Chapter 4

Result

Atmospheric Condition in Warehouses

After about 8 months, a lot of records from hygrometers were obtained. There were collected into graphs of relative humidity (%) and temperature T in °C versus duration (1 week or 1 month). Figure 4.1 demonstrates the kind of data.

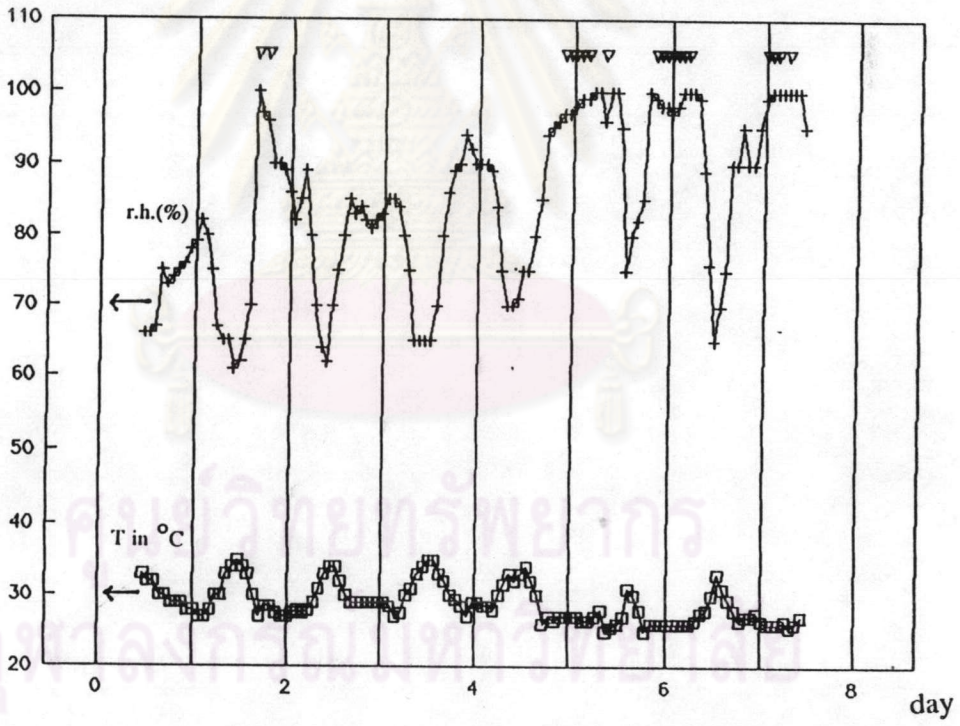
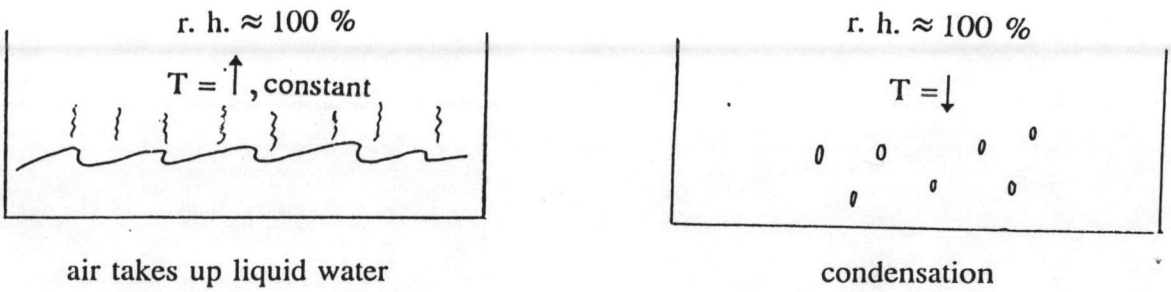


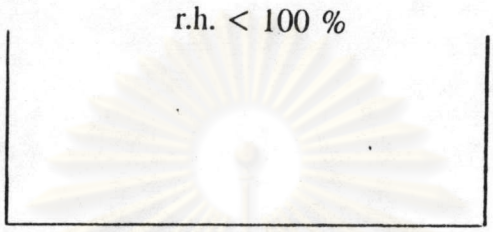
Fig 4.1 Results from hygrometer, warehouse 2 (WH 2), 29/06/95-06/07/95.

If the relative humidity exceeds 95 % and T drops, liquid water will occur. The following drawings are meant for better understanding.



air takes up liquid water

condensation



no liquid water present, "dry"

In figure 4.1, the symbol ∇ indicates condensation. For further records, see appendix B. Data of saturation temperatures in °C and absolute water content in g/m^3 can be seen in appendix C.

After investigation of all the records, it was found that the atmospheric condition among WH 1,WH 2, WH 4 are similar; condensation occurs as isolated event only. But in WH 8 the relative humidity is always high causing condensation which leads to the reaction at the glass surface.

Surface Analysis of Freshly Produced Glass Articles

1. Etching tests

The average dissolution depth calculated from weight loss as described in 2.2.4 of 8 glass samples from each step are presented in table 4.1. For comparison, samples of a container glass (BG) from different origin are shown, too.

Tab. 4.1 Dissolution depth of glass samples in nm after intervals of 15 sec of HF etching.

Etch no.	B1213 NA	B1213 A	B1408 NA	B1408 A	P0340 NA	P0340 A	BG NA	BG A
1	85	75	76	105	139	163	92	114
2	88	82	62	74	97	108	75	96
3	72	72	48	63	69	106	65	74
4	69	69	57	68	96	105	57	77
5	65	55	41	69	71	65	76	93
6	58	59	48	59	64	74	50	82
7	59	61	60	59	68	75	44	70

NA = non-annealed sample, A = annealed sample

The description of samples are presented again below

B1213: forming by press-blow, indirect lehr,

B0208: forming by press-blow, indirect lehr,

B1408: forming by press-blow, direct lehr,

P0340: forming by press-press, indirect lehr,

BG : forming by press-blow, indirect lehr, different glass composition

As seen from table 4.1, the dissolution depth of P0340 (the sample from press-press machine) was highest. Concerning the annealing process, the dissolution depths of the non-annealed samples seem to be smaller than for the annealed samples. In factory BG, the contrary is the case.

Each sample yielded 7 liquid samples of etching solution which then were measured for the concentration of sodium by flame photometer. The weight percent

of sodium oxide was calculated as described in 2.2.5. Table 4.2 below shows the results.

Tab. 4.2 Amount of Na_2O in etching solutions in nominal wt. % of the dissolved glass layer.

