 17 Aug 1995	1 week	WH 2 & free
17 Aug - 24 Aug 1995	1 week	WH 8 & free
24 Aug - 1 Sep 1995	1 week	WH 8 & free
1 Sep - 8 Sep 1995	1 week	WH 8 & free
13 Sep - 14 Oct 1995	1 month	WH 8 & free
13 Oct - 14 Nov 1995	1 month	WH 8 & free
13 Nov - 14 Dec 1995	1 month	WH 8 & free
13 Dec - 14 Jan 1996	1 month	WH 8 & free
13 Jan - 14 Feb 1996	1 month	WH 8 & free
13 Feb - 14 Mar 1996	1 month	WH 8 & free

\* = exposed to outside atmosphere in the gangway between WH3 and WH4, not exposed to direct rain

## 2. Surface analysis of glass articles

In an effort to identify the bloom present on the surfaces and to understand of the surface nature itself, experiments were performed using chemical methods. The following flow chart shows the details.

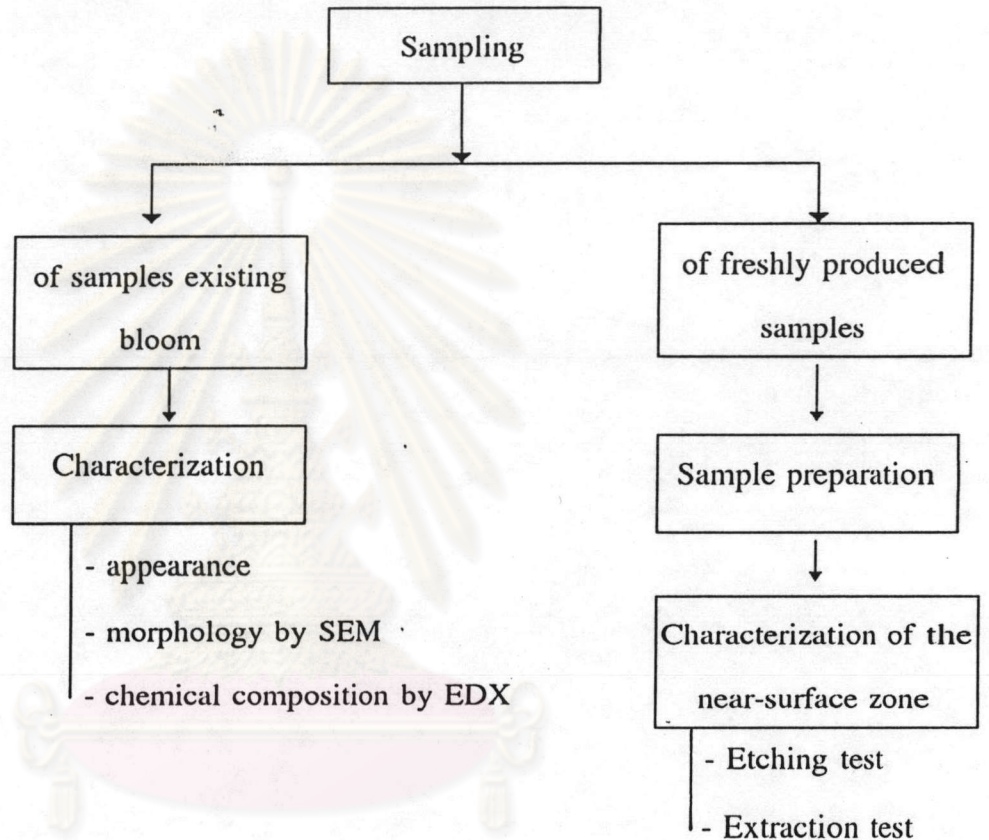


Fig. 3.2 Surface analysis description chart.

### Equipment and Procedure

Methods employed for the surface analysis of freshly produced glass surfaces are consecutive etching with hydrofluoric acid, and leaching in water (98 °C). The methods are supported by wet chemistry and electrochemical analysis.

## 2.1 Equipment

### 2.1.1 Water bath

The hydrofluoric acid solution was kept at constant temperature by means of a water bath (6 liter volume) with temperature controlled in the range of 30 to 100 °C.

### 2.1.2 Sodium ion sensitive electrode (Orion, 84-11)

Sodium can be measured in the detection range. It is necessary to constitute a calibration curve between the millivolt response and Na concentration. This is done by using a series of standards. The concentrations of the samples are determined by comparison to the standards. A specific reagent called Ionic Strength Adjuster (ISA) is added to all solutions to ensure that samples and standards have similar ionic strength and pH value. Analytical grade of NaCl was used for making a series of standard solutions. These were  $10^{-7}$ ,  $3 \times 10^{-7}$ ,  $10^{-6}$ ,  $2 \times 10^{-6}$ ,  $10^{-5}$ ,  $10^{-4}$  mol/l. DI water with a conductivity  $< 5 \mu\text{S}$  (typically  $2 \mu\text{S}$ ) was used.

In sodium measurement, the potential developed at a sodium selective membrane is measured through the use of two internal electrochemical cells. The membrane potential is added, in series, to the potential of the sensing reference cell, and their sum is measured against the potential of the second (reference) cell. Since the potentials of the two internal reference cells remain constant, changes in potential are due to changes in sodium concentration.

The measured potential corresponding to the level of sodium ion in solution is described by the Nernst equation:

$$E = E_0 + b \log(a) \quad \text{where:}$$

$E$  = measured electrode potential

$E_0$  = constant potential largely dependent on the reference electrode

$a$  = sodium ion activity or effective concentration of sodium

$b$  = electrode slope

The response of the electrode was detected by a millivolt meter. The calibration curve was constructed on semilogarithmic paper. Electrode potentials (mV) of standard solutions were measured and plotted on the linear axis against their concentrations on the log axis. Figure 3.3. shows the calibration curve.

