

CHAPTER III

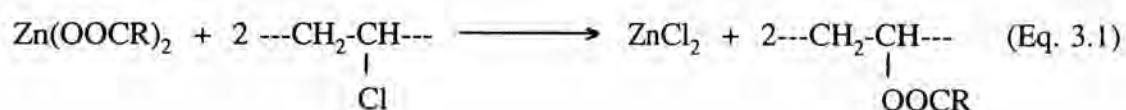
RESULTS AND DISCUSSION

3.1 Ca/Zn stabilizers and co-stabilizers for rigid PVC profile

Calcium stearate and zinc stearate are not used separately because they have different function for stabilizing PVC. They act as synergists.

Zinc stearate can improve the initial color of PVC. The use of calcium stearate without zinc stearate results in poor initial color of PVC (Fig.3.1). The stabilizing mechanism of zinc stearate is the displacement of labile chlorine atoms in the PVC chain in order to eliminate initial sites of degradation (Eq. 3.1)⁽⁴⁾. However, higher amount of zinc stearate can increase the tendency of PVC to degrade because the $ZnCl_2$ which is formed in this reaction can promote dehydrochlorination. $ZnCl_2$ is a strong Lewis acid and consequently it acts as a catalyst for dehydrochlorination. For this reason, lead stabilizers, which have no destabilizing effect are more powerful than zinc stabilizers (Fig. 3.2 shows some of the side-effects of stabilizers on the degradation of PVC)⁽⁴⁾. Therefore, zinc stabilizers are never used alone: it is necessary to add some additive which can inhibit the negative effect of $ZnCl_2$.

Calcium stearate can solve this problem, as it is an alkaline carboxylate which serves as a reservoir for the chloride ion that is liberated in the course of the degradation of the PVC chain. It can exchange one of its acidic ligands for the partially spent heavy metal chloride-carboxylate (Eq. 3.2)⁽⁵⁾. By this reaction the destabilizing effect of $ZnCl_2$ is blocked (at least temporarily).



**INITIAL COLOR
(MILLED SHEET)**

ROLL TEMPERATURE : 195 °C










Ca-stearate (phr)	Zn-stearate (phr)		
	0	1	2
3			
6			
8			

Fig. 3.1 : Effect of the Ca- and Zn-stearate amount on the initial color of rigid PVC profile

Additionally, calcium stearate can improve the long term heat stability of PVC. Fig. 3.3 indicates that the higher amount of calcium stearate is the better heat stabilizer of PVC. The stabilizing mechanism of calcium stearate is due to its absorption of HCl (Eq. 3.3) that has evolved during PVC degradation.

However, higher amounts of calcium stearate can lead to over-lubrication because calcium stearate is also a lubricant. Therefore the ratio of calcium stearate and zinc stearate must be optimised. Moreover, when calcium stearate is used in higher amounts, PVC has a tendency to a slight yellow discoloration. In order to mitigate this problem and improve performance of calcium/zinc stabilizers, epoxidized soybean oil (ESBO), tris(nonylphenyl)phosphite, stearoylbenzoylmethane (SBM), Mg/Al hydroxide carbonate and butylated hydroxy toluene (BHT) were used as co-stabilizers in this work. These co-stabilizers cannot be used alone because they work in the presence of $ZnCl_2$ which acts as a catalyst.

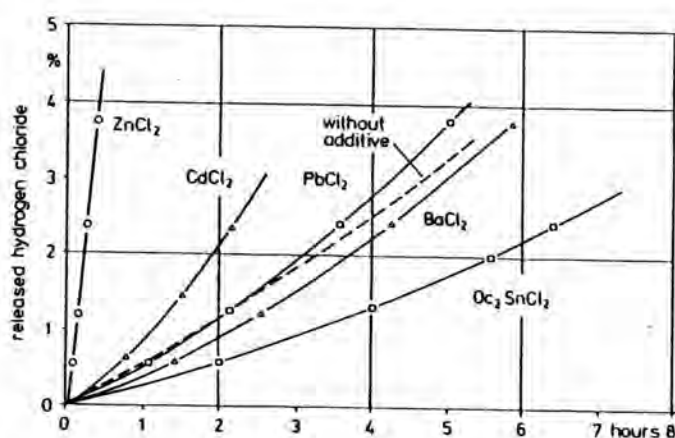


Fig 3.2 : Thermal dehydrochlorination of PVC in the presence of different metal chlorides ($175^{\circ}C$)