Etch no.	B1213 NA	B1213 A	B1408 NA	B1408 A	P0340 NA	P0340 A	BG NA	BG A
1	15.9	12.8	22.3	10.2	23.3	5.3	10.7	11.9
2	13.4	11.8	27.3	17.8	32.2	9.2	11.7	11.1
3	14.1	16.8	25.4	16.9	45.3	4.8	11.2	14.5
4	14.7	15.1	27.8	15.8	-	3.8	12.9	12.5
5	14.4	16.7	38.8	14.2	42.3	6.2	9.7	9.4
6	16.2	15.3	45.2	16.6	46.9	5.4	16.3	10.7
7	15.8	15.8	37.8	15.6	45.7	5.3	13.3	14.4

As shown in table 4.2, the amount of Na_2O in the surface of P0340 and B1408 was extremely high, but after annealing, it dropped remarkably. B1213 had the same tendency for the outermost surface zone. By contrast, The sample from factory BG showed quite low Na_2O levels from the beginning, and no further decrease during annealing.

The dissolution depth and weight percent of Na_2O obtained after the analysis of each sample is plotted independently versus the etching time (time interval = 15 sec). Profiles are shown in figures 4.2-4.5.

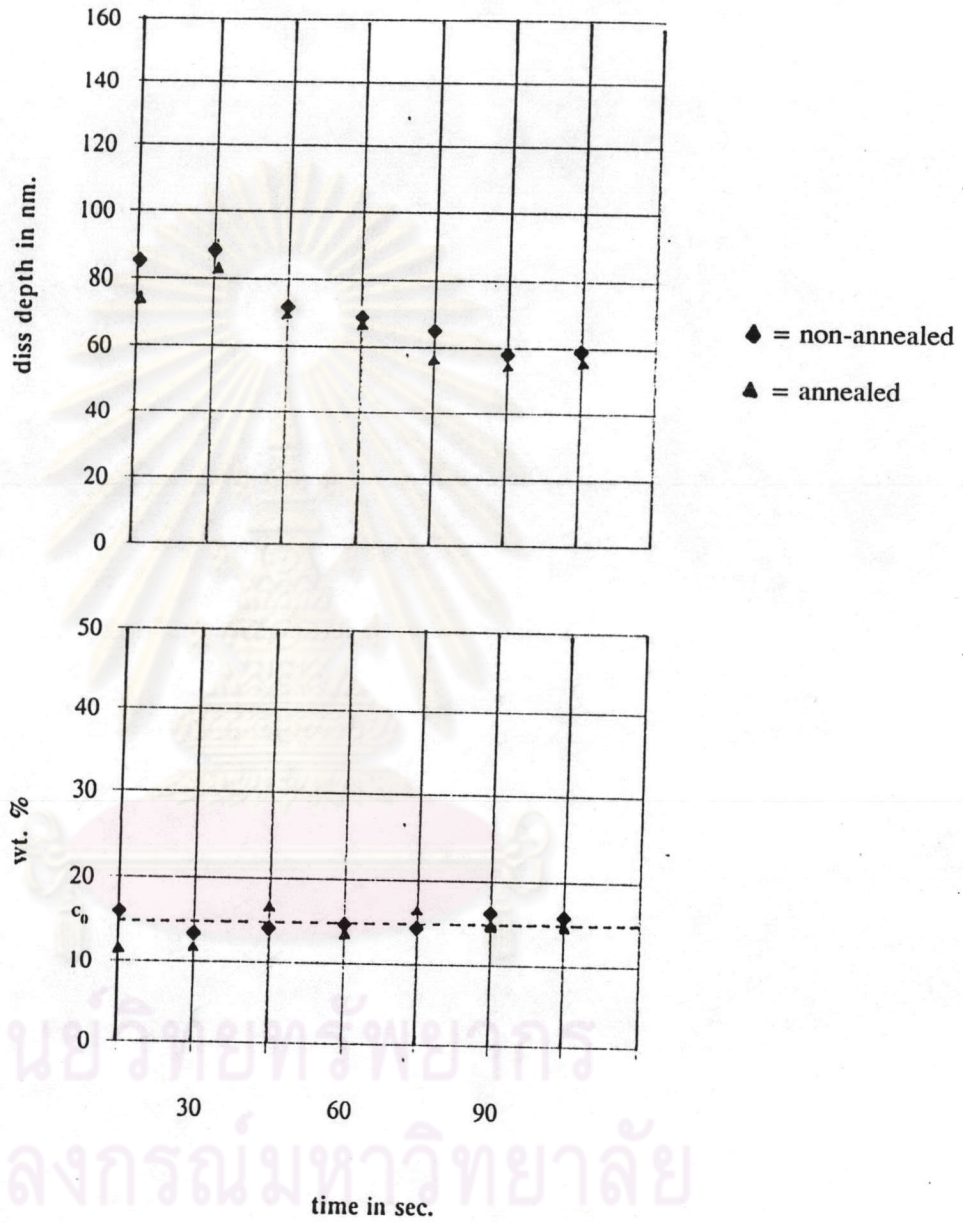


Fig 4.2 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of B1213NA and B1213A.