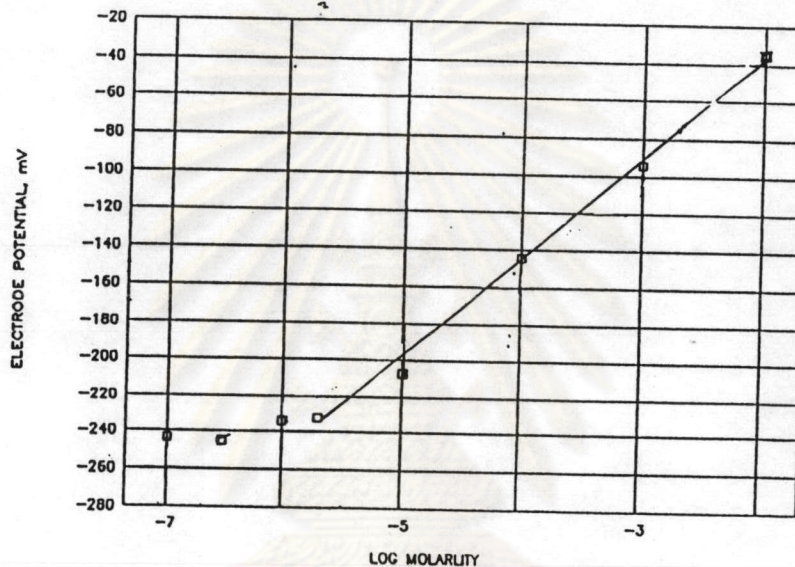


Fig. 3.3 Sodium electrode calibration curve.

The sodium concentrations of unknown samples were determined directly by this calibration curve.

### 2.1.3 Flame Photometer (Jenway, PFP7)

Flame Photometer relies upon the fact that most compounds of alkali and even some compounds of alkaline earth metals can be thermally dissociated in a flame. Dissociated atoms are excited to higher electronic energy levels. When relaxing to the ground state, they emit radiation which lies mainly in the visible region of the spectrum. Each element emits radiation at a series of



wavelengths specific for its electron levels. Flame photometry is restricted to the investigation of elements with easily excitable outer s electrons.

Over certain ranges of concentration, the intensity of the emission is directly proportional to the number of atoms returning to the ground state. This is in turn proportional to the absolute quantity of the species volatile in the flame, i.e., the light emitted is proportional to the sample concentration.

The light emitted by the element at the characteristic wavelengths is discriminated by an optical filter and the intensity is measured by a photodetector.

A calibration curve was constructed using standard solutions containing known sodium concentrations prepared in the same way as for the ion-sensitive electrode. The sodium concentration range covered by the calibration curve covered the expected concentration range ( mol/l ) so that the sample readings fall somewhere within the calibration curve.

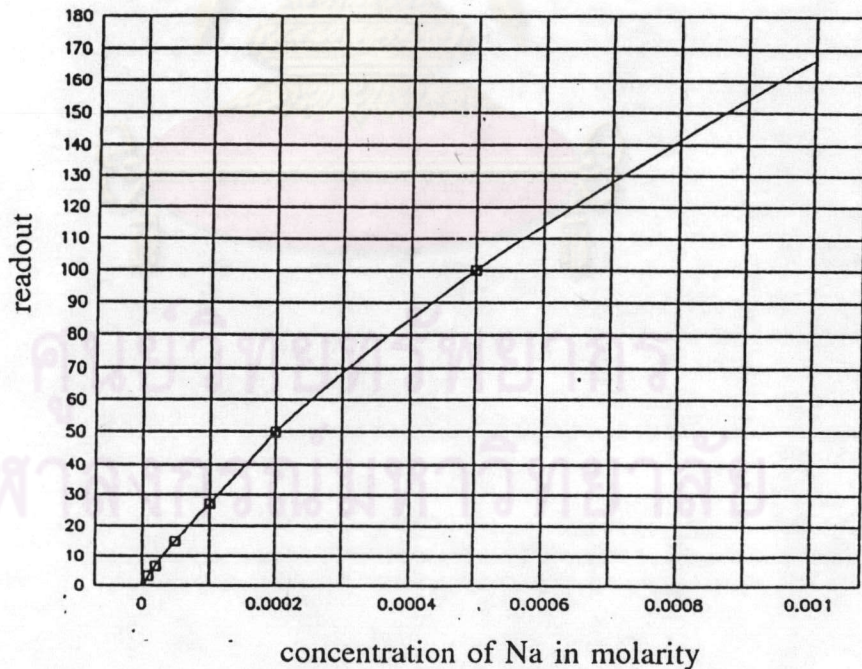


Fig. 3.4 Calibration curve of sodium .

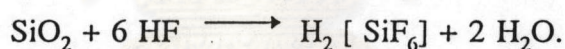
#### 2.1.4 Labware and Tweezers

In the experiments, all containers and tweezers are made of high grade plastic materials, white polypropylene (PP) labware, and brown high density polyethylene (HDPE) bottles for extraction test. Before testing, the plastic containers were cleaned with 0.1 % HCl.

Solutions were never in contacted with any metal or kept in glass bottles because glass containers release  $\text{Na}^+$  into a solution and metallic ions influence the surface reactions of glass in water.

#### 2.2 Etching

Of the better known reagents, it is only hydrofluoric acid which makes an immediately noticeable attack on glass. When applied as diluted acid, it brings the main components of glass into solution according to the formula



As a specific feature, this reaction dissolves silicate glasses in a congruent way. It can thus be used to remove glass slices step by step, by this allowing to analyze the near-surface zone of a glass.

