DESIGN OF NON-TOXIC ONE PACK STABILIZERS WITH DIFFERENT ZINC SALTS FOR THERMAL STABILITY OF RIGID POLY (VINYL CHLORIDE) APPLICATIONS.

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ABSTRACT:

In this research work nontoxic heat stabilizers containing zinc salt of stearate, laurate and benzoate have been studied. Influence of the different zinc salt as thermal stabilizers for poly (vinyl chloride) (PVC) was examined when used with combination of other assistant additives. The prepared one pack stabilizers were used for thermal stabilization of rigid poly (vinyl chloride) (PVC). Zinc benzoate (ZnB), zinc laurate (ZnL) and zinc stearate ($ZnSt_2$) are used with β-diketone and other assisting additives. The long-term heat stabilization efficiency of different salts was studied, on the basis of weight and percentage basis of $ZnSt_2$, when added to calcium/zinc one pack stabilizers and comparison with commercial lead stabilizer. The thermal stability was determined by Congo red test in air at 200^0C whereas discolouration test was examined by thermal aging test and torque rheology. Visual colour evolution and static thermal stability was examined at 190^0C in air, colour measured on colorscan. However, experimental results demonstrate that stabilizing effect of stabilizer with ZnL on thermal stability of PVC was more effective by scavenging hydrochloric acid which stops further degradation of PVC. ZnL exhibits greater long-term stabilizing efficiency than lead one pack and stabilizers contained benzoate and stearate salt.

Keywords: Poly(vinyl chloride) (PVC), Ca/Zn stabilizers, Thermal properties, Degradation, Rheology.

1. Introduction

Poly(vinyl chloride) PVC, is an important thermoplastic polymer and widely used in water pipes, floor, roof tiles, packaging films and sheets due to low economical cost. PVC has good physical and mechanical capacities and its high chemical and abrasion resistance [1-2]. Advantage of PVC is its non-flammable nature and good performance [3]. However, it is known that PVC is very thermally unstable at elevated temperatures and release hydrochloric acid (HCl) that accelerates degradation process. The processing range of temperature is much higher than glass transition temperature 70^0 C. PVC undergoes several changes in inherent structural chain. The thermal degradation creates autocatalytic dehydrochlorination reaction, which may produce unacceptable discoloration due to formation of conjugate double bonds or polyene sequences– $(–CH=CH–)–_n$, and loss of mechanical strength [4]. Mainly carboxylate salts of calcium and zinc, are mostly used for stabilization of PVC. Zinc carboxylate can produce $ZnCl_2$which can cause sudden dehydrochlorination of PVC during stabilization. The HCl released caused several colourations of polymer. The colour changes from white to yellow then brown and finally becomes black. It was due to labile sites for dehydrochlorination were prominent of allylic chlorines and tertiary chlorines. Proper stabilizers must be added to restrain the degradation of PVC during processing [5,6]. Stabilizers can inhibit degradation of removal of HCl due to their special properties of adsorption of HCl [7].

However, to retard dehydrochlorination of PVC, stabilizers such as lead salts, metal soaps, organotin and rare earth metals are used. However, some of them are toxic and cause environment issue, as most of them leave residue after degradation of polymer [8]. Applications of lead salts and organotin stabilizers are limited due to their toxicity and heavy metals though they have high efficiency to stabilize PVC. Ca/Zn stabilizers are restrained as they have low stabilizing efficiency. Industries except for exploring new kind of high efficiency stabilizers such as polyols [9, 10] and hydrotalcite (LDH) like materials have very important application in stabilization of PVC [11 - 14]. The researcher had done most of their study on Ca/Zn thermal stabilizers as they are nontoxic and environment friendly [15]. The synergistic mechanism of $CaSt_2$ and $ZnSt_2$ was widely investigated by many researchers [16]. Calcium stearate and zinc stearate play an important role in PVC stabilization as they are nontoxic. However, they need long term stabilization by adding some co-stabilizers for improvement [17]. Rigid PVC products, for examples pipes and profiles, require stronger stabilisers than, for example, cables and flexible calendered sheets. The zinc salts displace the labile chlorines and form zinc chloride. Zinc chloride is a good Lewis acid, and can catalyse dehydrochlorination of PVC. The calcium salt reacts with zinc chloride to regenerate the zinc salt and form calcium chloride.

Zinc laurate, stearate and benzoate studies in PVC have been proposed in this article. In this research article we have studied the efficacy of three zinc salts – zinc stearate, zinc laurate and zinc benzoate, in calcium-zinc stabilizer formulations. The three salts were chosen to understand the effect of chain length and a salt which is not linear and aliphatic but aromatic.

