

Synergistic Combination of Metal Stearates and β -Diketones with Hydrotalcites in Poly(vinyl chloride) Stabilization

Savita Gupta,¹ D. D. Agarwal,¹ Susanta Banerjee²

¹S.O.S.in chemistry, Jiwaji University, Gwalior-474011 (M.P.), India

²Materials science centre, IIT Kharagpur, Kharagpur-721302 (W.B.), India

Received 5 February 2008; accepted 20 October 2008

DOI 10.1002/app.29484

Published online 23 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A synergistic effect of synthetic hydrotalcites as long term stabilizer with metal soaps (the mixture of calcium and zinc stearate) and metal acetylacetonates on dehydrochlorination of PVC has been studied. A proper balance between color stabilization and HCl scavenging capacity has been obtained. Hydrotalcite was prepared by hydrothermal treatment and characterized by EDX, XRD, FTIR, TGA, and SEM techniques. The material is reasonably crystalline and suggests a relatively well ordered sheet arrangement with crystallite size 24.87 nm. The interlayer water content was calculated from the TGA curves and the suggested formula is $Mg_{0.76}Al_{0.24}(OH)_2(CO_3)_{0.12}\cdot 0.5H_2O$. Synergism in PVC stabilization has been studied by measuring the HCl evolution during the processing at 180°C. Oven aging method was used to study the color stabilization at higher temperature. PVC sheet with different formulation was prepared using Labcoater and subjected to oven for dif-

ferent time interval. The color development (polyene formation) on oven ageing was recorded using UV-visible spectroscopy. UV-visible studies shows that an average sized polyene gives pale yellow color, whereas red or brown color was developed due to long range polyene ($n = 10-14$) sequences. Hence, the HCl evolution depends on the rate of dehydrochlorination but color depends on the kind of polyene formed. Mechanism of stabilization suggests that adsorption and ion exchange, both phenomenon, are responsible for hydrotalcites as long term stabilizers. The acetylacetonate complex too substitute allylic chlorides and inhibit formation of long polyene responsible for darkening. A clear effect of synergism has been observed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1056–1062, 2009

Key words: hydrotalcites; poly(vinyl chloride); dehydrochlorination; thermal stabilizers

INTRODUCTION

Poly (vinyl chloride) is used in numerous domestic and industrial applications. But this polymer rapidly degrades (dehydrochlorinate) at processing temperature resulting in loss of properties. This deterioration can be minimized using stabilizers.¹⁻³ The stabilization effects of synergistic metal soaps^{4,5} is impaired by the excessive cool color producing metal chloride, that is, zinc blackening in PVC.^{6,7} To check this abrupt blackening and masking the cool-color, a costabilizer such as phosphates,⁸ diketones,⁹ polyols,¹⁰ amines,¹¹ and epoxides¹² have been used. They delay the induction period of degradation and are considered as short-term stabilizers.¹³ Because of their toxicity and high cost, these stabilizers are not considered as satisfactory solution of the problem. Apart from this, these stabilizers do not impart long term stability. Keeping the environmental issue and to achieve long term stabilization, a new class of

clay materials has been tried.¹⁴ The detailed stability behavior and possible mechanistic pathway is yet to be evaluated. In the present study, a number of formulations have been prepared by taking hydrotalcite as candidate of long term stabilizer. Hydrotalcites synthesized are layered double hydroxides (LDHs) or anionic clays having formula $[M_{(1-x)}^{II}M_x^{III}(OH)_2]^{y+}[A^{n-}]_{y/n}\cdot mH_2O$. Where M^{II} is Mg^{2+} , M^{III} is Al^{3+} , and A represents the anions like Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} etc. The techniques used to study the stabilization efficiency of these formulation are HCl evolution measurements, oven-aging, and UV-visible spectrophotometry.

EXPERIMENTAL

Materials

The materials used in the synthesis of hydrotalcites are: magnesium hydroxide, aluminum hydroxide, sodium bicarbonate, stearic acid, calcium hydroxide, sodium hydroxide, zinc sulfate, acetylacetone, dioctyl phthalate, etc. PVC resin having K value 67 was procured from IPCL Baroda (INDIA).

