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Influence of Pentaerythritol as Co Stabilizer for Calcium/Zinc One Pack System Stabilizers to Rigid Poly (Vinyl Chloride) Applications.

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ABSTRACT

The stabilization effect of zinc laurate (ZnL) with calcium stearate ($CaSt_2$) combined with β-diketone and pentaerythritol (PE) was studied in rigid poly (vinyl chloride) PVC application. The performance was characterized during thermal processing of PVC. The long-term heat stabilization efficiency of pentaerythritol was investigated, when added to calcium/zinc stabilizers and compare with conventional lead stabilizer. Investigation of prepared one pack thermal stabilizers was measured by Congo red test in air at 200^0C, thermal aging test and torque Rheometry study. Visual color evolution and thermal stability time was examined at 190^0C in air. The results revealed that combination of pentaerythritol and B-diketone with CaSt2/ZnL stabilizers enhance stabilization efficiency to poly (vinyl chloride) (PVC) and extended degradation time. Pentaerythritol and β-diketone with zinc laurate and calcium stearate exhibit better stability than the stabilizers containing zinc stearate stabilizers.

Keywords: Calcium/Zinc stabilizer, Degradation Polyvinyl chloride(PVC), Pentaerythritol,

I. INTRODUCTION

Poly (vinyl chloride) PVC, one of the most common thermoplastic polymer on accounts of its versatility and low cost. Poly (vinyl chloride) are widely used in many fields due their advantages of non-flammable nature and good performance and widely utilized in durable applications. PVC production is third largest after Polyethylene and polypropylene. It is very cost effective, highly versatile and is used in many construction applications as water, sewage and drainage pipes, and variety of extruded window profiles [1-4]. Poly (vinyl chloride) (PVC), which has superior mechanical and physical properties, high chemical and abrasion resistance [5]. Presently, calcium stearate and zinc stearate (CaSt2/ZnSt2) widely used to prevent dehydrochlorination of poly (vinyl chloride) (PVC) at processing temperature. Calcium stearate and zinc stearate, alkaline metal soaps combination when used shows good synergistic effect [6]. However, PVC has one major drawback is that it decomposes at lower temperature than its processing temperature. The degradation of PVC usually proceeds through dehydrochlorination process, the results of this formation of long chain of conjugate double bonds or polyene sequences, $-(CH=CH)_n-$, which cause color change [7, 8]. PVC, under the influence of temperature undergoes auto catalytic dehydrochlorination reaction and initial reaction of dehydrochlorination auto accelerates the evolution of HCl. The thermal degradation of PVC is results zipper dehydrochlorination [9, 10].

Because of this drawbacks in its structure, resulting in the degradation of polymer backbone and deterioration of polymer properties [9]. The zipper dehydrochlorination generates polyene sequences in polymer chain then produces undesirable color in the materials. Depending on number of conjugate double bonds, it becomes yellow, orange, red, brown and finally black. It was due to labile sites for dehydrochlorination were mainly the allylic chlorines and tertiary chlorines. This results in unacceptable discoloration of polymer during processing and drastic changes in polymers properties [11]. Therefore, it is necessary to add thermal stabilizers for improving thermal stability of PVC. Stabilizers can inhibit degradation of removal of HCl due to their capacity for HCl adsorption [12]. Metal soaps are most used heat stabilizers for PVC. The tertiary and allylic chlorine group substituted by carboxylate group of metal salts and stops initiation of dehydrochlorination according to Frye and Horst mechanism [13]. However, lead stabilizers are most efficient stabilizers, but they no longer used, as they are toxic and more restriction have been imposed [14]. Therefore, highly efficient environment friendly but cheap stabilizers have been given significant attention. Metal soaps are mostly used as stabilizers for PVC, one pack stabilizers containing calcium stearate and zinc stearate play significantly important roles because of non -toxic attributes. However, during process of PVC some unwanted zinc dichloride ($ZnCl_2$) produced during thermal stabilization of PVC. It accelerates dehydrochlorination of PVC through autocatalytic effect [15, 16]. The selection of thermal stabilizers for polymer processing is key important factor which determines the quality and final application of the finished product [17]. Most of stabilizers are expensive and less efficient than other stabilizers. Industries except for exploring new kind of high efficiency stabilizers such as polyols [18, 19]. Ca/Zn stabilizers already proposed as new alternative to lead based stabilizers for rigid applications. However, performance and price not being much attractive. New development makes more interest for researchers [20]. The synergistic mechanism of $CaSt_2$ and $ZnSt_2$ was widely investigated by many researcher [21, 22]. Zinc laurate and calcium stearate combination with increased amount of pentaerythritol which is works good than lead market control stabilizers.