2. Experimental work

2.1. Materials

The PVC, used in this work was PVC K value 67resin supplied by Reliance Industries Ltd, India, calcium carbonate was purchased from MRB, Vietnam.$CaSt_2$ (calcium content: 6.6%-7.1%) and $ZnSt_2$ (zinc stearate content: Zn:10.2%-10.5%) kindly supplied by FACI Singapore. Zinc benzoate (Zn content: 20.2%-20.7) provided by Mona Chem Vadodara, Zinc laurate (Zn content: 14.1-14.5%) was kindly supplied by FACI Singapore, used as received (metal percentage as per TDS). Lead stabilizer (Lead content: 19–21% as per TDS) supplied by Mona chem additives, Vadodara, India. Titanium dioxide was provided by Dupont India Ltd, and lubricants like polyethylene wax and oxidized polyethylene wax were kindly supplied by Honeywell corporation. B-22 impact modifier from Kaneka corporation. Method is described below.

2.2. PVC sample preparation:

All experiments were performed with master batch of PVC dry blend. The PVC samples for static oven test and evaluation of colour test were prepared by mixing master batch with additives as below.

Table 1. Specific components of the PVC master batch without stabilizer before milling:

Rigid PVC Formulation	Qty Phr
PVC K-67	100
$CaCO_3$	8
TiO_2	1
External Lubricant	1.2
Internal Lubricant	0.3
Impact modifier	4.3
Ca. St_2	0.7

Table 2. Stabilizer composition as below

All composition quantity in PHR					
Compounds	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
Zn St_2	0.5	0	0	0	0
Ca. St_2	0.45	0.45	0.45	0.45	0.45
Zn. L (wt/wt)	0	0	0	0.5	0
Zn L (% Basis)	0	0	0	0	0.36
Zn Benzoate(wt/wt)	0	0.5	0	0	0
Zn Benzoate (% Basis)	0	0	0.24	0	0
β-diketone	0.2	0.2	0.2	0.2	0.2
PVC Resin K-65	0	0	0.26	0	0.14
Assistant additives	1.35	1.35	1.35	1.35	1.35
Total	2.5	2.5	2.5	2.5	2.5

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The PVC master batch was prepared by blending of PVC having value K-67, CaCO3 (powder), Titanium dioxide pigment (powder), polyethylene wax (AC617A) as external lubricant, oxidized polyethylene wax (AC316A) as internal lubricant and $CaSt_2$ in high speed mixture for 2min. The specific components are shown in Table 1. Master batch was mixed with 2.5 phr (per hundred resin) Ca/Zn stabilizer for evaluation of stabilizing efficiency and 2phr of market control lead stabilizer. Then, above prepared PVC master batch (Table1) mixed together with 2.5phr experiment stabilizers, seventy grams of blend with stabilizer placed on Twin Roll Mill (Neoplast Ahmedabad, India). The front roll and rear roll temperatures were 195 deg C and 190 deg C respectively, sheet drawn after 3 min. The prepared sheet having thickness 1mm was used for investigation of further study.

2.3. Measurements

2.3.1. Congo Red Test:

A Congo red test was done to evaluate the rate of PVC dehydrochlorination when they were heated at 200^0C in air. Congo Red measurement test is done according to IS-5831. PVC film is prepared from above Table 1 with 2.5 phr of Ca/Zn and 2phr market control lead stabilizer. The thermal stability static time (tss) of stabilizer is obtained by heating 0.0500g of PVC sample (by fragmentation of PVC sheet into 0.2mm squares) in the test tube. Congo Red paper is placed at the top of the test tube. The test tube is placed in Congo Red stability apparatus [Made Veekay Apparatus, Mumbai] which having electrical heating at temp 200^0C ±1. Congo Red paper changes colour from red to blue by degradation of PVC sample, which was due to liberation of HCl. The time required for colour change is thermal stability of that sample.

2.3.2. Thermal ageing Test

The thermal aging test was carried out in hot air circulating temperature-controlled by oven [made by ELE Ahmedabad]. The thermal aging test was performed as per ASTM D-2115. The PVC samples were cut in to 30mm*20mm rectangular shapes strips and put into oven at 190^0C. Samples were removed after every 5min interval and subjected to visual examination. Colour scanning was done using colourscan 5100H [made by Premier colour scan 5100H]. Color measurement of PVC sheets were investigated by spectrophotometer instrument, whiteness and yellowness index values according to ASTM E313. The effect of stabilizers was evaluated by colour differences of PVC samples. Whiteness and yellowness index clearly indicate differences of stability of stabilizers.