Correspondence to: S. Gupta (savitagupta_16@yahoo.co.in).

Synthesis of hydrotalcite Mg-Al-CO₃

One pot hydrothermal reactions at higher temperature and autogenous pressure in aqueous media was carried out to obtain small and high surface area particles.¹⁵ In a typical reaction, Mg and Al hydroxides (metallic ratio 3 : 1) were taken and corresponding ratio of sodium bicarbonate was added as maintaining the pH 8.5. After aging the slurry, white precipitate was filtered, washed, and dried.

Synthesis of metal soaps and metal β -diketone complexes

Calcium stearate was prepared by fusing stearic acid (56.8 g) with calcium hydroxide (7.8 g).¹⁶ Zinc stearate was prepared by precipitation method.¹⁷ Magnesium acetylacetonate¹⁸ was prepared by refluxing magnesium hydroxide with acetylacetone in a ratio of 1 : 2.

Characterization techniques for hydrotalcite

The Mg^{II}/Al^{III} atomic ratios in hydrotalcite were measured using X-ray microanalysis with an energy dispersive spectrometer (EDS). XRD measurement of powdered samples using Cu-K α radiation with a graphite diffracted beam monochromator ($\lambda = 1.5418 \text{ \AA}$) with Rigaku's D-300 X-ray diffractometer was carried out. (Scan speed: 2^o per minute). Infra red spectra were recorded using Perkin-Elmer FTIR spectrometer in the range 4000–400 cm⁻¹ using KBr pellets. Thermal decomposition behavior was determined using TGA studies (in air with a temperature increase 10°C/min). The surface morphology of synthesized hydrotalcite was observed using JEOL JSM-5600 scanning electron microscope attached with a scintillation detector.

Procedure for thermal stability

Evaluation of thermal stabilizing efficiency (dehydrochlorination)

PVC sample for thermal degradation studies were prepared by mixing 100 parts per hundred (phr) PVC powder and two parts per hundred (phr) stabilizers and the resulting fine powder was heated at 180.0 \pm 1°C under steady flow of nitrogen. HCl evolution was measured periodically using acid–base indicator. The results obtained are an average of three comparable experiments.

Oven heat stability test (Astm D 2115-92) (Reapproved 2003)

PVC sheets were prepared using rolling machine. The sheets of dimension 1 cm \times 1 cm \times \sim 0.5 mm were placed in an oven at 180.0 \pm 1°C. Strips were

examined visually after every 10 min, 20 min, and 40 min during the first, second, and third hours, respectively.

Procedure for measurement of color intensity and pattern of double bond formation by UV–visible spectroscopy

The polymeric sheet was heated at 180°C in oven for different time intervals such as control, 40, 100, 160, and 280 min, respectively. The sheets were accurately weighed (each 0.05 g) and dissolved in tetrahydrofuran solvent (5 mL). UV–spectra of resultant solutions was recorded. The wavelength for measurement was 200 nm–800 nm and the mode was absorbance.

RESULTS AND DISCUSSION

Structure of hydrotalcite Mg-Al-CO₃

Mg : Al atomic ratio was measured using X-ray microanalysis and found 3.16, which is in good agreement with the metallic ratio (3) taken in solution. The value of x [$x = M^{III}/M^{II} + M^{III}$] was found to be 0.24, which suggest the purity of hydrotalcite.¹⁹ The interlayer water contents were calculated from the TGA curves and the following formula has been suggested Mg_{0.76} Al_{0.24}(OH)₂(CO₃)_{0.12}·0.5H₂O.

The FTIR spectra of Mg-Al-CO₃ (Fig. 1) shows a band near 3479 cm⁻¹, which corresponds to the vibration bands of hydroxyls (ν OH). A weak shoulder recorded around 3200 cm⁻¹ has been ascribed²⁰ to the OH stretching mode of interlayer water molecules, hydrogen bonded to interlayer carbonate anions. The bending mode of water molecules appeared at 1654 cm⁻¹. The sharp intense band at 1366 cm⁻¹ in Mg-Al-CO₃ is due to ν_3 anti-symmetric stretching of interlayer carbonate. This shows that CO₃²⁻ in hydrotalcite got shifted because of strong hydrogen bonding with hydroxyl sheets and water molecules in the interlayer.²¹ The bands recorded below 1000 cm⁻¹ can be ascribed to ν_2 of carbonate such as at 823 cm⁻¹ and ν_4 band at