The dissolved matter from the glass eventually accumulates in the solution and changed its activities. If a solubility limit is reached, then compound formation and precipitation will occur, preferentially in the vicinity of the glass surface. That is why the ratio of the surface area of the glass to the volume of the etching solution ( $\text{s in cm}^{-1}$ ) is an important parameter which must be fixed in these experiment.

HF and  $\text{HNO}_3$  were used as etching solution to avoid calcium fluoride precipitation on the surface of the samples. The etching solution is changed for each

each etching step. In this way the amount of constituents per unit surface area can be deduced as a function of reaction time at fixed temperature and solution conditions. A number of techniques have been developed for determining depth profiles; most require that the sample surface be etched layer-by-layer or sputtered away in successive steps.

Dissolution depth were calculated from weight loss measurements gained from each etching step. The following flow chart shows the details of the etching test

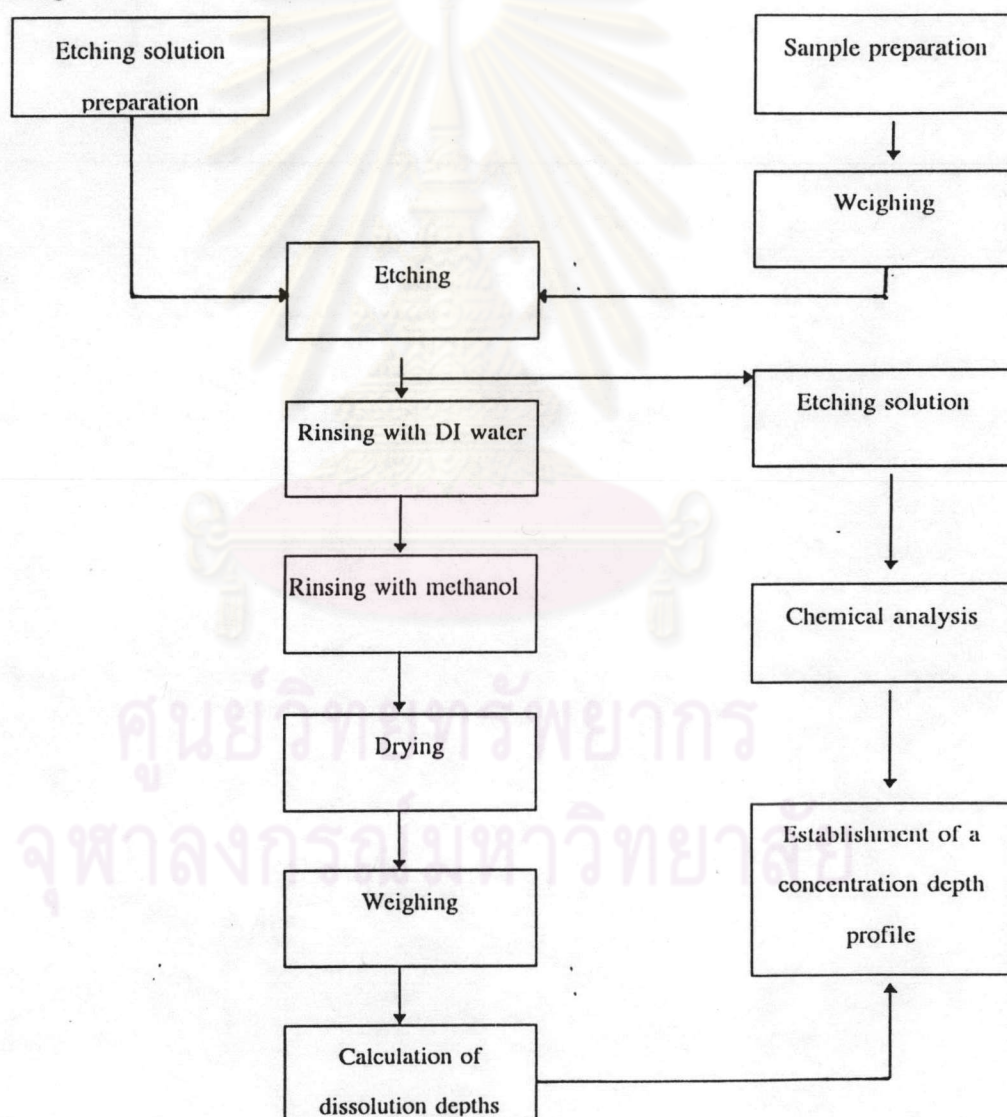


Fig. 3.5. Illustration of etching process.

### 2.2.1 Sample Preparation

Freshly produced samples were used in the experiments for pre-tests. The sample called PB5 was investigated in order to search for the optimum solution condition and etching times. The  $s$  parameter and the leaching temperature  $T$  were fixed throughout the experiment ( $s = 0.2 \text{ cm}^{-1}$ ,  $T = 45\text{-}46 \text{ }^\circ\text{C}$ ).

Sample were cut into a crackless chips with controlled surface area (A) of approximately  $10 \text{ cm}^2$ . Hence, the etching solution quantity was 50 ml. The samples were cleaned with trichloroethylene and kept in the desiccator before testing.

### 2.2.2 Etching Solution Preparation

The two different conditions of the etching solution were

1. 0.5 % HF + 2 %  $\text{HNO}_3$
2. 0.3 % HF + 2 %  $\text{HNO}_3$ .

It was important to use fresh deionized water for dilution and mixing.

### 2.2.3 Weighing

This was a most important and sensitive step because the accuracy of weight determination was the key to the reliability of the results. Each glass chip was weighed with great attention and patience not less than 7 times to the nearest  $0.00001 \text{ g}$ . After that the average value and the standard deviation were calculated. The maximum limit of the deviation allowed was  $2 \times 10^{-5} \text{ g}$ . Data exceeding the standard deviation were rejected. Weighing was continued until a set of data with at least 7 members and with the desired standard deviation was obtained. The balance was calibrated every time before weighing.