2.3.3. Rheological study of stabilizers on Brabender

In this study Brabender torque rheometer was used to study the processability of PVC compound with stabilizers. The shear flow properties of PVC master batch with experimental stabilizers has carried out on Brabender plasticodore PL2000. Fusion behaviour and degradation time of compounds carried out using

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Brabender torque plastogram at 200^0C at rotor speed at 60 rpm. Above prepared master batch Table 1 taken 65 gms with stabilizers mixed together which to be evaluated, was placed in mixing chamber. A 5 kgs loading chute was used to introduced material into the mixer chamber quickly as possible to get reproducibility. The fusion behaviour was study by observation of changes torque, temperature and time.

3. Results and Discussion

3.1. Congo red testing of different stabilizers.

As shown in Figure 1, the rate of dehydrochlorination of PVC thermal stabilizers was studied by Congo red test as thermal stability time (ts). Low the stability time higher is the dehydrochlorination. The Congo red stability time data are obtained are shown in Table 3. To get proper thermal heat stability of PVC, it needs strong heat stabilizers. The stabilizer is made from $ZnSt_2$, ZnL and ZnB with other additives as shown in Expt no.1 to 5. The result shows that stabilizer expt no.5, content of ZnL on percentage basis of $Znst_2$shows better thermal stability time (ts) of PVC when compare with lead stabilizer. All expt. stabilizers tested at fixed phr level except lead stabilizer. It is seen that thermal stability time (ts) of PVC incorporation of ZnL wt/wt basis was28 min, whereas PVC containing with $ZnSt_{2,}$ ZnB shows only 18 and 21min, which is comparatively low thermal stability could be due to liberation of chlorine and autocatalytic action, and $ZnCl_2$ might be responsible for further dehydrochlorination of PVC. ZnL on percentage basis with expt no.5shows higher thermal stability time32 min, which have higher retardancy efficiency of HCl. Whereas ZnL on wt basis shows 28 min Congo red stability when compared with lead stabilizer. [Stabilizer prepared on metal percentage basis quantity reduced less to 2.5phr. Expt No 3 and 5 make 2.5 phr by adding PVC Resin]

The proposed formulation of stabilizer is given in Table 2

Table 3. Congo red stability Chart:

Congo Red Test	
Stabilizer	Stability time (ts) min
Market control Lead	23
Expt.No.1(Zn St)	18
Expt.No.2 (ZnB wt basis)	21
Expt.No.3 (ZnB %)	23
Expt.No.4 (Zn L Wt basis)	28
Expt.No.5 (ZnL %)	32

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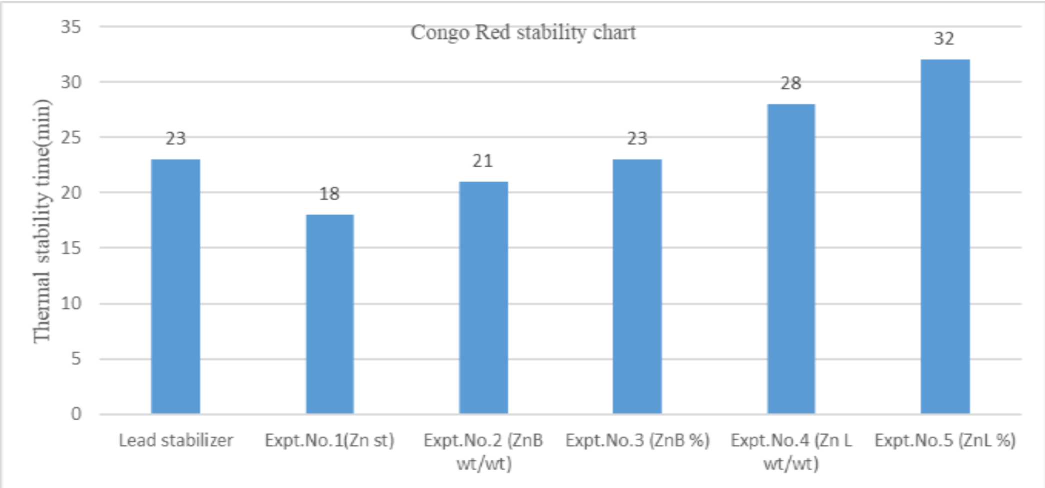

Fig 1. Comparison of thermal stability time of different experimental stabilizer with market control lead stabilizer.