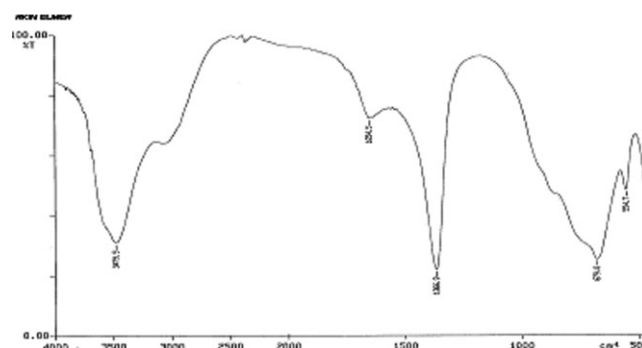


Figure 1 FTIR graph of hydrotalcite Mg-Al-CO₃.

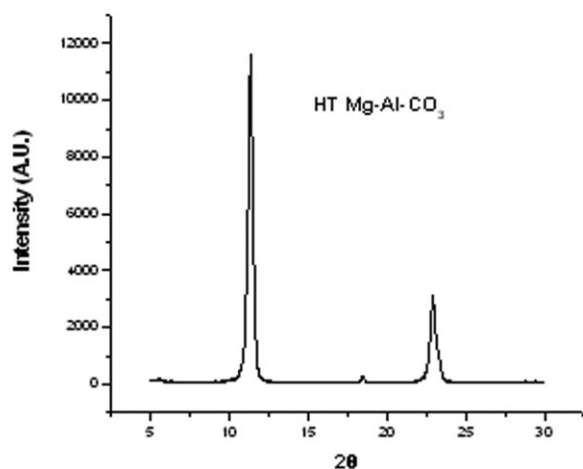


Figure 2 PXRD Spectra of hydrotalcite Mg-Al-CO₃.

679 cm⁻¹. The bands observed at the lower frequency correspond to the lattice vibration modes and can be attributed to M—O and O—M—O vibration.²²

The PXRD pattern for sample Mg-Al-CO₃ is shown in Figure 2. It shows a $c/3$ value 7.76 Å⁰. This indicates a gallery height of 2.96 Å⁰ (assuming a thickness of 4.8 Å⁰ for the cationic sheets). The material is reasonably crystalline and suggests a relatively well-ordered sheet arrangement.²⁰ The crystallite size of this sample was found 24.87 nm as calculated using Scherrer formula.²³ Figure 3 represents the TGA curves of the Mg-Al-CO₃ hydrotalcite. The TGA curve exhibits three main region in the temperature range 30–220°C, 220–420°C, and 420–748°C, respectively, which involves a total weight loss of 44.55%. The TGA results indicate that the LDH is thermally stable upto 220°C. The second weight loss between 220 and 420°C has been ascribed to the dehydroxylation of the brucite like layers along with anion decomposition (decarbonation process) leaving a Mg, Al oxohydroxide upto 420°C. Finally, the third weight loss has been assigned to progressive elimination of hydroxyl ions and produce metal oxides and spinel structure.²⁴

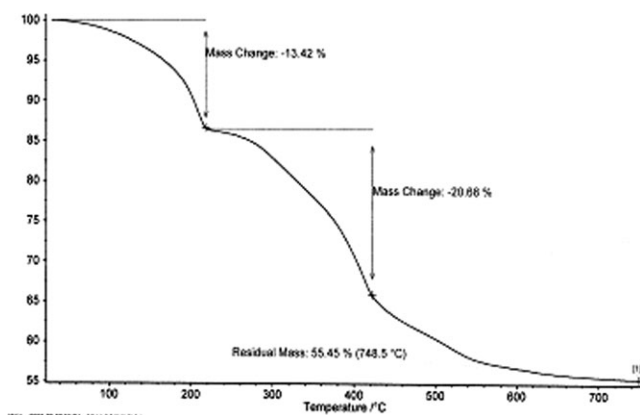


Figure 3 TGA graph of hydrotalcite Mg-Al-CO₃.