For example, weighing of the PB5 chip sample yielded 2.40543, 2.40542, 2.40544, 2.40543, 2.40544, 2.40545, 2.40544

$$\text{average} = 2.40544 \quad \text{SD} = 0.00001_1$$

The layer-by-layer method in HF solution is one of the various kinds of surface analysis measurements to be used instead of X-ray photoelectron spectroscopy (XPS). It is a typical microanalysis method. Errors during the experimentation were inevitable. Each step of the test was done with great care to avoid any error as much as possible. Yet the relative accuracies and precisions obtained must not be mixed up with the requirements of conventional chemical analysis. For microanalysis, a precision of  $\pm 30\%$  is still an acceptable result.

#### 2.2.4 Calculation.

The weight loss upon dissolution after etching lead to the calculated depth as following;

$$\begin{aligned} \text{weight loss} &= m \\ \text{surface area} &= A \\ \text{weight loss per surface area} &= q = m/A \quad \text{mg/cm}^2 \\ \text{dissolution rate} &= r = q/t \quad \text{mg/cm}^2 \cdot \text{day} \\ \text{dissolution depth} &= d = q/\rho \quad \text{cm or nm} \\ \text{dissolution velocity} &= v = r/\rho \quad \text{cm/day} \\ \text{density } (\rho) \text{ of the glass sample} &= 2.47 \text{ g/cm}^3 \end{aligned}$$

#### 2.2.5 Etching

The PB5 sample was prepared as described above. Etching was done in a water bath at 45-46 °C.

Three conditions of leaching test was designed as follows:

1. 0.5 % HF + 2 % HNO<sub>3</sub>, etching time = 30 seconds

2. 0.5 % HF + 2 % HNO<sub>3</sub>, etching time = 15 seconds

3. 0.3 % HF + 2 % HNO<sub>3</sub>, etching time = 10 seconds.

In each condition, 5 pieces of PB5 chips were etched in the solution independently as described in figure 3.5. Mass loss obtained after etching brings along the dissolution depth by the calculation described in 2.2.4. Five values of dissolution depth are averaged.

Table 3.5 Demonstration of the calculation of dissolution depths.

0.5% HF + 2% HNO <sub>3</sub> , etching time 30 seconds						
Etching no.	Surface area (cm <sup>2</sup> )	Weight before etching (g)	Weight after etching (g)	Mass loss (g)	q (μg/cm <sup>2</sup> )	d = q/ρ (nm)
1	9.4881	2.14793	2.14760	0.00033	34.7	141
2	9.7231	1.85510	1.85471	0.00039	40.1	162
3	9.8910	1.91145	1.91113	0.00032	32.4	131
4	10.0184	2.04235	2.04198	0.00037	36.9	150
5	10.0633	1.72896	1.72854	0.00042	41.7	169
averaged dissolution depth = 154 nm						

The results of the leaching test of PB5 are shown in the table next

page






Tab. 3.6 Etching test of PB5

No.	Etching condition	Average dissolution depth (nm)
1	0.5 % HF + 2 % HNO <sub>3</sub> , 30 sec	154
2	0.5 % HF + 2 % HNO <sub>3</sub> , 15 sec	90
3	0.3 % HF + 2 % HNO <sub>3</sub> , 10 sec	52

The target dissolution depth for etching is 100 nm at most. The etching condition no. 2 seemed to be close to the expectation.

After the pre-test of PB5, the guidelines for the etching process were obtained. There were 8 samples collected from each of the four feed lines both before and after annealing. The description is given in table 3.7

Tab. 3.7 Description of samples.

Sample No.	Forming	Lehr	Image
B 1213 *	press - blow	indirect **	
B 0208 *	press - blow	indirect **	
B 1408 *	press - blow	direct **	
P 0340 *	press - press	indirect **	
BG *	press - blow	indirect **	

\* = no cold end coating

\*\* = no decoration

Sample B 1213 and B 0208 are similar in process. For this reason, only B 1213, B 1408 and P 0340 were selected for surface analysis. In addition,

samples from a container factory was also investigated for reasons of comparison. The samples are called BG.

The etching procedure was similar to pre-test no. 2. But there were some slight changes. The etching step was extended to 7 steps, and 3 pieces of sample (same code no.) were etched subsequently in the same solution in order to increase the concentration of dissolved sodium so as to be sufficient for the detection by electrode or flame photometer.

The etching solutions were further examined by wet chemical analysis using sodium electrode and flame photometer (FES). The purpose was the determination of the amount of leached sodium.

Before measuring the etching solutions from samples in table 3.7, it was necessary to test the efficiency of the electrode. A new B 1213NA was etched again (only one piece). Table 3.8 shows the result of this etching process.

Tab. 3.8 Etching of B 1213NA

Surface area = 9.7548 cm<sup>2</sup>

Etching no.	Wt.(bef) (g)	Wt(aft) (g)	Mass loss (g)	q (µg/cm <sup>2</sup> )	d (nm)
1	1.63113	1.63092	0.00021	21.5	87
2	1.63092	1.63072	0.00020	2.05	83
3	1.63072	1.63050	0.00022	2.25	91
4	1.63050	1.63031	0.00019	1.95	79
5	1.63031	1.63014	0.00017	1.74	71
6	1.63014	1.62998	0.00016	1.64	66
7	1.62998	1.62985	0.00013	1.33	54



The etching solution from each step was brought to electrode measurement. The test was conducted 6 times for each solution to get a good average. Table 3.9 summarizes the mV obtained from the multimeter.