3.2. Thermal Stability of PVC Samples

To conduct the static thermal aging tests to observe discolouration PVC strip with stabilizer are heated in hot air circulating oven. The PVC sheet prepared were subjected to oven stability test at 190^0C. The efficiency of stabilizers was evaluated by discolouration of test. The gradual colour change was observed and represented graphically in Figure 2. The time needed for colour changes is measured as stabilizing efficiency of those stabilizers. The difference in colour of PVC dry blend with stabilizers whiteness index are shown in Figure 3. The PVC strip that content Lead one pack stabilizer initially shows good whiteness which is necessary for industrial pipe production. The colour began to change at 5 min light brown and onward gradually became brown and dark brown at 25,30 and 35 min, it degrades completely, whereas stabilizer containing ZnB on weight and percentage basis shows initial excellent whiteness but long- term stability is weaker than lead one pack stabilizer, its completely become black at 25 min. PVC formulation containing $ZnSt_2$ shows good thermal stability up to 10 min and later on faint yellow and becomes black completely. Blackening is due to formation of $ZnCl_2$, which accelerates dehydrochlorination of PVC. The efficiency of $ZnCl_2$ in the reaction, it has also tendency to form $H^+ZnCl_3^-$ [18], this creating labile chlorine the PVC chain. However, it has been also stated that $ZnCl_2$concentration after reaching certain level it promotes dehydrochlorination [18, 19-20]. The thermal stabilizer containing ZnL has exhibited not only good initial colour but also long-term thermal stability. Significant improvement was observed that ZnL on percentage basis extends degradation of PVC, compared with $ZnSt_2$ and ZnB, its color holding properties are very good till 20 min. Colour strip-maintained whiteness till 10 min. Then it becomes pale yellow at 25and 30 min. Figure 3 shows that ZnL on percentage basis inhibit formation of polyene sequence. It’s good HCl scavenger and extends blackening time and imparts long term stability.

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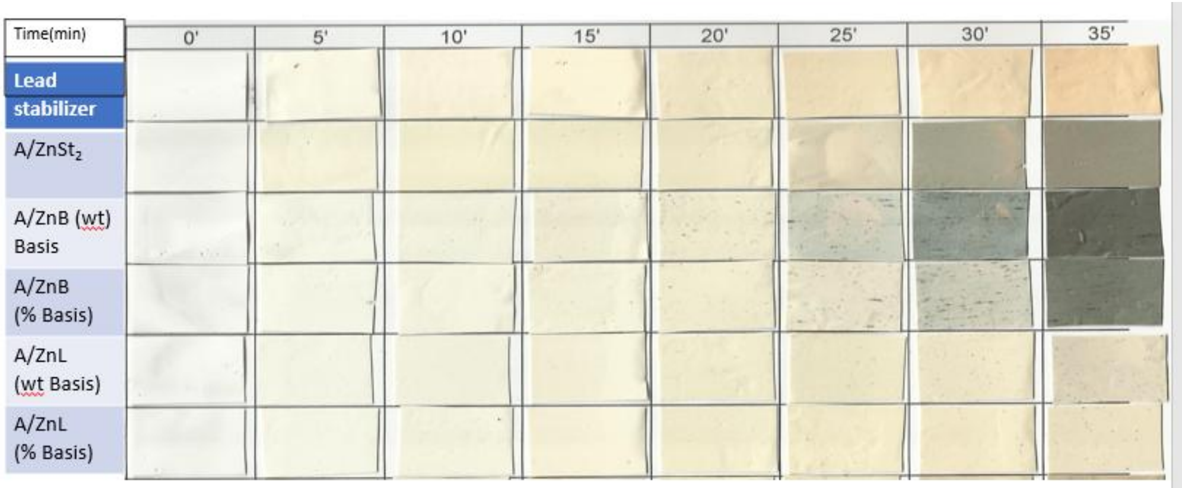

Fig. 2. Static thermal Stability test for stabilizers. Color changes of PVC strips at 190^0C.

Stabilizer containing ZnL on percentage basis has good initial colour holding ability with long term thermal stability than stearate and benzoate and market control lead stabilizer.

Mechanism of metal soaps stabilizer

GROUP IIB METALS: Zn

- Can neutralize HCl

$$(RCOO)_2Zn + 2\,HCl \longrightarrow 2RCOOH + ZnCl_2$$

$$ZnCl_2 + Ca\,(OOCR)_2 \longrightarrow (RCOO)_2Zn + CaCl_2$$

- They can also displace Labile chlorines

Colorimeter data obtained for above PVC strips in figure 2 are given in below.