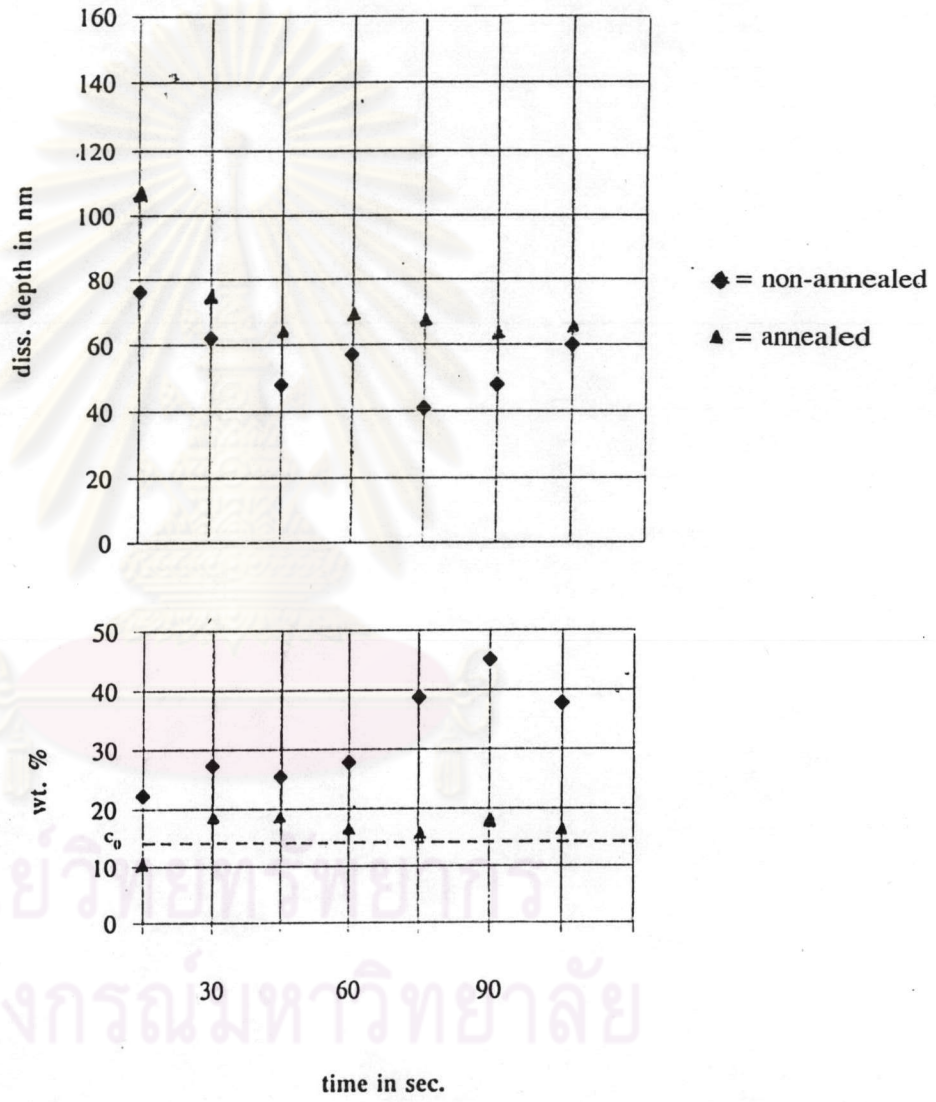


Fig 4.3 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of B1408NA and B1408A.

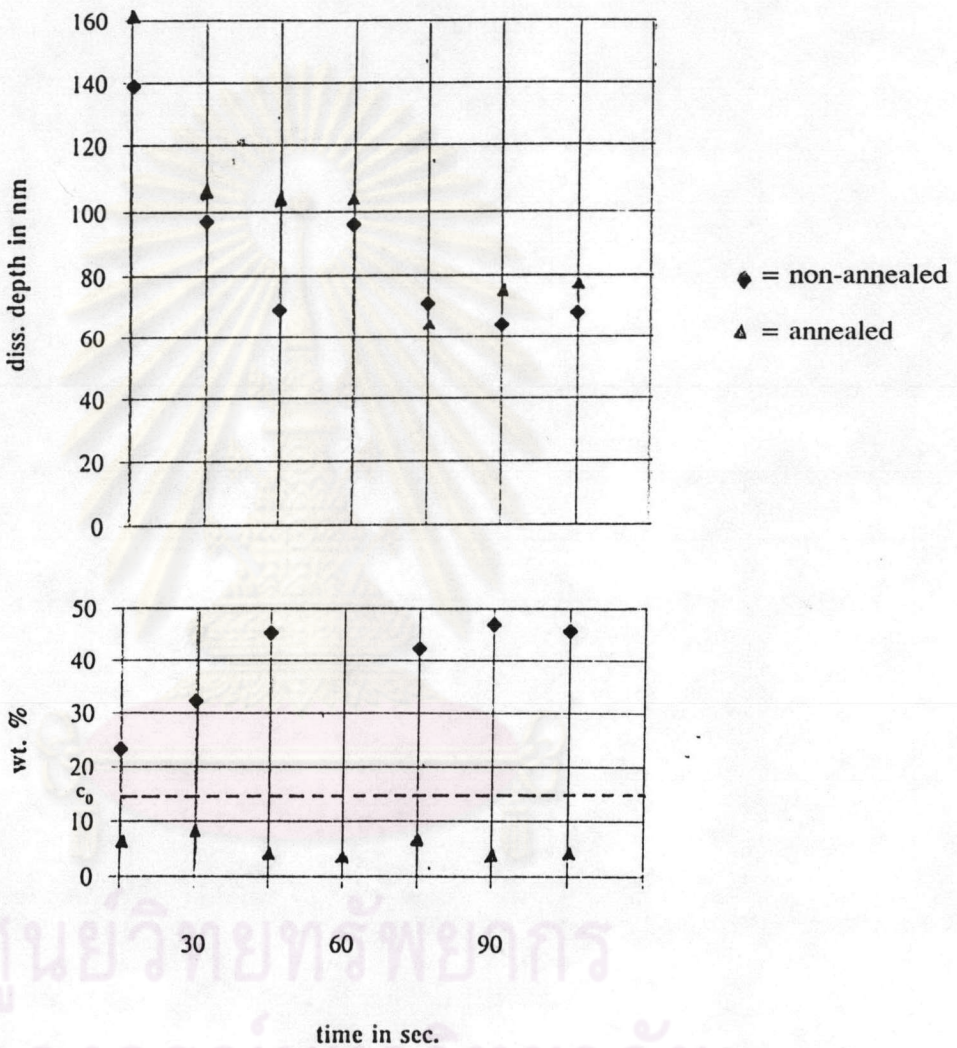


Fig 4.4 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of P0340NA and P0340A