II. EXPERIMENTAL WORK

2.1. Materials

The Poly (vinyl chloride), used in this work was PVC K value = 57 and K=67. Resin supply by IPCL Baroda (INDIA), Calcium carbonate stearic acid coated used in this work purchased from MRB Vietnam. Zinc laurate (zinc: 1 content kindly supplied by FACI PTE Singapore. Stearoyl benzoyl methane (β-diketone) purchased from Brenntag agency, Nashik, India. Pentaerythritol purchased from BASF. Zinc stearate and calcium stearate purchased from MLA group Kanpur, UP (India) both are commercial grade. Lead one pack stabilizer supplied by Monachem Baroda, India. Titanium dioxide provided by Dupont India Ltd. Lubricants kindly supplied by Honeywell corporation AC617A and AC316A.

2.2. Sample preparation

Master batch of PVC dry blend was prepared. The PVC samples for static oven test and evaluation of visual color test were prepared by mixing master batch with additives as below.

Specific additives of the PVC master batch without stabilizer before milling on Two Roll Mill:

Table No:1

Components	PVC	CaCO3	TiO2	AC 617A	AC316A
Mass in g	**100**	**13**	**1**	**1.2**	**0.3**

The PVC master batch was prepared by blending of PVC having value K-57, CaCO3, Titanium pigment, AC617 (EL), AC316A(IL) in high speed mixture for 2min. The specific components shown in table no1. Master batch was mixed with 2.5 phr (per hundred resin) Ca/Zn stabilizer for evaluation of stabilizing efficiency and 2phr for lead stabilizer.

Then, 70 g of above prepared PVC master batch (Table No.1) mixed with 2.5phr stabilizer. having different ratio of pentaerythritol with $CaSt_2$/ZnL composition in the presence of β-diketone and lubricants placed on Twin Roll Mill (Neoplast Ahmedabad, India) for 3 min at 195^0c. The thickness was drawn out of sheets was 1mm ± 0.1mm. The prepared sheet was used for investigation of further study like static heat stability and Congo red testing.

2.3. Measurements

2.3.1. Congo Red Test:

Congo Red measurement test done according to standard method of ASTM D4202. PVC film prepared from above table no.1 with 2.5 phr Ca/Zn and 2phr market control lead stabilizer. The thermal stability static time(tss) of stabilizer obtained by heating 0.0500g of PVC sample (by fragmentation of PVC sheet into 0.2mm squares) in the test tube. Congo Red paper place at the top of the test tube. The test tube placed in Congo Red stability apparatus [Made Veekay Apparatus] which having electrical heating at temp 200^0c ±1. Congo red paper changes color from red to blue by degradation of PVC sample, the time required to color change is static thermal stability of that sample.

Stabilizer chart:

A = (0.37/0.33 g ZnL/$CaSt_{2)}$ + 0.06g β-diketone + 0.45g PE wax

Table No.2.

Serial number	A+ Pentaerythritol
Lead one pack	0
RS-27	Blank PVC
RS-27A	A + 0.0
RS-39	A + 0.03
RS-40	A + 0.06
RS-41	A + 0.12g

2.3.2. Thermal aging Test

To conduct the thermal aging tests by observing color change of samples. The thermal aging test was carried out in Hot Air Circulating temperature controlled oven [Made by ELE Ahmedabad, India]. The PVC samples were cut in to 30mm*20mm rectangular shapes strips and put it in oven at 190 ^{0}C ± 1.0^{0}c. Sample were removed after every 5-min interval and subjected to visual examination. Color scanning done using color scan 5100H [made by Premier colour scan 5100H]. The effect of stabilizers was evaluated by color differences of PVC samples. Whiteness and Yellowing index clearly indicate differences of stability of stabilizers.

2.3.3. Torque Rheometry study:

Specific components of the PVC master batch without stabilizer for Torque rheometry study:

Table No. 3

Component	PVC	CaCO3	TiO2
Mass in g	100	13	1

Rheological test performed on Brabender plasticodore PL 2000 GmBH. The PVC master batch was prepared as shown in Table no.2 used for Torque rheometer study at 60 rpm and 200^{0}C. The PVC master batch was prepared by blending of PVC value K-67, CaCO3, Titanium dioxide pigment in high speed mixture for 2min. Master batch of 65gms was mixed with 2.5 phr (per hundred resin) Ca/Zn stabilizers for evaluation of stabilizing efficiency and compare with 2phr market control one pack lead stabilizer.