Table 4. Whiteness index at 0 min sample at oven stability test

Stabilizer	Expt.no	Whiteness
Lead one pack	-	63.868
A/$ZnSt_2$	1	62.048
A/ZnB (wt basis)	2	64.016
A/ZnB (%basis)	3	63.431
A/ZnL (wt basis)	4	63.806
A/ZnL (% basis)	5	64.264

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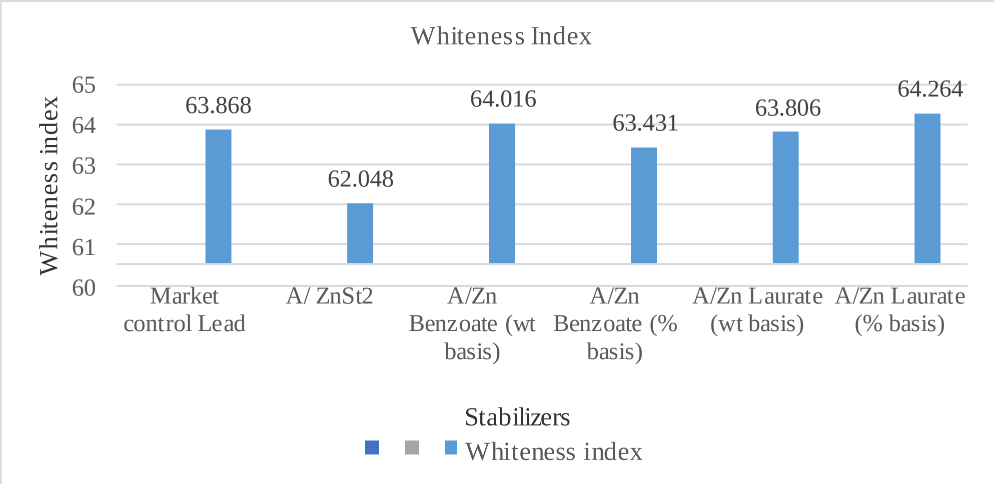

Fig. 3. Colorimeter data of whiteness for PVC strip made with different stabilizers.

The colour changes for PVC with different contents of zinc salts Table 5

Table 5. Yellowness index measured on colorscan 5100H instrument.

Time (min)	0	5	10	15	20	25	30	35
Lead stabilizer	5.131	18.736	25.15	29.298	33.254	37.353	45.347	50.152
Expt.no.1 A/Znst	15.011	40.402	45.893	47.904	55.604	48.782	-	-
Expt.no.2 A/ZnB	7.425	14.233	22.156	26.633	38.887	40.916	-	-
Expt.no.3 A/ZnB wt%	4.834	11.32	22.203	28.979	40.841	45.399	-	-
Expt.no.4 A/ZnL	5.274	12.7	20.825	24.659	30.311	33.261	37.49	41.689
Expt.no.5 A/ZnL wt%	4.208	10.361	18.455	22.926	28.824	33.324	33.652	38.568