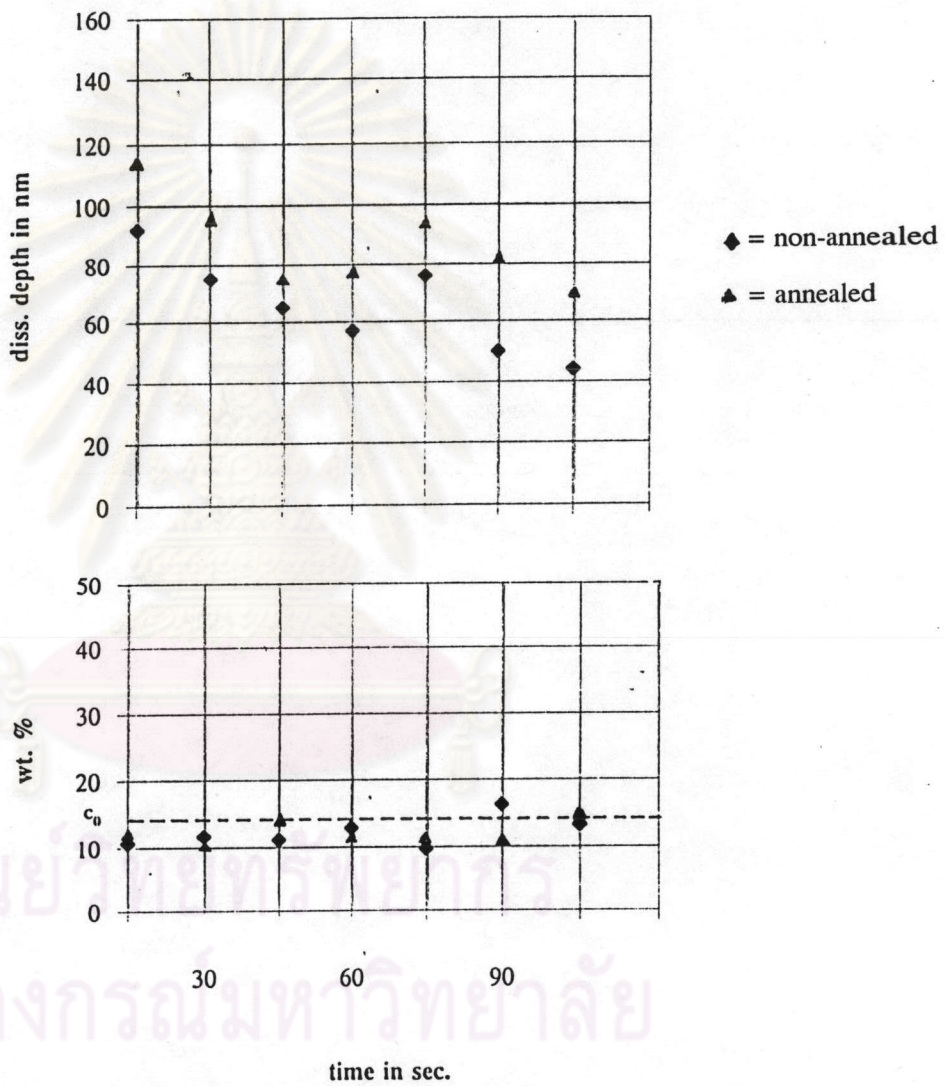


Fig 4.5 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of BG-NA and BG-A.

2. Extraction tests

The procedure of extraction tests was already described in 2.3.1. The surface area and conductivity data are shown in table 4.3.

Tab. 4.3 Raw data of extraction test.

Sample	Surface area (cm^2)	Conductivity (μs)
B0208	NA: 41.6315	NA: 33.4
	A: 27.2423	A: 34.5
B1213	NA: 27.0275	NA: 18.0
	A: 37.6357	A: 45.4
B1408	NA: 38.4239	NA: 43.7
	A: 31.0262	A: 31.5
P0340	NA: 26.3403	NA: 33.9
	A: 29.4092	A: 39.8
BG	NA: 25.2633	NA: 13.4
	A: 29.5206	A: 15.2

* Conductivity of blank (DI water) = 4.2 μS

Calculation could be done following 2.3.2. The results of concentration of Na are presented in table 4.4.

Tab. 4.4 Results of extraction test

Sample	µmol equivalent of Na/cm^2
B0208	NA: 33
	A: 52
B1213	NA: 27
	A: 50
B1408 *	NA: 47
	A: 42
P0340 **	NA: 53
	A: 56
BG	NA: 21
	A: 21

* = sample from direct annealing furnace

** = sample from press-press forming machine

As seen from the above table, among the results of B0208, B1213, B1408, P0340, (samples from the same factory), B1408 was different from the rest. The results for annealed samples were smaller than the non-annealed ones. The rest showed the opposite behavior. This goes together well with the finding that the SiO_2 network of B1408 became stronger during annealing, while it weakened for the other samples. The result of P0340 supported the result of its dissolution depth, i, e., the surface of press-press samples was weak. As an interesting result, the samples from BG factory, showed that the annealing process is designed well.

For cross checking of the measurement, the results from flame photometer and conductivity meter were compared in units of mol Na/cm^2. For the flame photometer, results of the etching step 1 and step 2 were selected and averaged.

Tab. 4.5 Comparison between the flame photometry and conductivity tests

Sample		FES test (μmol Na/cm^2)			Extraction test (μmol Na/cm^2)
		step 1	step 2	averages	
B1213	NA	32.4	28.2	30.3	27
	A	23	23	23	
B1408	NA	40.7	40.1	40.4	47
	A	25.5	31.7	28.6	
P0340	NA	77.5	74.7	76.1	53
	A	16	13.7	14.9	56
BG	NA	23.4	21	22.2	21
	A	32.2	25.8	29	

Results shows that the two measurements were compactible. The ratio of μmol Na for the non-annealed samples by FES and by the extraction test is 1.12 ± 0.21. For the annealed samples, no correlation was found.

Surface Analysis of the Reformulated Glass.

Like in table 4.2, the following results including leaching test and extraction test are presented in table 4.6 and table 4.7, respectively.

Tab. 4.6 Dissolution depths of the reformulated glass in nm after intervals of 15 sec of HF etching.

Etch no.	Original glass	N13.5	N13.0	N12.5
1	135	115	123	135
2	105	80	95	105
3	95	85	82	75
4	80	75	74	75
5	60	50	83	80
6	80	70	60	60
7	60	55	71	50

The trend of the dissolution depth profile was similar to the previous group of samples.

The concentration of sodium in the etching solution was detected by flame photometry. Then the weight percent of Na_2O was calculated.

Tab. 4.7 Amount of Na_2O in etching solution of the reformulated glass in nominal wt. % of the dissolved glass layers.

Etch no.	Original glass	N13.5	N13.0	N12.5
1	11.8	10.1	9.2	8.9
2	10.6	11.1	12.1	8.1
3	10.1	12.5	8.6	10.2
4	12.0	13.9	9.7	10.2
5	14.8	12.4	10.4	8.7
6	11.1	13.8	10.4	10.6
7	14.8	6.5	10.6	12.7

At the first step of etching, the results showed that the amount of Na_2O in the near surface zone of the glass was decreased as the wt. % of Na_2O in the glass formula decreased.

Similar to the freshly produced samples (see figures 4.6-4.9), the profiles of the dissolution depth and the amount of Na_2O distribution in the near surface zone are presented versus the etching time.