STATIC HEAT STABILITY

OIL BATH TEMPERATURE 190°C

TIME (min.)	BATCH NO.										
	1	2	3	4	5	6	7	8	9		
0											
5											
15											
25											
30											
45											
50											
60											
70											
80											
90											
95											
A*	3	3	3	6	6	6	8	8	8		
B*	0	1	2	0	1	2	0	1	2		

Remark : A* = Ca-stearate (phr), B* = Zn-stearate (phr)

Fig. 3.3 : Static heat stability of rigid PVC profile by variation of the Ca- and Zn-stearate ratio

ESBO can improve the long term heat stability of calcium/zinc stabilizers. Fig.3.4 indicates that the higher the amount of ESBO the better is the heat stability of PVC. The stabilizing mechanism of ESBO is due to its absorption of HCl (Eq. 3.4) and the displacement of labile chlorine atoms in the PVC chain (Eq. 3.5). $ZnCl_2$ is thought to function as catalyst of the displacement of labile chlorine atoms (Eq. 3.5)

For this reason, ESBO can retard dehydrochlorination. Therefore, ESBO is used to replace Ca-stearate for hydrogen chloride absorption thereby reducing the over-lubrication problem. However, higher amounts of ESBO can decrease the vicat temperature (softening temperature), because ESBO is considered as a secondary plasticizer. Fig.3.5 indicates the effect of ESBO on the vicat temperature of PVC. Therefore, the amount of ESBO must be optimized.

Tris(nonylphenyl)phosphite can improve the initial color of PVC (Fig3.6). Its stabilizing mechanism is due to its displacement of labile chlorine atoms of the PVC chain which forms in the presence of $ZnCl_2$. Therefore, it can mitigate the yellow tint problem of Ca-stearate (Eq. 3.6).

Furthermore, tris(nonylphenyl)phosphite is a secondary antioxidant and consequently it can retard dehydrochlorination by elimination of initiation sites which form by oxygen attack on the PVC chain.

STATIC HEAT STABILITY

OIL BATH TEMPERATURE 190°C

TIME (min.)	BATCH NO.					
	10	11	12	13	14	15
0						
5						
15						
25						
35						
45						
50						
60						
75						
85						
95						
100						
110						
A*	6/1	6/1	6/1	6/1	6/1	6/1
B*	0/0	0/0.5	0/1	3/0	3/0.5	3/1

Remark : A* = Ca/Zn-St (phr), B* = ESBO/tris(nonylphenyl)phosphite (phr)

Fig. 3.4 : Static heat stability of rigid PVC profile by variation of ESBO and tris(nonylphenyl)phosphite