III. RESULTS AND DISCUSSION

3.1. Congo Red testing:

In order to get proper thermal heat stability of PVC, it need strong heat stabilizers. The evaluation of calcium zinc stability, different amount of pentaerythritol added to PVC formulation with other additives. The result shows influence of different ration of pentaerythritol with CaSt2/ZnL (0.3/0.3) g +0.06 g Rh-55P+0.45g lubricant shows equal static stability time (tss) of PVC when compare with market control lead one pack stabilizer. It is seen that static stability time (tss) of PVC incorporation of A is 34 min, while PVC containing with increased amount of pentaerythritol shows increased in tss. Ca/Zn one pack stabilizer with 0.12g with A shows equal static stability time 41 min, when compare with Market control lead one pack stabilizer having lead 35% which is strongest in performance which have Congo red stability.

Stabilizers composition:

A = (0.37/0.33 g ZnL/$CaSt_{2)}$ + 0.06g β-diketone + 0.45g PE wax

Table No. 4

Stabilizers	composition	Stabilizers in phr
Lead stabilizer	Lead one pack	2
RS-27	Blank PVC	0
RS-27A	A / PE (0.00g)	2.5
RS-39	A / PE (0.03g)	2.5
RS-40	A / PE (0.06g)	2.5
RS-41	A / PE (0.12g)	2.5

Table No.5

Stabilizers	CongoRed Time(min)
Lead stabilizer	39
RS-27Blank PVC	08
RS-27A	28
RS-39	30
RS-40	37
RS-41	42

Thermal stability time (min) of stabilizers.

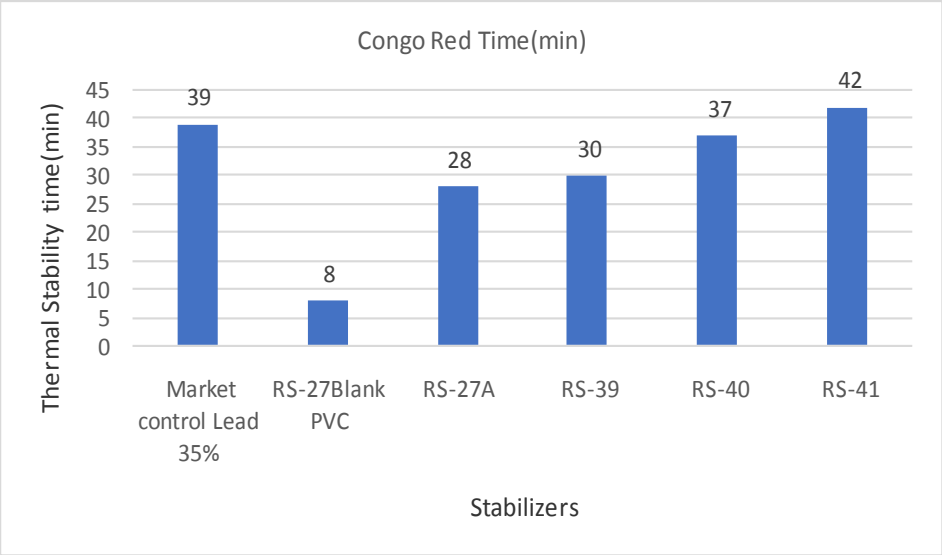

Fig.1. Congo Red stability chart of stabilizers

3.3. Thermal stability of PVC samples:

The PVC sheet prepared subjected to oven stability test at 190^{0}C degree celcius. The gradual color change was observed and listed in figure 3. Market control lead one pack stabiliser with 2phr and other stabilisers used 2.5 phr used. The time needed for color changes measured as stabilizing efficiency of stabilizers. Lead one pack sample started faint brown from 5 min onward become gradually brown and dark brown at 25,30 min, it degrades completely, while stabilizer containing ZnL initial whiteness is more than lead one pack stabilizer, but 5min to 20 min its shows yellowness saturated and degraded at 25, 30 min i.e. toward black. PVC formulation containing pentaerythritol e shows good thermal stability up to 10 min later on yellow and become brown but better than stabilizer containing ZnL. Stabilizer formulation containing A/0.12g of PE has exhibit better thermal

stability than other. Significant improvement was observed that 0.12g of PE could delay degradation time, compared with 0.03g of PE, its color holding properties very good till 20 min. Color strip maintained whiteness till 10 min. Then color become pale yellow at 25 and 30 min. Figure 2 shows that PE of 0.12g with A formulation has goodthermal stability against lead one pack stabilizer.