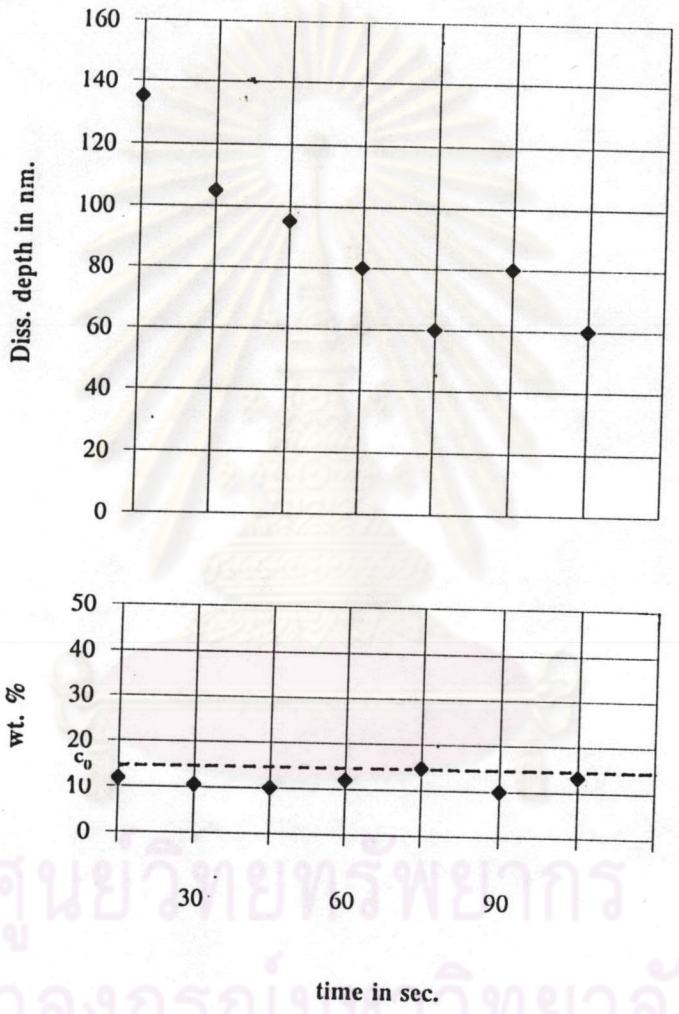


Fig 4.6 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of the original formula.

SATURATION TEMPERATURES IN °C

T/°C	% r.H. 45	50	55	60	65	70	75	80	85	90	95	100
15.0	2.4	4.0	5.4	6.8	8.0	9.2	10.3	11.4	12.3	13.3	14.2	15.0
16.0	3.3	4.9	6.4	7.7	9.0	10.2	11.3	12.3	13.3	14.3	15.1	16.0
17.0	4.2	5.8	7.3	8.7	10.0	11.1	12.3	13.3	14.3	15.2	16.1	17.0
18.0	5.1	6.7	8.2	9.6	10.9	12.1	13.2	14.3	15.3	16.2	17.1	18.0
19.0	6.0	7.7	9.2	10.6	11.9	13.1	14.2	15.3	16.3	17.2	18.1	19.0
20.0	6.9	8.6	10.1	11.5	12.8	14.0	15.2	16.2	17.2	18.2	19.1	20.0
21.0	7.9	9.5	11.0	12.5	13.8	15.0	16.1	17.2	18.2	19.2	20.1	21.0
22.0	8.8	10.4	12.0	13.4	14.7	15.9	17.1	18.2	19.2	20.2	21.1	22.0
23.0	9.7	11.4	12.9	14.3	15.7	16.9	18.1	19.1	20.2	21.2	22.1	23.0
24.0	10.6	12.3	13.8	15.3	16.6	17.9	19.0	20.1	21.2	22.2	23.1	24.0
25.0	11.5	13.2	14.8	16.2	17.6	18.8	20.0	21.1	22.1	23.1	24.1	25.0
26.0	12.4	14.1	15.7	17.2	18.5	19.8	20.9	22.1	23.1	24.1	25.1	26.0
27.0	13.3	15.0	16.6	18.1	19.4	20.7	21.9	23.0	24.1	25.1	26.1	27.0
28.0	14.2	16.0	17.6	19.0	20.4	21.7	22.9	24.0	25.1	26.1	27.1	28.0
29.0	15.1	16.9	18.5	20.0	21.3	22.6	23.8	25.0	26.1	27.1	28.1	29.0
30.0	16.0	17.8	19.4	20.9	22.3	23.6	24.8	25.9	27.0	28.1	29.1	30.0
31.0	16.9	18.7	20.3	21.8	23.2	24.5	25.8	26.9	28.0	29.1	30.0	31.0
32.0	17.8	19.6	21.2	22.8	24.2	25.5	26.7	27.9	29.0	30.0	31.0	32.0
33.0	18.7	20.5	22.2	23.7	25.1	26.4	27.7	28.9	30.0	31.0	32.0	33.0
34.0	19.6	21.4	23.1	24.6	26.0	27.4	28.6	29.8	30.9	32.0	33.0	34.0
35.0	20.5	22.3	24.0	25.6	27.0	28.3	29.6	30.8	31.9	33.0	34.0	35.0
36.0	21.4	23.2	24.9	26.5	27.9	29.3	30.6	31.8	32.9	34.0	35.0	36.0
37.0	22.3	24.2	25.8	27.4	28.9	30.2	31.5	32.7	33.9	35.0	36.0	37.0
38.0	23.2	25.1	26.8	28.3	29.8	31.2	32.5	33.7	34.8	35.9	37.0	38.0
39.0	24.1	26.0	27.7	29.3	30.7	32.1	33.4	34.7	35.8	36.9	38.0	39.0
40.0	25.0	26.9	28.6	30.2	31.7	33.1	34.4	35.6	36.8	37.9	39.0	40.0
41.0	25.9	27.8	29.5	31.1	32.6	34.0	35.3	36.6	37.8	38.9	40.0	41.0
42.0	26.7	28.7	30.4	32.0	33.5	35.0	36.3	37.5	38.7	39.9	41.0	42.0
43.0	27.6	29.6	31.3	33.0	34.5	35.9	37.2	38.5	39.7	40.9	42.0	43.0
44.0	28.5	30.4	32.2	33.9	35.4	36.8	38.2	39.5	40.7	41.8	42.9	44.0
45.0	29.4	31.3	33.1	34.8	36.3	37.8	39.1	40.4	41.7	42.8	43.9	45.0