Tab. 3.9 Data of electrode testing (in mV).

no.							average
1	-149	-150	-149	-150	-151	-151	-150
2	156	-154	-155	-155	-156	-157	-156
3	-159	-160	-160	-163	-162	-163	-151
4	-149	-153	-150	-150	-150	-150	-150
5	-150	-151	-150	-152	-151	-151	-151
6	-160	-160	-161	-162	-161	-160	-160
7	-160	-162	-161	-162	-162	-162	-162

From the calibration curve (see figure 3.3), the log molarity was detected and then converted to molarity.

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Tab. 3.10 Concentration of sodium by electrode.

mV.	log molarity.	molarity(*10 <sup>-5</sup> )
-150	-4.15	7.07
-156	-4.25	5.62
-151	-4.35	4.47
-150	-4.15	7.08
-151	-4.17	6.76
-160	-4.32	4.79
-162	-4.37	4.27

#### Example of calculation

The amount of solution was 50 ml, from etching step 1 with the dissolution depth = 87 nm

$$\begin{aligned}
 7.07 * 10^{-5} \text{ mol/l} &= (50 * 7.05 * 10^{-5}) / 1000 && \text{mol/slice} \\
 &= (50 * 7.05 * 10^{-5}) / (1000 * \text{depth} * A) && \text{mol/cm}^3 \\
 &= (50 * 7.05 * 10^{-5}) / (1000 * 8.7 * 10^{-6} * 9.7548) && \text{mol/cm}^3 \\
 &= 0.0415 && \text{mol/cm}^3 \\
 1 \text{ mol Na} = 23 \text{ g} &= 0.0415 * 23 = 0.95 && \text{g/cm}^3
 \end{aligned}$$

Below the results of each step of the calculation are shown.

Tab. 3.11 The amount of sodium in etching solution.

Depth in nm	Molarity	Amount of etched Na (g/cm <sup>3</sup> )
87	$7.07 \cdot 10^{-5}$	0.95
83	$5.62 \cdot 10^{-5}$	0.79
91	$4.47 \cdot 10^{-5}$	0.58
79	$7.08 \cdot 10^{-5}$	1.06
71	$6.76 \cdot 10^{-5}$	1.12
66	$4.79 \cdot 10^{-5}$	0.86
54	$4.27 \cdot 10^{-5}$	0.93

The results were surprising because the actual amount of Na<sup>+</sup> in the soda glass is approximately 0.2 g/cm<sup>3</sup> only (see appendix A). The results prove that there is an interference of Na<sup>+</sup> ion from glass electrode bulb: therefore, flame photometry was used for the analysis of etching solution consequently.

#### 2.2.5 Procedure for the Flame Phometer

1. Fresh DI water was sucked into the system to flush impurities within the inner tubes approximately 10 minutes before carrying out the experiment.
2. The calibration curve which had been constructed previously was re-checked.
3. Then the sample solution were aspirated and determined subsequently. The reproducible readout was recorded.

4. From the calibration curve, the readings for the sample solutions were compared to the curve to allow the sample concentrations to be established. The readings were converted to concentration by means of the calibration curve.

#### 2.2.6 Calculation of the Concentration of $\text{Na}_2\text{O}$ in the Etching Solution

$\text{Na}_2\text{O}$  concentrations were calculated from both the results from the etching process and flame photometer as followings:

from etching:

average depth  $\rightarrow$  average mass per slice in  $\mu\text{g}$  (m)

$m = \text{depth} * \text{surface area} * \text{density}$

from FES:

concentration of Na (c)  $\rightarrow c * 50 / 1000 = \text{mol Na per slice.}$

mol Na per slice \* 31 (gram atom of  $1/2\text{Na}_2\text{O}$ ) = mass  $\text{Na}_2\text{O}$  per slice

=  $m_{\text{Na}_2\text{O}}$

$\therefore \text{wt\% of } \text{Na}_2\text{O} = 100 * m_{\text{Na}_2\text{O}} / m$

#### 2.3 Extraction Test.

The rate of the extraction of sodium relates to the electrical conductivity of the glass.

##### 2.3.1 Procedure

The flow chart below shows the details of the extraction procedure.

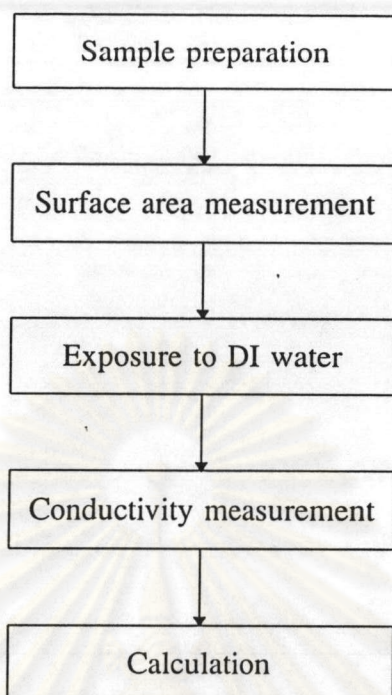


Fig. 3.6 Flow chart of the extraction procedure.

The same series of samples including BG and B 0208 were prepared as chips and cleaned in the same way as mentioned previously. Afterwards, the surface area of chip samples was measured.

HDPE brown bottles which can withstand 98 °C were used. The amount of DI water was 50 milliliters. The chips were hanging on clean threads so that they were surrounded by water and did not contact the container walls.

Extraction test were performed in a water bath at 98 °C. The duration of treatment was 4 hours. After this, the samples were taken, the water was cooled down and the conductivity was measured.