Yellowness index graphically represent as below

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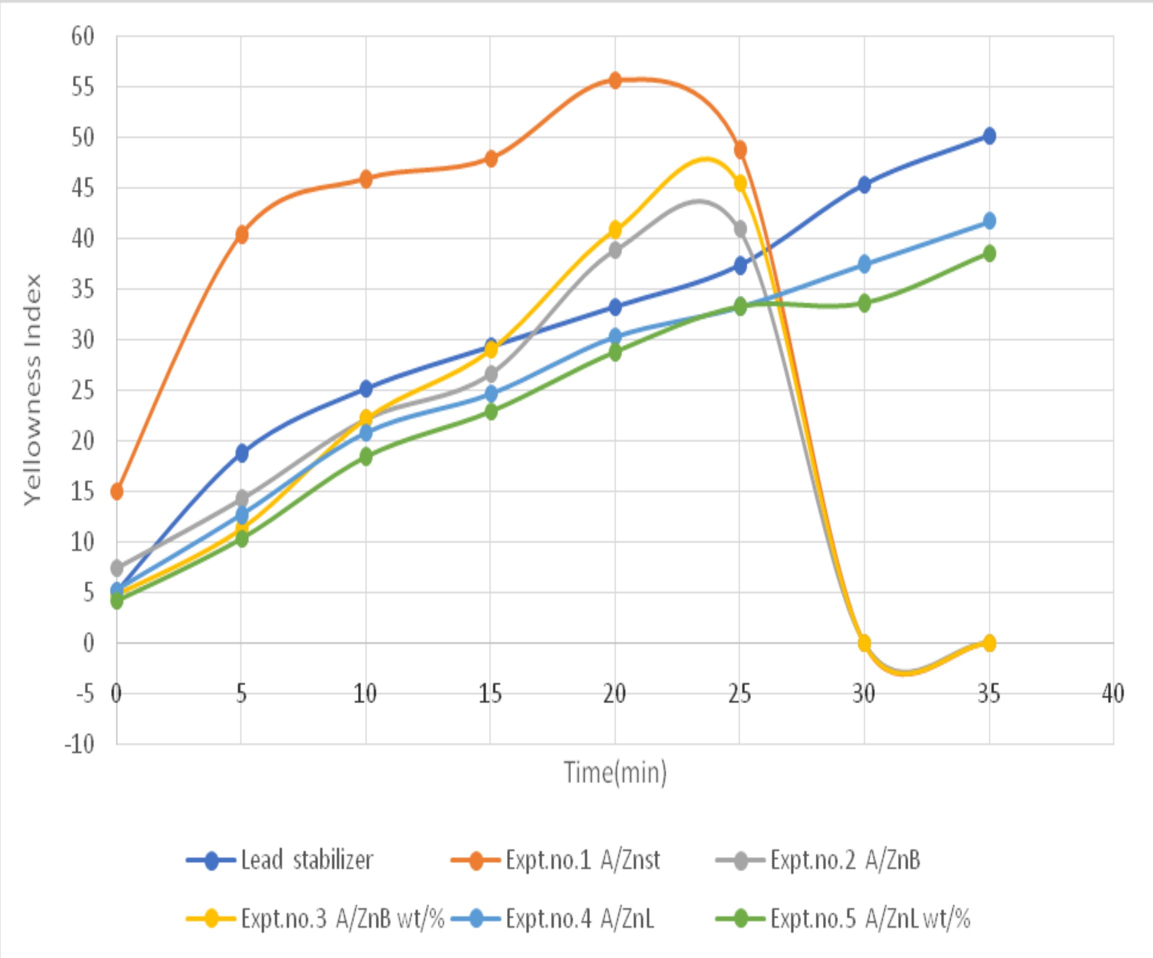

Fig. 4. Thermal stability of experimental stabilizers compared with lead stabilizer. Color changes for PVC samples in oven stability test @190^{0}C till 30 min [yellowness index].

Yellowness value of (expt. No.1) Zn laurate stabilizer on percentage basis, almost lower side indicates that stabilizer efficiency is good than other stabilizers. Stabilizer containing $ZnSt_2$ shows good initial early color but from 10 min it degrades fast and black at end, long term stability shows weak.

3.3. Torque Rheology study of Stabilizer.

The effect of different zinc salts content stabilizers upon fusion torque, fusion time and degradation time was studied. Stabilizer fusion time and toque as given below. For experiment number refer table no.2. Rheology done for selective stabilizes (which have good thermal stability in static stability test).

3.4. Brabender Plastogram

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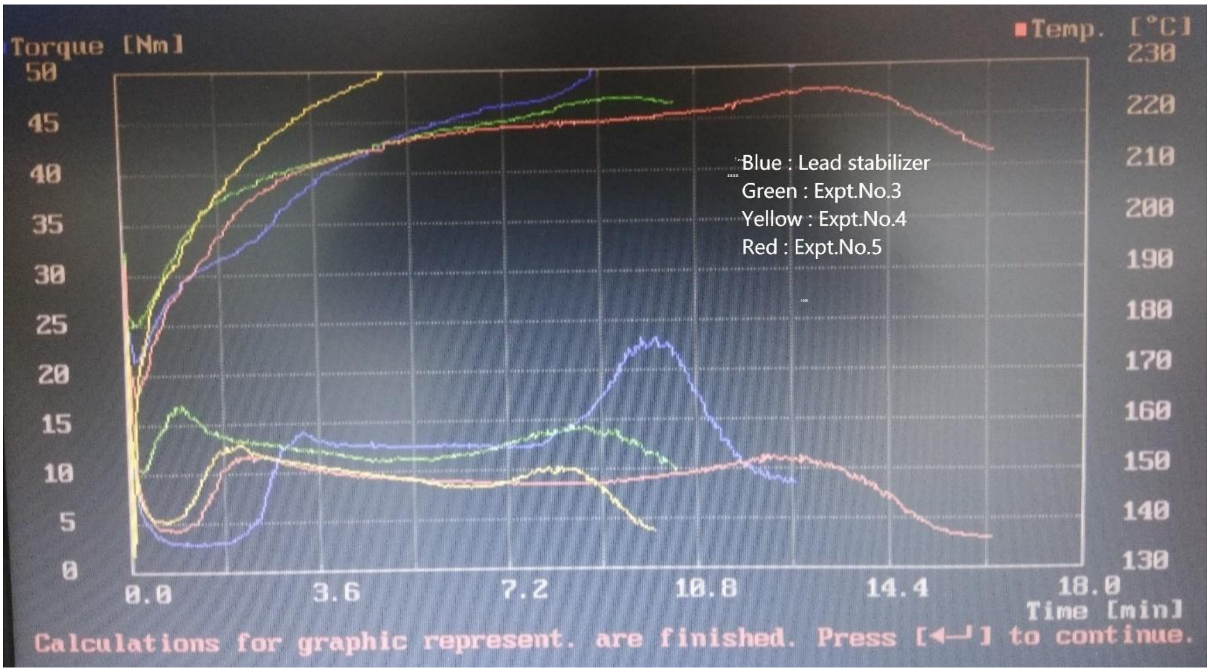