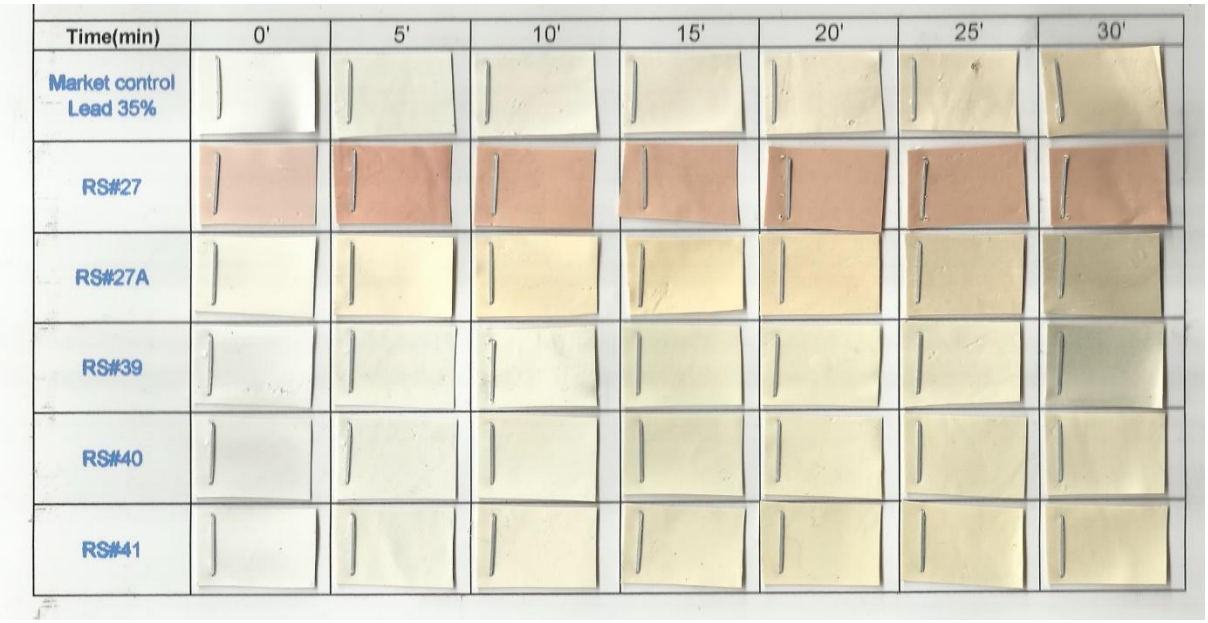

Fig. 2. Oven Stability test for stabilizers. Color changes of PVC strips at 190^{0}C.[RS- research sample]

Stabilizer containing pentaerythritol having value of 0.12g with formulation **A** shows good long-term stability. Colorimeter Data for above PVC strips, whiteness and yellowness index as shown in table no.6 and 7 respectively.

Table 6.Whiteness Index at 0 min sample at oven stability test

Time (min)	0
Market control one pack Lead 35%	62.665
RS#27	15.284
RS#27A	54.052
RS#39	63.333
RS#40	64.388
RS#41	66.031

Whiteness index of above samples shows that pentaerythritol having quantity 0.12g has more whiteness than other, when compared with market control lead sample having lead 35%.