### 2.3.2 Calculation.

The conductometer measures the conductance  $C$  (i.e., the reciprocal resistance) of electrolyte solutions in units of S (Siemens);  $1 \text{ S} = 1 \text{ ohm}^{-1}$ . The cell

used has a cell constant of  $a = 1 \text{ cm}^{-1}$ . Hence the conductance  $C$  is linked to the overall conductivity  $k$  of the solution by

$$C = k/a$$

According to the Debye - Hueckel theory of electrolyte solutions,  $k$  is given by

$$K = (c/100) \cdot K + k(\text{H}_2\text{O}),$$

where  $c$  is the electrolyte concentration in mol/l,  $k(\text{H}_2\text{O})$  is the conductivity of theoretically pure water, and  $K$  is the so-called equivalent conductivity of the electrolyte. For sufficiently low concentrations, i. e., when the hydration shells of the individual ions do not overlap, the  $K$  obeys the Kohlrausch law

$$K = K_0 + b \cdot \sqrt{c}.$$

The range of validity of this law is also called the range of independent ion motion.  $K_0$  is the equivalent conductance at infinite dilution, and  $b$  is a slope. As a direct consequence of independent ion motion,  $K_0$  is given by the sum of cationic and anionic contributions. For NaOH as electrolyte, this reads

$$K_0(\text{NaOH}) = K_0(\text{Na}^+) + K_0(\text{OH}^-).$$

The quantities needed have the following values at 25 °C:

$k(\text{H}_2\text{O})$	$4.0 \cdot 10^{-8}$	$\text{ohm}^{-1} \cdot \text{cm}^{-1}$ ,
$K_0(\text{Na}^+)$	50.1	$\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$ ,
$K_0(\text{OH}^-)$	198.6	$\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$ ,
$b$	-446.1	$\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-3/2}$ .

For a conversion of  $K_0(\text{Na}^+)$  and  $K_0(\text{OH}^-)$  to other temperatures, a temperature coefficient of  $+2 \text{ cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  is valid. With the formulae and data given above, the conductance values  $C$  read from the conductometer can be readily translated to NaOH concentration. The contributions of minor amounts of any other ions, such as  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ , etc., are included in the equivalent NaOH value. Since  $\text{Na}^+$  is the major species, this is an acceptable approximation. The result of the above calculation are presented in figure 3.7.

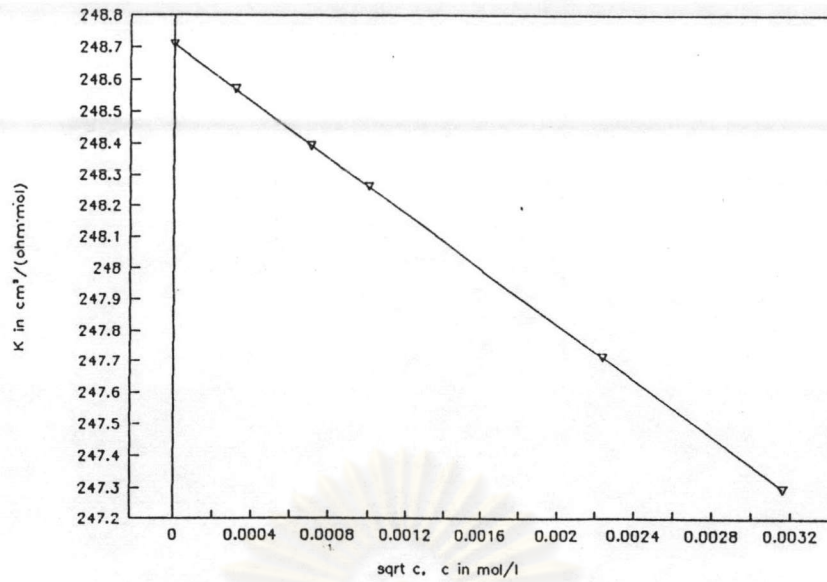


Fig. 3.7 Calibration curve for extraction test.

### 3. Reformulation of Glass Formula

Generally, the rate of extraction from glass by aqueous solutions is largely determined by the composition of glass. The rate decreases with decreasing alkali content of glass.

This part is concerned about the improvement of the glass formula by lowering sodium oxide. The objective was to determine if there were an actual decrease in the amount of leached sodium. The replacement was performed under the boundary condition of constant workability. The significant difference expected was the better stability of the reformulated glass.

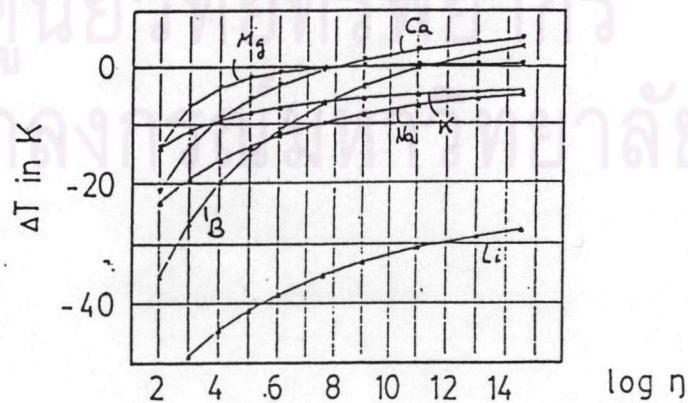


Fig. 3.8 Effect of replacement of SiO<sub>2</sub>(1wt. %) in a commercial mass glass by other oxides, Lakatos et al., 1976.

Figure 3.8 shows the effect of a replacement of 1 wt. % of  $\text{SiO}_2$  in a mass glass by different oxides. Obviously,  $\text{Li}_2\text{O}$  is by far the strongest viscosity flux.  $\text{B}_2\text{O}_3$  is also a strong viscosity flux but only for  $\log \eta < 11$   $\text{Na}_2\text{O}$  is less strong than  $\text{Li}_2\text{O}$ .

### 3.1 Procedure

The following flow chart shows the procedure of this part.