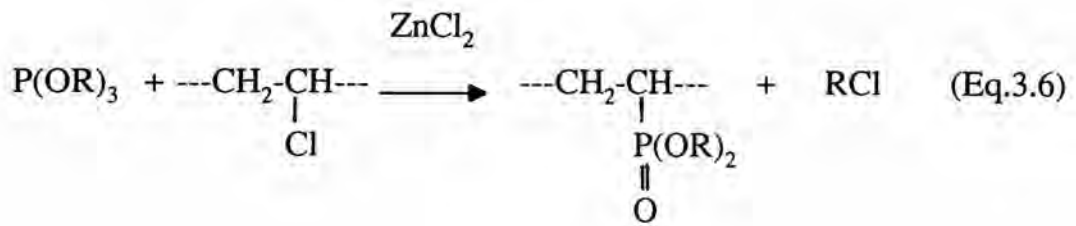
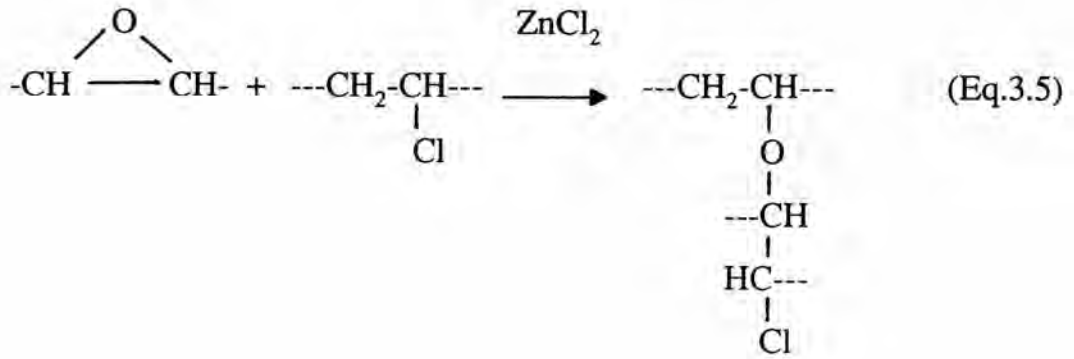
STATIC HEAT STABILITY

OIL BATH TEMPERATURE 190°C

TIME (min.)	BATCH NO.					
	16	17	18	19	20	21
0						
5						
15						
30						
45						
60						
75						
85						
95						
110						
120						
130						
140						
A*	6/1	6/1	6/1	6/1	6/1	6/1
B*	5/0	5/0.5	5/1	7/0	7/0.5	7/1

Remark : A* = Ca/Zn-St (phr), B* = ESBO/tris(nonylphenyl)phosphite (phr)

Fig. 3.4 : Static heat stability of rigid PVC profile by variation of ESBO and tris(nonylphenyl)phosphite (Continued)