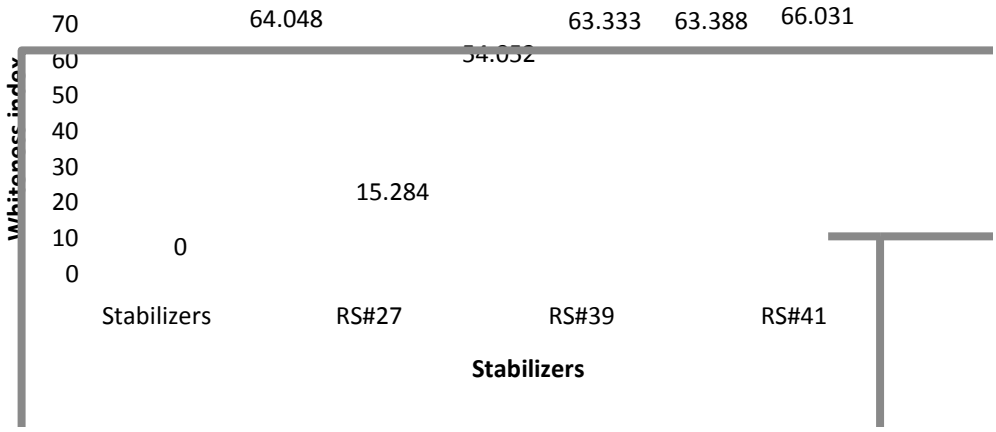

Fig. 3.Whiteness Index chart of stabilizers. Yellowness index of stabilizers:

Table No.7

Time (min)	0	5	10	15	20	25	30
Market control Lead 35%	7.131	18.736	25.15	29.298	33.254	37.353	45.347
RS#27	34.876	63.724	64.981	66.071	64.294	59.408	59.381
RS#27A	15.011	40.402	45.893	47.904	55.604	48.782	46.108
RS#39	7.425	14.233	22.156	26.633	38.887	40.916	46.374
RS#40	7.32	13.089	21.579	26.266	36.526	39.969	44.194
RS#41	7.074	12.7	20.825	24.659	30.311	33.261	37.49

The color changes for polyvinyl chloride (PVC) with different contents of pentaerythritol. The graph clearly indicates that RS#41 which has pentaerythritol 0.12g shows less yellowing index as compare to market control lead sample. The plotted time against Yellowness index as shown in fig. 4.

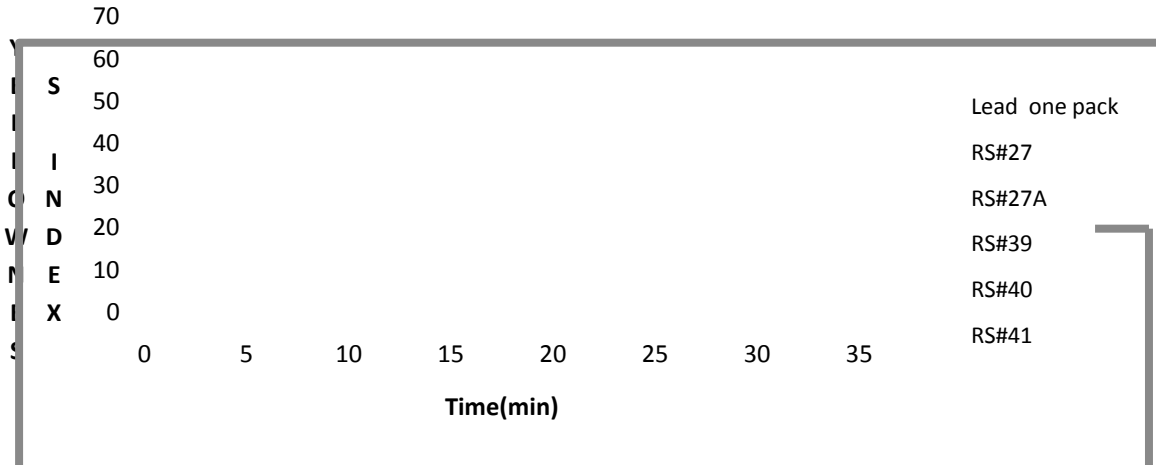

Fig.4. Color changes for PVC samples in Oven Stability Test @190^{0}C till 30 min [Yellowness Index].

3.4. Torque Rheometry Study

Market control lead one pack stabilizer, compare with Ca/Zn one pack stabilizers containing different zinc salts, such as stearate, laurate and levulinate on Brabender plasticodore. Mechanical properties of stabilizers study were done. Lead one pack stabilizer shows fusion torque at 14 Nm with gelation time 4.22min with thermal stability time in Brabender 4.39min. Stabilizer containing zinc levulinate shows torque 11.5 Nm and fusion time required 2.39min. Stability time in Brabender plasticodore is 8.0 min which is greater than lead one pack stabilizer.