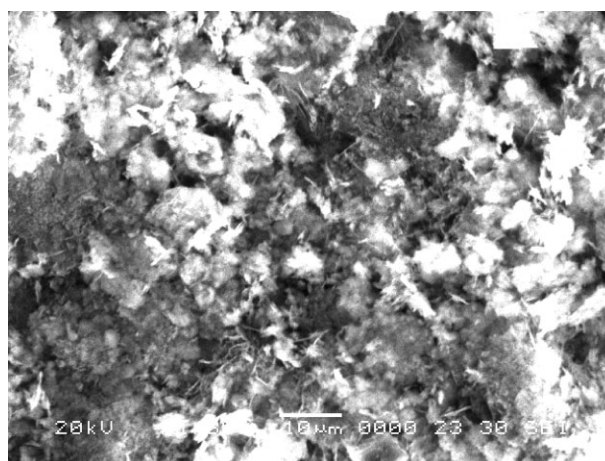


Figure 4 SEM photograph of hydrotalcite Mg-Al-CO₃.

Typical SEM images of Mg-Al-CO₃ hydrotalcite is shown in Figure 4. This figure indicates the existence of lamellar particles looks like rounded hexagonal shape and typical of hydrotalcite like material. The material was found mesoporous with the surface area 90 m²/g.

Thermal stability testing of prepared PVC formulation

HCl evolution measurement

Results of HCl evolution using different PVC formulation are presented in (Table I and Fig. 5). It is clear from Table I that in presence of hydrotalcite (Mg-Al-CO₃) (Exp. No.8) evolution of HCl (2 mmol) took 497 min, whereas in blank PVC (Exp. No.1), it was just 50 min. When hydrotalcite was replaced by CaSt₂ (Exp. No.3) the HCl evolution required 386 min. This shows that hydrotalcite provide long term stability. When ZnSt₂ (Exp. No.2) alone and in combination with CaSt₂ (Exp. No.4) was used, it showed unsatisfactory result. Concentration of ZnSt₂ also plays a significant role in synergism. When a combination of hydrotalcite + CaSt₂ + ZnSt₂ in the ratio of 1 + 0.5 + 0.5 (total 2 phr) (Exp. No.5) was used, HCl evolution took just 48 min. The HCl evolution got increased to 128 min, when concentration of ZnSt₂ was reduced from 0.5 to 0.25 phr. Conclusively, the stabilizer combination hydrotalcites + CaSt₂ + ZnSt₂ (1 + 0.75 + 0.25) (Exp. No.6) prove better. When ZnSt₂ was excluded from the system and combination of Mg-Al-CO₃ and CaSt₂ (1 phr each) (Exp. No.9) was tried, then the significant improvement was observed and HCl evolution time was 260 min. When magnesium acetylacetonate was tried in place of CaSt₂ (Exp. No.7), then it showed better results as far of HCl evolution time and color stability is concerned (Fig. 6). A combination of CaSt₂ + hydrotalcite + Magnesium acetylacetonate (1 + 0.5 + 0.5 phr)

TABLE I
Effect of Stabilizers on HCl Evolution and Degradation Time at 180°C

Exp. No.	Components	Quantity (phr)	Induction period (min)	Time for 2 mmol HCl evolution (min)
1	PVC (blank)	100	8	50
2	PVC + ZnSt ₂	100 + 2	4	16
3	PVC + CaSt ₂	100 + 2	30	386
4	PVC + CaSt ₂ + ZnSt ₂	100 + 1 + 1	7	55
5	PVC + CaSt ₂ + ZnSt ₂ + Mg-Al-CO ₃	100 + 0.5 + 0.5 + 1	11	48
6	PVC + CaSt ₂ + ZnSt ₂ + Mg-Al-CO ₃	100 + 0.75 + 0.25 + 1	20	128
7	PVC + Mg-Al-CO ₃ + Mg(acac) ₂	100 + 1 + 1	14	275
8	PVC + Mg-Al-CO ₃	100 + 2	22	497
9	PVC + CaSt ₂ + Mg-Al-CO ₃	100 + 1 + 1	20	260
10	PVC + CaSt ₂ + Mg-Al-CO ₃ + Mg(acac) ₂	100 + 1 + 0.5 + 0.5	9	206

(Exp. No.10) was also tried. It showed little bit poor synergism then Exp. No.7 and 9. This may be due to lower concentration of hydrotalcites (from 1 phr to 0.5 phr) and the HCl evolution becomes fast.