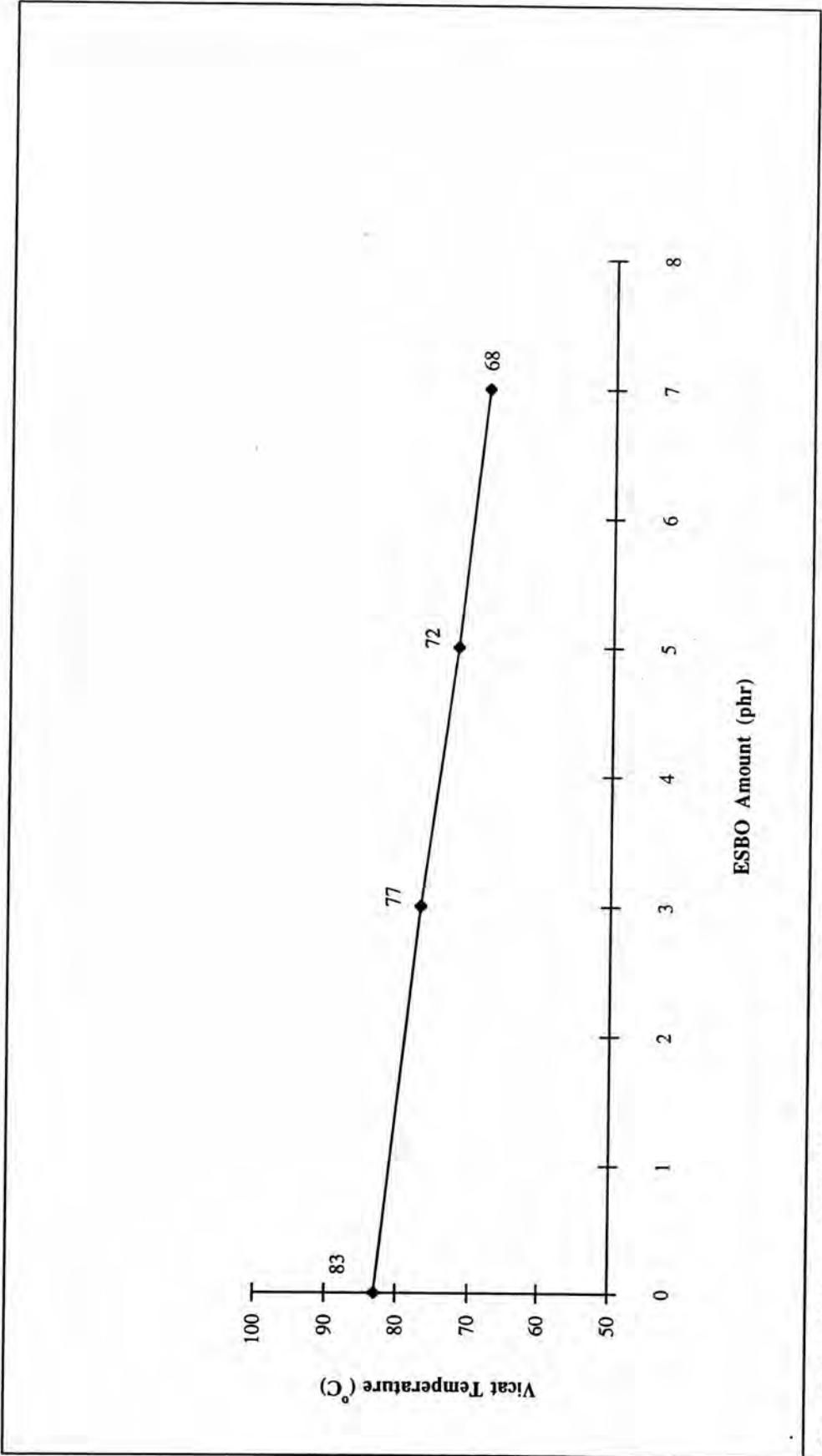


Fig. 3.5 : Effect of ESBO amount on vicat temperature of the rigid PVC profile

**INITIAL COLOR
(MILLED SHEET)**

ROLL TEMPERATURE : 195 °C

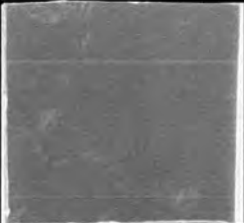

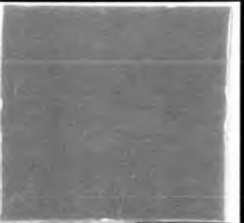




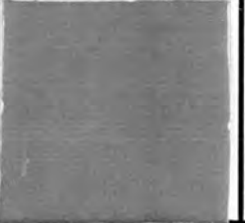
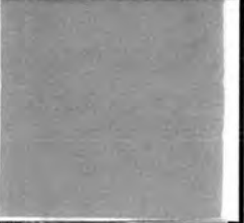
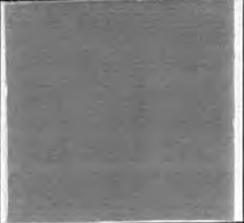
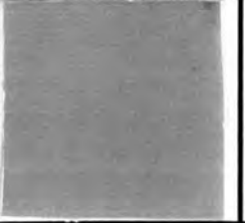
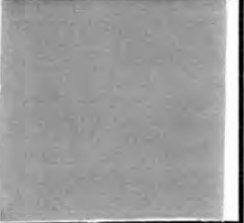
ESBO (phr)	Tris(nonylphenyl)phosphite (phr)		
	0	0.5	1
0			
3			
5			
7			

Fig. 3.6 : Effect of ESBO and tris(nonylphenyl)phosphite amount on the initial color of the rigid PVC profile

Even though ESBO and tris(nonylphenyl)phosphite are added to the Ca/Zn stabilizer system, the color of the milled sheet is still more yellow than it would be using a lead stabilizer. Therefore, it is necessary to add a co-stabilizer which acts as the polyene sequence for color improvement.