Fig. 5. Torque curve of new experimental stabilizers with market control Lead one pack stabilizer.

Table 6. Fusion torque of stabilizer

Stabilizer	Fusion torque (Nm)
Lead stabilizer	14
Expt no.3 A/ZnB wt/%	16
Expt.no.4 A/ZnL	12.5
Expt.no.5 A/Znst wt/%	11.5

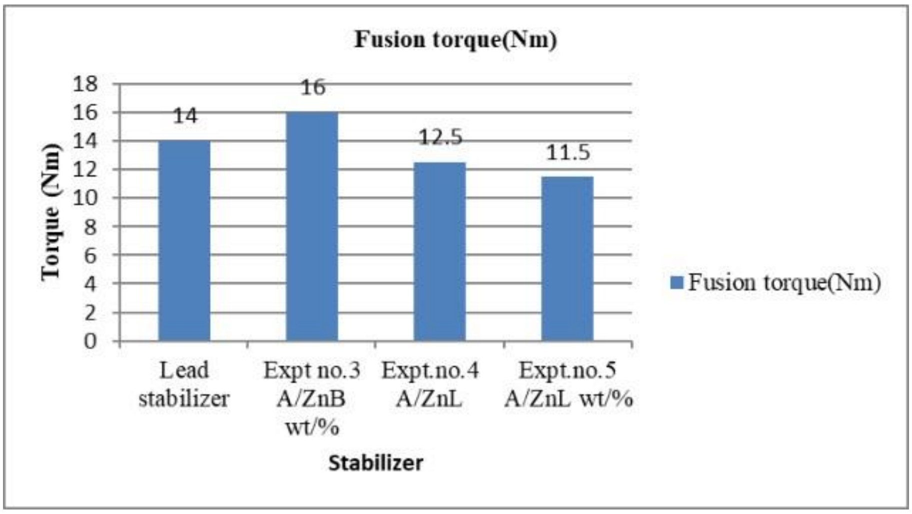

Fig. 6. Fusion torque of Stabilizer

Fusion time chart of stabilizer

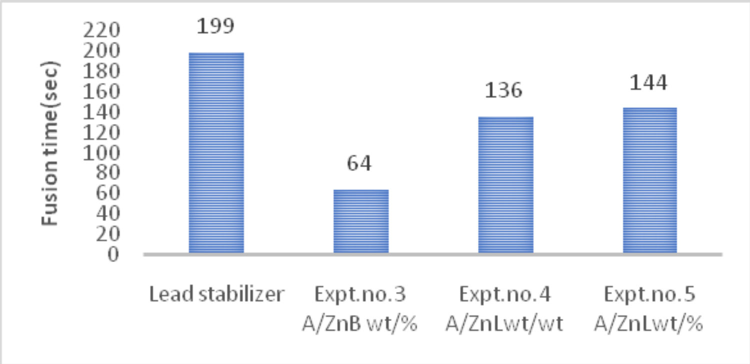

Fig.7. Fusion time (sec) of stabilizer

Brabender test measuring fusion torque and time for new experimental stabilizer against market control lead stabilizer. Lead stabilizer shows higher fusion torque and early gelation which is better for processing. Above chart indicates that expt. no. 4 and 5 have gelation time higher than other experimental stabilizers. Expt no 4 and 5 have much better than lead stabilizers. Rheological behaviour much better than lead stabilizer. Thermal stability time of lead have less than new developed stabilizers. Expt.no.3 with Zinc benzoate on percentage basis have higher fusion torque but stability is very weak due to zinc burning effect, degradation time is less than other. Expt no.5 has been designed much better than standard market control stabilizer in terms of rheological and fusion behaviours and also nontoxic environment friendly.