Oven-ageing test for color stability measurement

In Figure 6, oven-aging test results are shown. The blank (Exp. No.1) when heated at 180°C remains white upto 20 min but it turned yellow in 30 min. Brown color was observed in 50 min and after that its discoloration was very fast and become black in 360 min. Addition of CaSt₂ as thermal stabilizer (Exp. No.3) shows 20 min additional color stability. Color chart also reveals that blackening time has also increased to 400 min. The sheet of Exp. No.4 was prepared by using 1 phr CaSt₂ and 1 phr ZnSt₂ as stabilizer to evaluate the synergistic effect. The Figure 6 reveals that except the little improvement in color intensity between 80 and 120 min whole pattern is similar. The sheet of Exp. No.8 was prepared by mixing hydrotalcite Mg-Al-CO₃. This sheet

become pink in 30 min and brown color was observed after 80 min heating. A very noticeable result obtained here was that blackening time of this sheet was 800 min, that is, a marked improvement. Thus suggesting that hydrotalcite Mg-Al-CO₃ provided long-term stability.

Sheet of Exp. No.9 was prepared by using stabilizer combination 1 phr CaSt₂ and 1 phr hydrotalcite Mg-Al-CO₃. A slight pink color was observed in 20 min and it remained pink up to 80 min. Later it turned yellow in 100 min and to brown in 120 min but the blackening time of this sheet was 800 min. In Sheet of Exp. No. 10, a stabilizer mixture 1 phr CaSt₂, 0.5 phr hydrotalcites Mg-Al-CO₃, 0.5 phr magnesium acetylacetonate was used having total stabilizer concentration 2 phr in 100 phr PVC. A remarkable improvement was that it maintained white color upto 80 min. It changed to yellow in 100 min and brown in 140 min. This color becomes gradually darker and turned to black in 400 min. It clearly reveals that by adding magnesium acetylacetonate although initial color stability is markedly

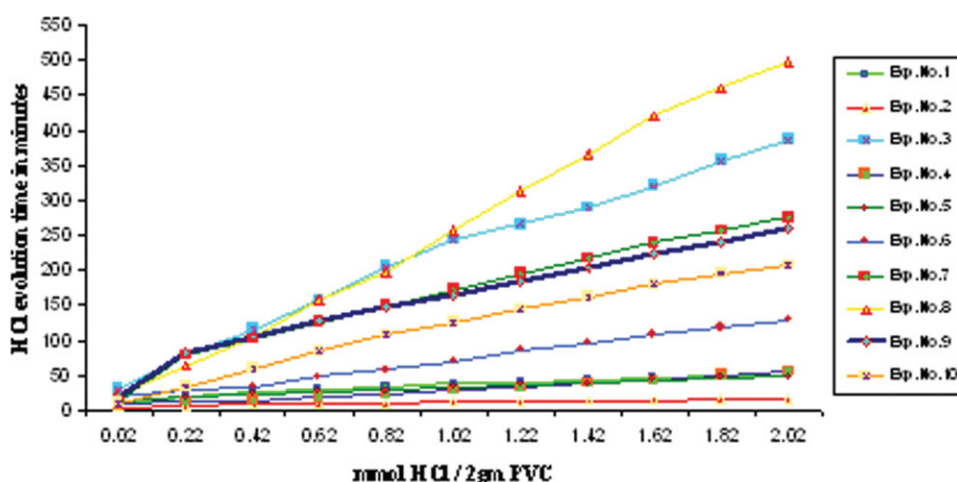


Figure 5 Evolution of HCl (dehydrochlorination of PVC) at 180°C in presence of 2 phr stabilizer system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