Table No:8

Sr. No.	Stabilizer	Torque Nm	Fusion time(min)	Stability time(min)
1	Lead One pack	14	4.22	4.39
2	A/0.03g PE	10.5	3	3.33
3	A/0.06g PE	10	2.39	5.46
4	A/0.12gPE	11.5	2.39	8

Brabender plastogram

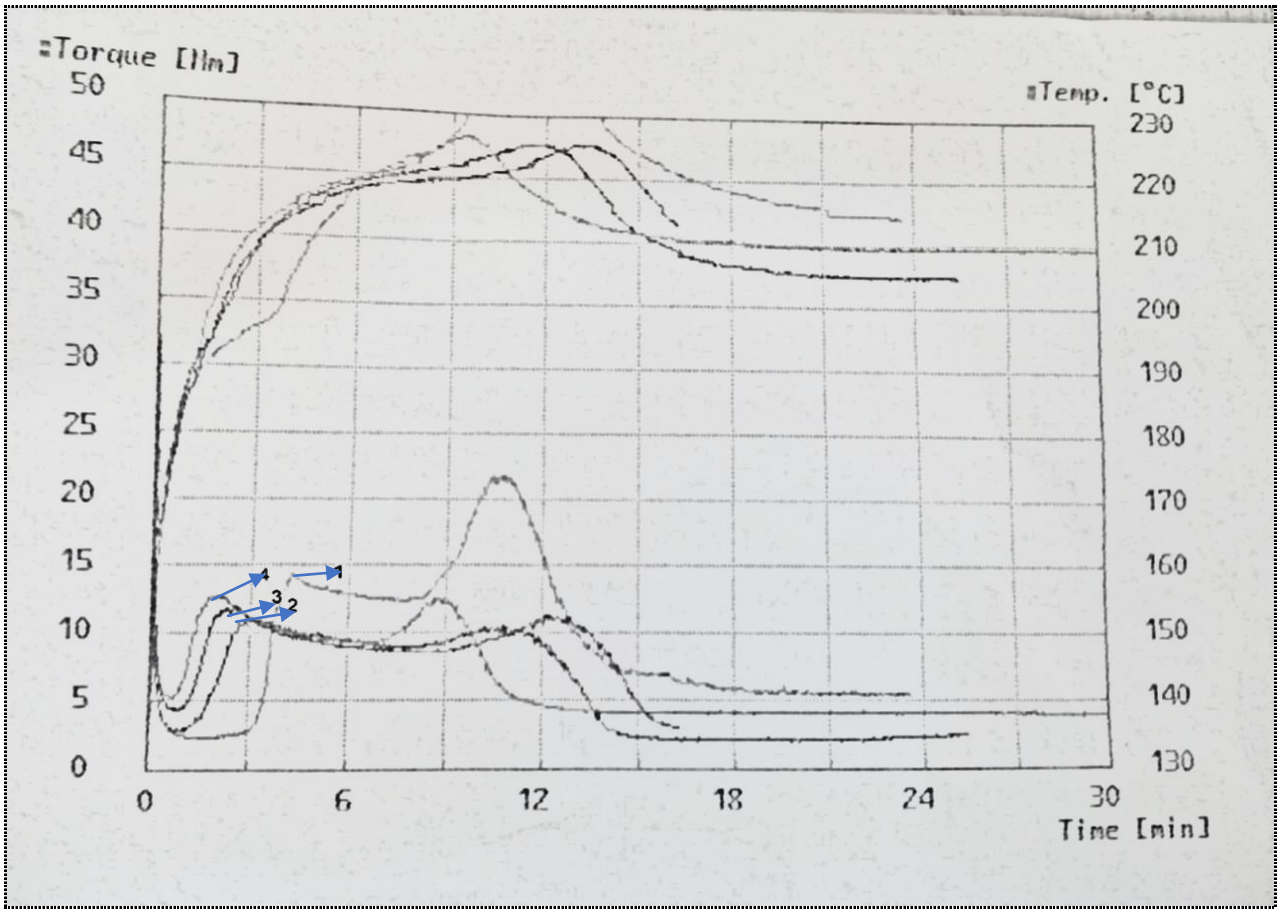

Fig.5.Content on fusion time, torque and stability time.

1 ─ Lead one pack
2 ─ A/0.03g of PE(RS-39)
3 ─ A/0.06 g of PE(RS-40)
4 ─ A/0.12g of PE(RS-41)

IV. CONCLUSIONS

Pentaerythritol with Calcium stearate and zinc laurate with other additives shows good initial whiteness and long-term stability than other stabilizers and conventional market control lead stabilizer. It demonstrates that initial color stability was markedly improved and thermal stability time was extended. Colorimeter data shows yellowness index has lower value than lead stabilizers mean strong thermal stability. Brabender study shows long term stability of stabilizer containing 0.12g of pentaerythritol.

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