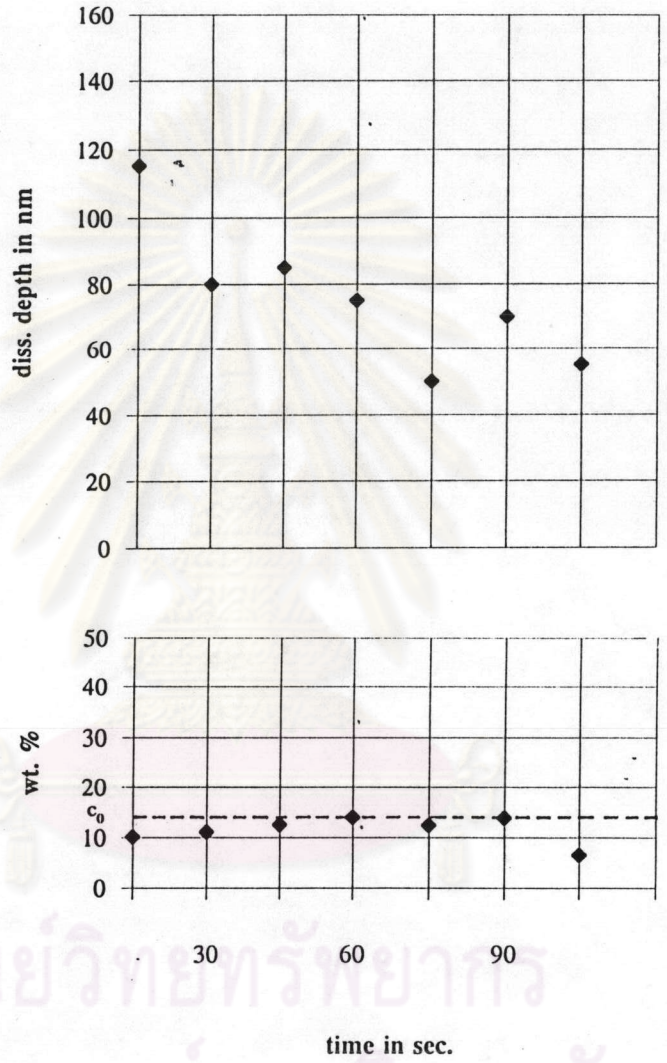


Fig 4.7 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of N13.5.

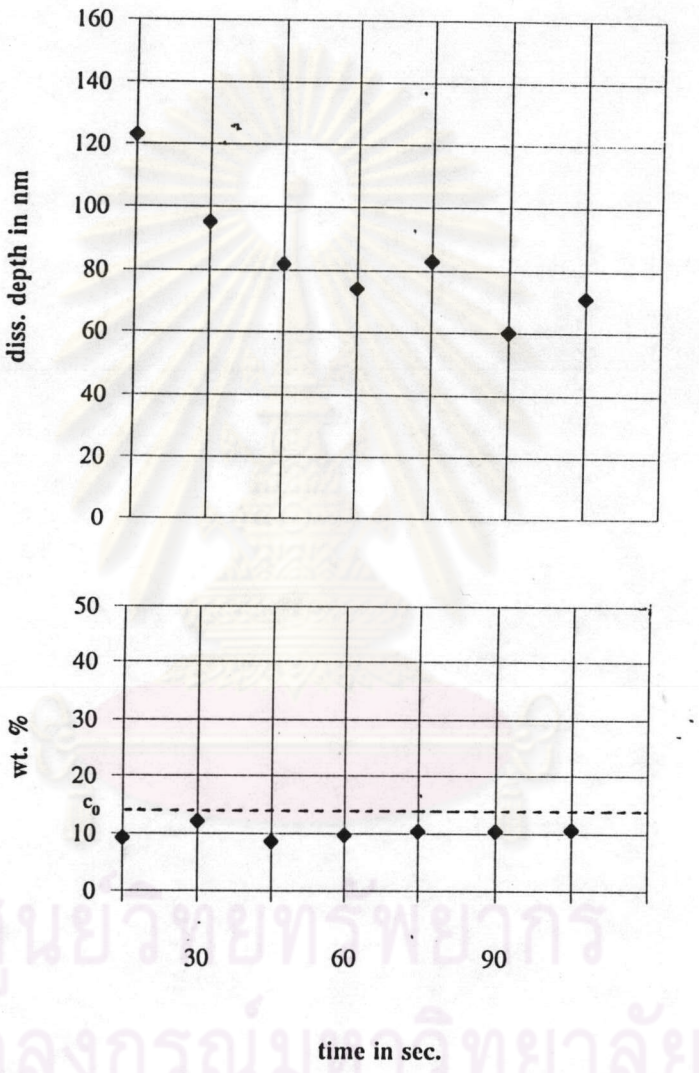


Fig 4.8 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of N13.0.

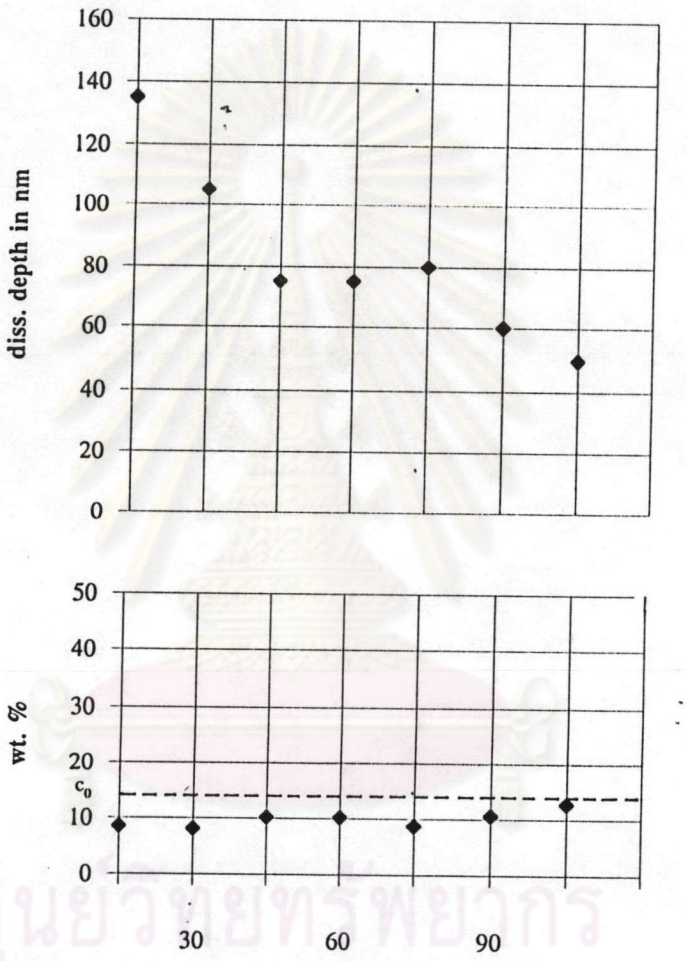


Fig 4.9 Profiles of dissolution depth in nm and the amount of Na_2O in etching solution in nominal wt. % of the dissolved glass layers versus time of N12.5.