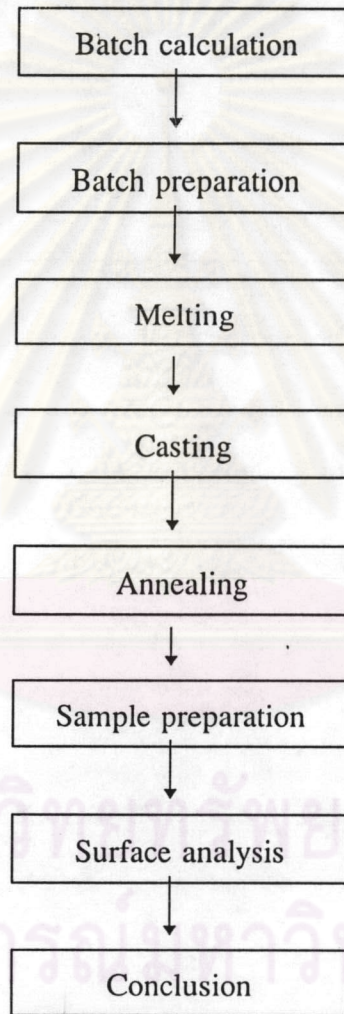


Fig. 3.9 Flow chart of the reformulation.

### 3.2 Batch Calculation

The commercial chemical composition of Ocean Glass Public Co., Ltd. and its characteristic temperatures is shown in table 3.12



Tab. 3.12 Chemical composition of the commercial glass (original formula).

Chemical composition in wt. %	
SiO <sub>2</sub>	72.38
Fe <sub>2</sub> O <sub>3</sub>	0.04
Al <sub>2</sub> O <sub>3</sub>	1.61
CaO	7.74
MgO	3.36
SO <sub>3</sub>	0.18
Na <sub>2</sub> O	14.30

characteristic temperatures and related viscosity, written as T (log η)	
liquidus temperature	= 1018 °C
refining temperature	= T (2.0) = 1465 °C
gob temperature	= T (3) = 1206 °C
Littleton temperature	= T (7.6) = 727 °C
transformation temperature	= T (13.0) = 546 °C
redox number	= 16.89

The original formula was reformulated. The main raw materials such as sand and dolomite were supplied from Ocean Glass Public Co., Ltd. The lithium spar from Australia was used in this experiment.

The chemical analysis of raw materials are summarized as followings.

Tab. 3.13 Chemical analysis of raw materials.

Component wt. %	Raw materials		
	Sand	Dolomite	Li-spar
SiO <sub>2</sub>	99.53	-	76.55
Fe <sub>2</sub> O <sub>3</sub>	0.017	0.050	0.10
Al <sub>2</sub> O <sub>3</sub>	0.40*	-	18.24
CaO	0.016	35.52	0.07
MgO	0.007	17.15	-
Na <sub>2</sub> O	0.009	-	0.26
K <sub>2</sub> O	0.033	-	0.24
Li <sub>2</sub> O	-	-	4.85
P <sub>2</sub> O <sub>5</sub>	-	-	0.08
TiO <sub>2</sub>	-	-	0.01
Cr <sub>2</sub> O <sub>3</sub>	1.88**	4.99**	-
MnO	5.63**	27.22**	0.03
Loss	0.15	-	0.24

\* had to be corrected to 0.27 (see later explanation)

\*\* in ppm

The chemical analysis of raw materials were used for the batch calculation. Batch calculation was performed by the matrix method using software UNIGLASS (Conradt, 1995). As usual in glass technology, the real formula shifts a little bit from the target one due to the use of natural raw materials.

### 3.3 Reformulation

It is recognized that glass from a tank furnace in a factory and the glass from a crucible in a laboratory are quite different. Therefore, for comparison, it is necessary to produce the original glass in the laboratory as well.

The amount of alkali (sodium) in the original glass formula is 14.30 wt. %. It was reduced to 13.50, 13.0, 12.5 wt. % respectively. Viscosity was adjusted by  $B_2O_3$  and  $Li_2O$ . There were totally 4 glass formula in this study.

A target glass composition was designed semi-automatically by varying the oxide composition and by observing the glass properties calculated and displayed on-line. When the glass composition met the desired property profile, the task was finished. The gob temperature T(3.0) was adjusted with first priority. Table 3.14 shows the comparison of the target formula and the real formula calculated on screen.

Tab. 3.14 Comparison of glass formulas.

Components	Target formula (wt. %)	Real formula (wt. %)
$SiO_2$	72.38	72.40
$Fe_2O_3$	0.00	0.02
$Al_2O_3$	1.61	1.71
CaO	7.74	7.76
MgO	3.36	3.75
$K_2O$	-	0.02
$Na_2O$	14.30	14.34

As seen from the above table, target and real formula show a remarkable difference in  $Al_2O_3$ . It was important to keep the  $Al_2O_3$  content fixed

because of its effectiveness on chemical durability. During the preliminary calculations, it was discovered that the data on glass composition and raw material compositions communicated by the contractor were incompatible. This was corrected by assuming that the glass composition had been determined without error; the alumina content of sand was corrected accordingly from 0.40 % to 0.27 %. Eventually the adapted real glass formula calculated had the composition as follows.



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Tab. 3.15 Chemical composition of original glass formula.

Chemical composition in wt. %	
SiO <sub>2</sub>	72.46
Fe <sub>2</sub> O <sub>3</sub>	0.02
Al <sub>2</sub> O <sub>3</sub>	1.61
CaO	7.77
MgO	3.75
K <sub>2</sub> O	0.02
Na <sub>2</sub> O	14.36
mol % total alkali oxide = 13.76	
characteristic temperatures and related viscosity	
liquidus temperature	= 1015 °C
refining temperature	= T (2.0) = 1464 °C
gob temperature	= T (3) = 1205 °C
Littleton temperature	= T (7.6) = 726 °C
transformation temperature	= T (13.0) = 546 °C
redox number	= 16.89

The other three formulas called N13.5, N13.0, N12.5 were designed in the same way as described above (see tables 3.16 to 3.18).