3.5. Conclusions

One pack stabilizer containing zinc laurate on weight and percentage basis both shows good initial colour holding ability than the other stabilizers. Congo Red thermal stability and long- term stability equal or better than the reference lead stabilizer. Thermal stability of PVC sheet studied by oven stability test. It demonstrates that initial colour stability was markedly improved and thermal stability time was extended by stabilizer containing zinc salt of lauric acid. Colorimeter data shows that yellowness index has lower value than other stabilizers mean strong thermal stability. Brabender study shows long term stability of stabilizer containing zinc laurate. Better synergism was observed in stabilizer content percentage basis of zinc stabilizing system on the thermal stability of PVC when compared with market control lead stabilizer.

References:

1. G. M. Chen, Preparation of a poly (vinyl chloride)/layered double hydroxide nano composite with a reduced heavy-metal thermal stabilizer. J. Appl. Polym. Sci. 2007, 106, 817–820.
2. D. Li, M. Zhou, L. Xie, X. Yu.; Y. Yu.; H. Ai; S. Tang, Polym. J. 2012, 45, 775.
3. O. M. Folarin, E. R. Sadiku, Thermal stabilizers for poly (vinyl chloride): A review International journal of materials science. 6 (18), 4323-4330, 2011.

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4. S. Y. Tawfi, J. N. Asaad, MW. Sabaa, Thermal and mechanical behaviour of flexible poly(vinyl chloride) mixed with saturated polyester. Polym Degrad stab, 2006;91(2):385-9.
5. WH Jr. Stranes, Structural and mechanistic aspect of thermal degradation of poly (vinyl chloride). J Polym Sci Part A Polychem, 2005;43: 2451-2467.
6. WH Jr. Stranes, Structural and mechanistic aspects of the thermal degradation of Poly(vinyl chloride). Prog Poym Sci 2002;2133- 2170.
7. J. Murphy, Heat stabilizers. Plastic.Add. Compound. 1999, 1, 24-29.
8. M W. Sabaa, RR Mohamed, Organic thermal stabilizers for rigid poly (vinyl chloride). Part XIII. Eugenol (4-allyl-2- methoxyphenol). Polym Degrad stab. 2007; 92(4):587- 95.
9. Z. H. Yang, W. Y. Shu, H.Z. Long, Li, X, H. Influence of rare earth heating stabilizer on heating stabilizing property of PVC. Chin. Rare Earths 1999, 20, 60-62.
10. J. Steenwijk, R. Langerock, DS Vanes, JV Haveren, JW Geus, Long-term heat Stabilization by natural polyols in heavy metal and zinc free poly (vinyl chloride). Polym Degrad Stab 2006; 91:52-9.
11. Y J Li, JR Wang, DG Evans, DQ. Li. Layered and intercalated hydrotalcite-like materials as thermal stabilizers in PVC resin, J Phys Chem Solids 2006; 67:998- 1001.
12. A. Vaccari, Preparation and catalytic properties of cationic and anionic clays. Catal Today 1998,41,53-71.
13. A. Vaccari, Clays and catalysis: A promising future. Appl, Clay Sci. 1999, 14, 161-198.
14. L.Van der Ven.; Van Gemert, M.L.M.; L.F. Batenburg; JJ. Keern, L.H. Gielgens, T.P.M. Koster, Fischer, H.R. On the action of hydrotalcite-like clay materials as stabilizers in polyvinylchloride. Appl. Clay Sci. 2000, 17, 25-34.
15. Xu SL, Li D. G., Yu XJ. Study on pentaerythritol zinc as novel thermal stabilizer for rigid poly (vinyl chloride). J. Appl Polym Sci. 2012;126(2):569-74.
16. K. B. Abbas, E. Sorvik, Heat stabilizer for poly (vinyl chloride). I. Synergistic systems based on calcium/zinc stearate. J. Vinyl Additives Technol 1980; 2:87–94.
17. W. Manzoor; S. M. Yousaf; Z. Ahmad. Polym. Degrad. Stab. 1996, 51, 295.
18. L. J. Gonzalez-Ortiz, M. Arellano, M.J. Sanchez-Pena, E. Mendizabal, Effect of stearate preheating on the thermal stability of plasticized PVC compounds. Polym. Degrad. Stab., 2715, 91(2006).
19. R. Bacaloglu, M. H. Fisch. PVC stabilizers. In: Zweifel H, editor. Plastics additives handbook. 5th ed. Munich: Hanser; 2001 [chapter 3].
20. E. D. Owen, K. J. Msayib, Catalyzed degradation of poly(vinyl chloride). III. Zinc (II) chloride catalysis, J Polym. Sci. Part A Polym. Chem., 399, 27(1989).