The extraction test of the reformulated glass measured by the conductivity meter had raw data as follows:

Tab 4.8 Data of the extraction test.

Sample	Surface area (cm^2)	Conductivity (μS)
Original glass	29.9560	15.5
N13.5	29.8012	19.5
N13.0	26.5439	23.9
N12.5	40.0941	44.5

Conductivity of blank (DI water) = 1.2 (μS)

The calculation was followed as described in 2.3.2.Table 4.8 shows the results after the calculation.

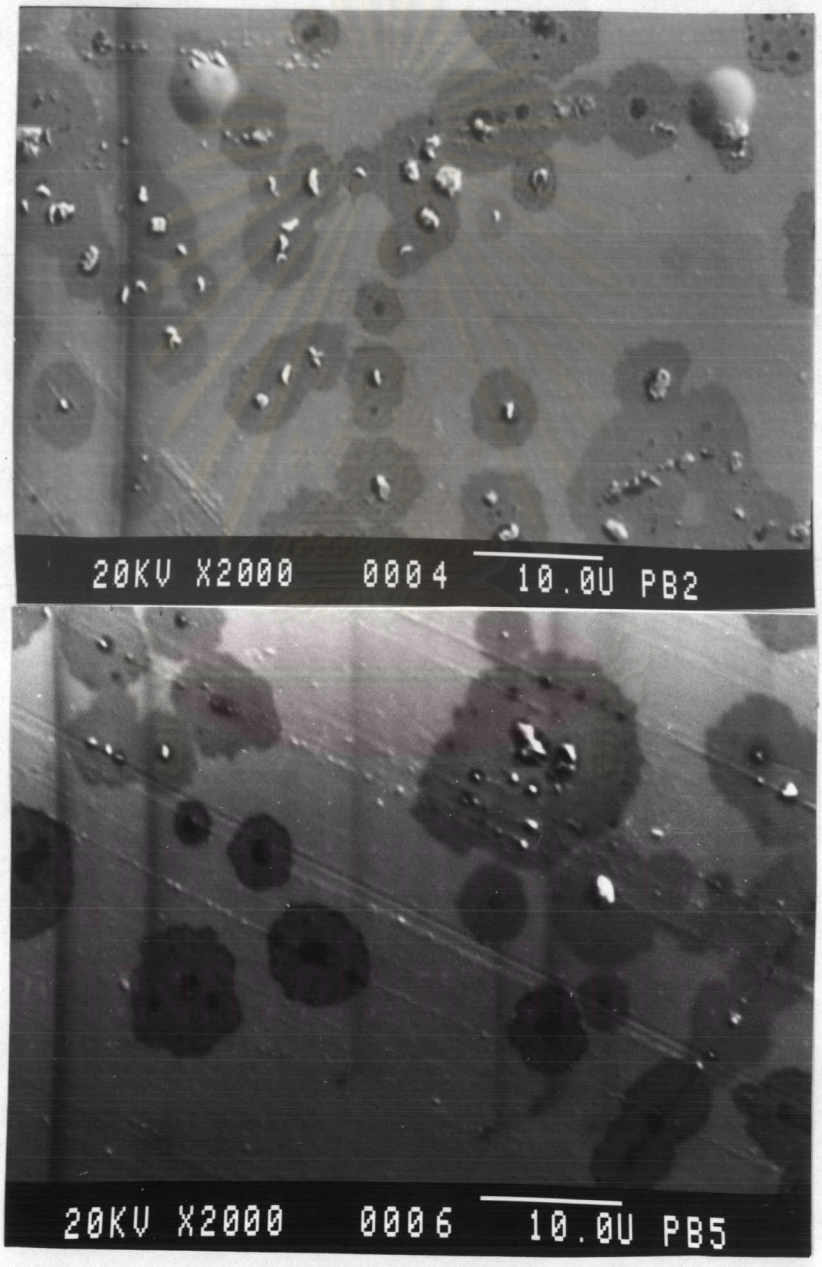
Tab. 4.9 Results of the extraction of the reformulated glass.

Sample	μmole equivalent of Na/cm^2
Original glass	46
N13.5	37
N13.0	27
N12.5	21

As seen from table 4.9, the results very clearly followed the Na_2O level in the glass and supported the results from table 4.7. A regression analysis of the mol % of total alkali versus the amount of leached alkali yield a square regression coefficient of $r^2 = 0.998$.

Characterization of the Existing Bloom

The inspection of the existing bloom was carried out by SEM on samples kept in the warehouse for a long time. PB2 and PB5 which had a different features of bloom (seen by the naked eye) were examined. Figure 4.10 shows the morphology of the glass surfaces.



(a)

(b)

Fig. 4.10 Illustrations of glass surfaces with bloom: a, = PB2 , b = PB5.

The scattered dark phases and crystals located at their centres were found both from PB2 and PB5. The chemical compositions of crystals on the glass surfaces were analyzed by EDX. Table 4.10 shows the results.

Tab. 4.10 Chemical analysis by EDX.