Tab. 3.16 Chemical composition of N 13.50.

Chemical composition in wt. %	
SiO <sub>2</sub>	72.80
Fe <sub>2</sub> O <sub>3</sub>	0.03
Al <sub>2</sub> O <sub>3</sub>	1.61
CaO	7.76
MgO	3.75
K <sub>2</sub> O	0.02
Na <sub>2</sub> O	13.46
B <sub>2</sub> O <sub>3</sub>	0.46
Li <sub>2</sub> O	0.11
mol % total alkali oxide	= 13.36
characteristic temperatures and related viscosity	
liquidus temperature	= 1039 °C
refining temperature	= T (2.0) = 1463 °C
gob temperature	= T (3) = 1204 °C
Littleton temperature	= T (7.6) = 729 °C
transformation temperature	= T (13.0) = 549 °C
redox number	= 16.89

Tab. 3.17 Chemical composition of N 13.00.

Chemical composition in wt. %	
SiO <sub>2</sub>	73.13
Fe <sub>2</sub> O <sub>3</sub>	0.03
Al <sub>2</sub> O <sub>3</sub>	1.61
CaO	7.82
MgO	3.77
K <sub>2</sub> O	0.02
Na <sub>2</sub> O	13.07
B <sub>2</sub> O <sub>3</sub>	0.58
Li <sub>2</sub> O	0.15
mol % total alkali oxide = 12.79	
characteristic temperatures and related viscosity	
liquidus temperature	= 1044 °C
refining temperature	= T (2.0) = 1463 °C
gob temperature	= T (3) = 1204 °C
Littleton temperature	= T (7.6) = 729 °C
transformation temperature	= T (13.0) = 550 °C
redox number	= 16.89

Tab. 3.18 Chemical composition of N 12.50.

Chemical composition in wt. %	
SiO <sub>2</sub>	73.15
Fe <sub>2</sub> O <sub>3</sub>	0.03
Al <sub>2</sub> O <sub>3</sub>	1.61
CaO	7.91
MgO	3.70
K <sub>2</sub> O	0.04
Na <sub>2</sub> O	12.51
B <sub>2</sub> O <sub>3</sub>	0.80
Li <sub>2</sub> O	0.25
mol % total alkali oxide	= 12.49
characteristic temperatures and related viscosity	
liquidus temperature	= 1069 °C
refining temperature	= T (2.0) = 1463 °C
gob temperature	= T (3) = 1205 °C
Littleton temperature	= T (7.6) = 731 °C
transformation temperature	= T (13.0) = 552 °C
redox number	= 16.89



### 3.4 Batch Preparation

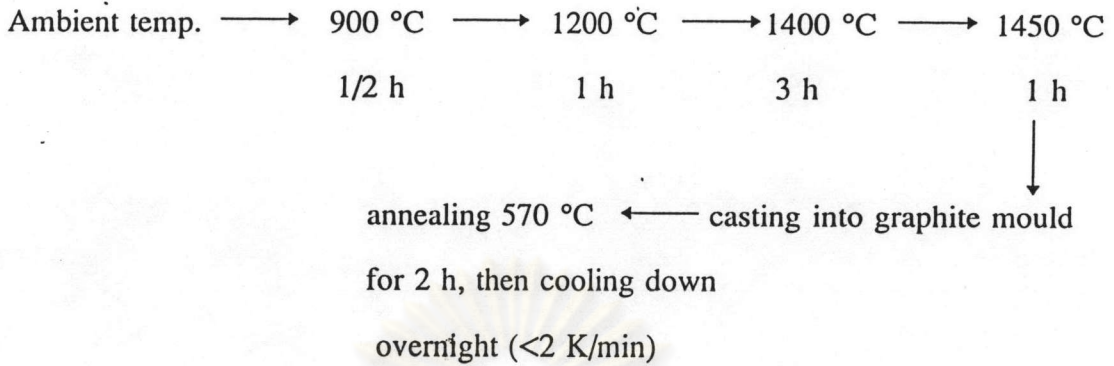
After the glass compositions were calculated, they were converted into a batch composition referred to raw materials dried at 110 °C. Table 3.19 shows the batch compositions in 100 g of total batch.

Tab 3.19 Batch composition of reformulated formulas.

Raw materials	Original	N13.5	N13.0	N12.5
Sand	60.13	59.2	59.07	57.9
Soda ash	19.74	18.32	17.75	16.88
Dolomite	18.04	18.09	18.25	17.95
Alumina	1.17	0.88	0.46	0.41
Borax.5H <sub>2</sub> O	-	0.62	0.78	1.07
Boric acid	-	0.15	0.20	0.28
Limestone	-	-	-	0.35
Li-spar	-	1.89	2.59	4.29
Na <sub>2</sub> SO <sub>4</sub>	0.56	0.54	0.54	0.53
NaNO <sub>3</sub>	1.33	0.33	0.32	0.32
Sb <sub>2</sub> O <sub>3</sub>	0.04	0.04	0.03	0.03

### 3.5 Melting and Annealing

The melting was performed in an electrical furnace in a chamotte crucible. The maximum melting temperature was 1450 °C. The melting schedule is shown below.



### 3.6 Surface Analysis

After the melting was completed, the four glass samples obtained were cut into chips for further surface analysis measurements. These were etching tests and extraction tests (see 2.2 and 2.3 ). Each parameter had to be exactly the same as in the previous measurements. The results were compared among the original glass formula and the reformulated ones.

### 4. Characterization of Existing Bloom

In the factory, the glass articles with bloom are classified into many levels due to the appearance and property of bloom. The level no. 5 on the sample called PB5 is the most serious one. The glass surface looks dirty and translucent because of the permanent bloom which cannot be wiped off by water.

The glass surface and its chemical composition of bloom were investigated by SEM and EDX.