Stearoylbenzoylmethane is used for this purpose in order to preclude the formation of conjugated double bonds. Conjugated double bonds absorb electromagnetic radiation of various wavelengths, depending on the number of double bonds in the chain. With relatively few units, the absorption occurs in the ultraviolet region, but as the number of conjugated double bonds exceeds seven, or thereabouts, yellowing of the polymer becomes evident⁽⁵⁾. Fig. 3.7 shows that addition of stearoylbenzoylmethane results in excellent initial color. Furthermore, it can improve long term heat stability because it is able to react with the labile allylic chlorine atom through carbon alkylation. The substitution is catalysed by $ZnCl_2$.

Butylated hydroxy toluene (BHT) is used as an antioxidant. Its function is to protect the PVC chain from oxygen attack which leads to the new initiation site. But in this work addition of BHT results in poor heat stability because the use of phenolic antioxidant in the presence of tris(nonylphenyl)phosphite which has an antioxidant effect inherent is an over-dosage of antioxidant⁽⁴⁾.

STATIC HEAT STABILITY

OIL BATH TEMPERATURE 190°C

TIME (min.)	BATCH NO.					
	17	22	23			
0						
15						
45						
60						
75						
80						
90						
100						
120						
130						
140						
150						
A*	6/1	6/1	6/1			
B*	5/0.5	5/0.5	5/0.5			
C*	-	0.5/-	0.5/0.5			

Remark : A* = Ca/Zn-St (phr), B* = ESBO/tris(nonylphenyl)phosphite (phr)

C* = SBM/BHT (phr)

Fig. 3.7 : Effect of SBM and BHT on the static heat stability

3.2 The effect of lubricants and the optimum formulation for heat stability and processability

3.2.1 The effect of lubricants

When choosing a stabilizer, the proposed lubricant system must also be considered. This process is known as the correction of the stabilizer/lubricant balance. This is an important factor as some lubricants have a stabilizing action while some stabilizers have a lubricant action. Thus synergistic effects can arise and lead to undesirable results such as poor surface appearance and a plate-out effect.

In this work, lubricants did not effect the heat stability as shown by comparison of batches no. 22 and 24 by the static and dynamic heat stability test (Fig. 3.8, 3.9). However, the surface appearance is effected as shown by comparison of batch no. 22 with 24 by the extrusion test (Fig. 3.10). Batch no. 22 (which has no lubricant) shows a rough surface at the edge of strip (specimen) while batch no. 24 which contained lubricant, results in a smooth surface at the same position.

Additionally, lubricants can effect the flow which is shown by the Melt Index (MI), Table3.1.

TABLE 3.1 : Effect of lubricants on melt index

Batch no.	Unit	22	24	25	26
Ca/Zn stearate	phr	6/1	6/1	4/1	4/1
Lubricant	phr	-	1.5	1.5	1.5
Mg/Al hydroxide carbonate	phr	-	-	-	0.5
Melt index	g/10 min	5.4	16.6	4.6	3.2

STATIC HEAT STABILITY

OIL BATH TEMPERATURE 190°C

TIME (min.)	BATCH NO.					
	22	24	25	26	Pb	
0						
15						
30						
45						
60						
75						
90						
105						
120						
135						
150						
165						
A*	6/1/5/0.5	6/1/5/0.5	4/1/5/0.5	4/1/5/0.5	Refer to	
B*	0.5/-	0.5/-	0.5/-	0.5/-	TABLE D	
C*	-	-1.5	-1.5	0.5/1.5		

Remark : A* = Ca-St/Zn-st/ESBO/Tris(nonylphenyl)phosphite (phr)

B* = SBM/BHT (phr), C* = Mg/Al hydroxide carbonate/lubricant (phr)

Fig. 3.8 : Effect of Mg/Al hydroxide carbonate on static heat stability

DYNAMIC HEAT STABILITY

ROLL TEMPERATURE 195 °C

TIME (min.)	BATCH NO.					
	17	22	24	25	26	Pb
5						
15						
25						
35						
45						
55						
65						
75						
80						
90						
95						
100						
A*	6/1/5/0.5	6/1/5/0.5	6/1/5/0.5	4/1/5/0.5	4/1/5/0.5	Refer to
B*	-	0.5/-	0.5/-	0.5/-	0.5/-	TABLE D
C*	-	-	-1.5	-1.5	0.5/1.5	