EDX analysis of bloom,

g/mol			40.08	28.09	26.98	24.31	22.99	196.97
			Ca	Si	Al	Mg	Na	Au
peak height, raw EDX data:								
bloom	PB501	high	91.3	-	114.1	44.1	26.5	-
		low	10.2	77.9	13.8	4.5	3.3	82.7
bloom	PB502	high	54.2	-	49.1	19.5	11.9	-
		low	12.5	79.5	11.8	4.0	1.9	80.9
glass	PB502	high	56.8	-	26.0	23.0	19.6	-
		low	13.1	124.0	6.1	5.5	4.0	58.8
peak height per g mol:								
bloom	PB501	high	2.28	-	4.23	1.81	1.15	-
		low	0.25	2.77	0.51	0.19	0.14	0.42
bloom	PB502	high	1.35	-	1.82	0.80	0.52	-
		low	0.31	2.83	0.44	0.16	0.08	0.41
glass	PB502	high	1.42	-	0.96	0.95	0.85	-
		low	0.33	4.42	0.23	0.23	0.17	0.30
"molar" ratios per Al:								
bloom	PB501	high	0.54	-	1.00	0.43	0.27	-
		low	0.50	5.42	1.00	0.36	0.28	0.82
bloom	PB502	high	0.74	-	1.00	0.44	0.28	-
		low	0.71	6.47	1.00	0.38	0.19	0.94
glass	PB502	high	1.47	-	1.00	0.98	0.88	-
		low	1.45	19.53	1.00	1.00	0.77	1.32

The chemical analysis from the above table indicates that the composition of bloom is similar to the glass composition itself, except for the molar ratios. In the bloom, the ratios are close to natural minerals in cementic and feldspartic groups such as CASH phases, NAS_4H_2, $C_5S_6H_{10.5}$, AS_2H_2, CAH_{10} ($N=Na_2O$, $C=CaO$, $A=Al_2O_3$, $S=SiO_2$, $H=H_20$).

After the surfaces of PB5 was observed, scratches with the dark phases were found as shown in figure 4.11.

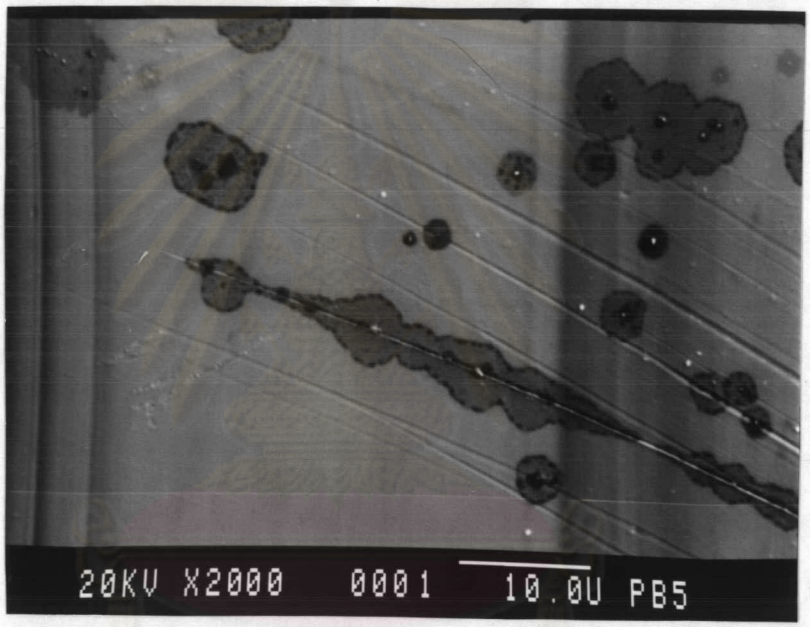
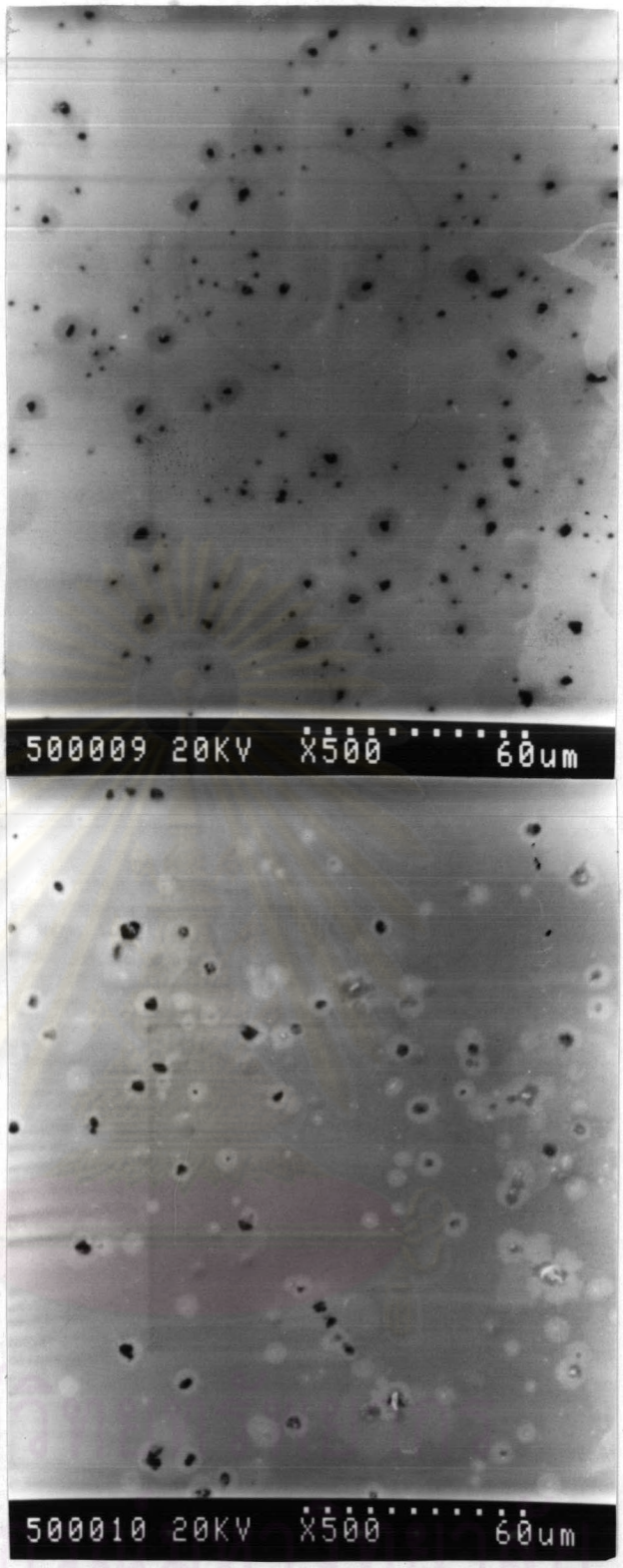


Fig. 4.11 Micrograph of PB5 surface with scratches.

This scratches and dark phases might be caused by the forming process. In an effort to check whether the dark phases are oil depositions, the samples were cleaned with tissue soaked in benzene and observed by SEM again. Oil should dissappear under such treatment.



(a)

(b)

Fig 4.12 Glass surfaces after cleaning with benzene a = PB2, b = PB5.

The dark phases were still there, but the crystallites had been swept away by the tissue, leaving holes behind.