Remark : A* = Ca-St/Zn-st/ESBO/Tris(nonylphenyl)phosphite (phr)

B* = SBM/BHT (phr), C* = Mg/Al hydroxide carbonate/lubricant (phr)

Fig. 3.9 : Dynamic heat stability comparison between Ca/Zn and Pb stabilizer system

STRIP TEST

Extruder temperature : Z1 = 160, Z2 = 165, Z3 = 167, Die = 170 ($^{\circ}$ C)

Screw speed : 50 rpm





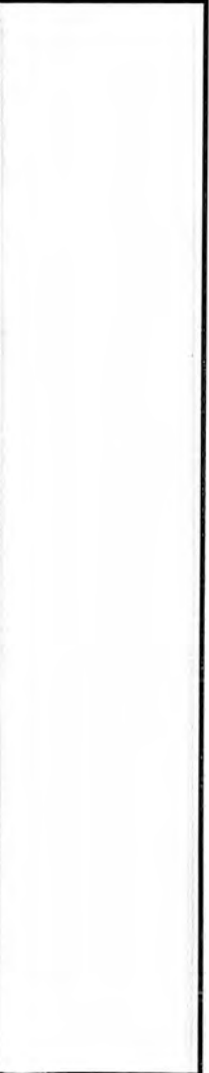
BATCH NO.				
17	22	24	26	Pb
				

Fig. 3.10 : Extrusion test (strip test) shown surface appearance and initial color of rigid PVC profile in Ca/Zn stabilizer system compared to Pb-stabilizer system

**INITIAL COLOR
(MILLED SHEET)**

ROLL TEMPERATURE : 195 °C


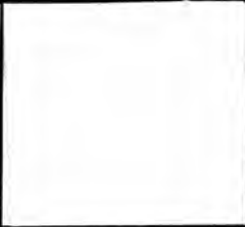
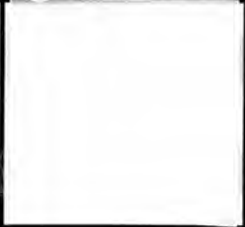
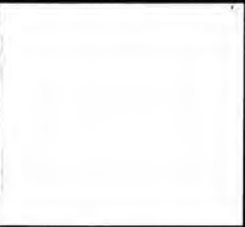
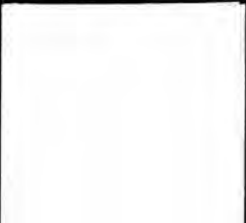



Batch no.			
17	22	23	24
			
Batch no.			
25	26	Pb	
			

Fig. 3.11 : Initial color of rigid PVC profile in Ca/Zn stabilizer system compared to the Pb stabilizer system

Lubricants can increase flow because of the decreased friction during blending and processing. With increasing temperature, PVC begins to soften and the lubricant melts and penetrates between the PVC particles. At which point in the barrel of the extruder this occurs is the determinant for the flow. Thus, the melting point, as well as the melt viscosity of the lubricants, have an influence on this effect.

The rate of penetration of the lubricant into PVC is controlled by its solubility, which depends on the structure of the lubricant molecule as well as its polarity in relation to that of PVC⁽⁴⁾.

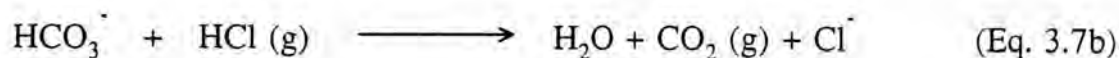
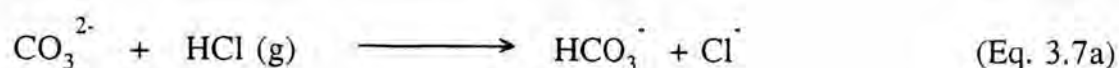
By variation of the bonding strength between polymer and plasticizer, fine-tuning is possible: the weaker the strength of the interaction, the more mobile and incompatible the lubricant molecules. Under high pressure they are actually squeezed out of the space between the polymer particles⁽⁵⁾. They cover the surface and act as a lubricant between the thermoplastic material and the walls of the machine. In the extreme, and undesirable, case they build up a release film which totally prevents the indispensable adherence to the wall. This is a disadvantage during processing for it disturbs the plasticization and smooth flow as a result of over-lubrication. The art of effective processing consist of finding the right system which provides the correct ratio of internal and external lubrication at the right place in the right concentration.

3.2.2 The optimum formulation for heat stability and processability

The information obtained from sections 3.1 and 3.2.1 is considered to be the optimum formulation for rigid PVC profile.

Although there are already five components in the stabilizer system (Ca-stearate, Zn-stearate, ESBO, tris(nonylphenyl)phosphite and stearylbenzoylmethane), the heat stability of the finished product is still lower than its that of the lead stabilizer system.

Recently Mg/Al hydroxide carbonate has been used to improve long term heat stability without a destabilizing effect. This effect is due to its unique crystal structure. Mg/Al hydroxide carbonate consist of positive charged basic layers $[\text{Mg/Al}(\text{OH})_2]^+$ and negative charged middle layers $[(\text{CO}_3) \cdot 2\text{H}_2\text{O}]^-$ which neutralizes the positive charge of the basic layer and hence maintains electrical neutrality. The CO_3^{2-} ion functions as an anion exchanger and neutralizer, therefore Mg/Al hydroxide carbonate neutralizes the hydrogen chloride generated by the thermal decomposition of PVC and thereby mops up Cl^- . Al and Mg in the basic layer is inactive to HCl while CO_3^{2-} reacts with HCl (Eq. 3.7). Mg/Al hydroxide carbonate imparts the best heat stability compared with the other heat stabilizers. But, it has the disadvantage of causing early reddish coloring to appear due to its strong electron donating property derived from replacing Aluminium for magnesium in the basic layer. Therefore, it needs co-stabilizers to reduce the color.



After adjustment of the amount of stabilizer and lubricant, the final formulation is batch no. 26. Details are shown in Table 3.2.

TABLE 3.2 : Properties of rigid PVC profile in a Ca/Zn stabilizer system

Item	Unit	Pb	Ca/Zn
1. Appearance			
-Color (yellowness index)	-	33	55
-Surface	-	smooth	smooth
2. Heat stability	min.	165	150
3. Melt index	g/10 min	1.2	3.2
4. Vicat temperature	°C	84	69
5. Izod impact strength	Kg-cm/cm	14	41

The surface appearance and heat stability compared to the product with a Pb-stabilizer system is acceptable. Color tint is slightly more yellow than that with the Pb-stabilizer system (Fig. 3.11), because the effect of the Mg/Al hydroxide carbonate, but it could be compensated for increasing the white pigment content ⁽¹⁾. Melt index(MI) is higher than that with the Pb-stabilizer system because the more amount of lubricant required for surface

appearance improvement and the Ca-stearate in this formulation has a lubricant action. Vicat temperature is obviously lower than that with the Pb-stabilizer system because ESBO in this formulation has a plasticizer effect. Reduction of the amount of ESBO results in rough surface (batch no.27 in Fig. 3.12). This problem may be solved by adjusting the amount of processing aid to obtain a more homogeneous compound. The izod impact strength is higher than that with the Pb-stabilizer system because the effect of the ESBO will effect the vicat temperature, resulting in a more flexible compound.

STRIP TEST

Extruder temperature : Z1 = 160, Z2 = 165, Z3 = 167, Die = 170 (°C)

Screw speed : 50 rpm

BATCH NO.				
25	26	27	Pb	

Fig. 3.12 : Surface appearance comparison between batch no. 26 and 27