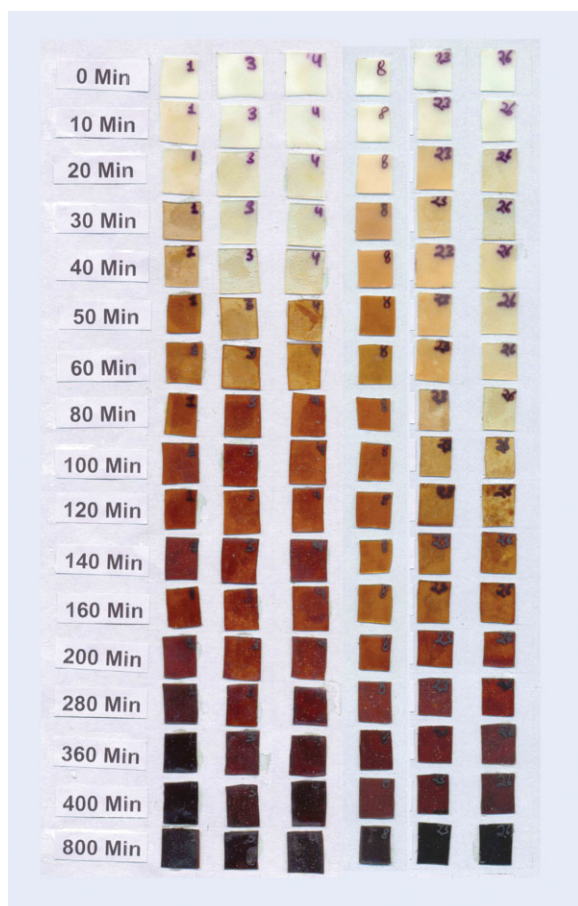


Figure 6 Change of color of sheet with time at 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

improved but due to early consumption and less concentration of hydroaltalcite long term stability is markedly impaired. These observations also suggest that hydroaltalcites works as along term stabilizer and 1 phr concentration is sufficient to maintain long term color stability.

Polyene formation

The Figures 7 and 8 shows polyene formation during oven-aging. The UV-visible spectra of the blank PVC (Exp. No.1) in THF at 308 nm shows the presence of 3-conjugated double bond. Figure 7 shows that there is slight increase in absorbance when sheet was heated upto 40 min. On further heating to 100 min, the absorbance at 308 nm increased very rapidly and this behavior continues upto 280 min. This suggests that from 0 to 40 min formation of short chain polyene ($n = 3$ double bond) takes place slowly but formation of short chain polyene was very fast when PVC was heated for longer duration, that is, 100, 160, and 280 min. Addition of CaSt_2 to PVC (Exp. No. 3) and spectra at 308 nm shows that

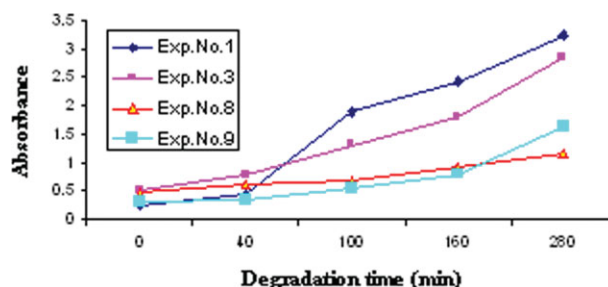


Figure 7 Plot of absorbance versus degradation time (min) in presence of stabilizer using UV-visible spectrophotometer at λ_{max} 308 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

there is decrease in absorbance at 100, 160, and 280 min. It shows that CaSt_2 addition decreases short chain polyene formation. In the presence of hydroaltalcite Mg-Al-CO_3 (Exp. No.8), the short range polyene formation is very slow and uniform as shown by the low absorbance at 308 nm. The addition of $\text{Mg-Al-CO}_3 + \text{CaSt}_2$ to PVC (Exp. No.9) shows that the formation of short range polyene is slow during 40 to 160 min. After 160 min, polyene formation increases rapidly. The spectrum of blank PVC at 400 nm corresponds to 6–8 double bonds ($n = 6-8$). It shows that upto 40 min very less number of polyene is formed and between 20 and 40 min very light yellow color develops. After 40 min, formation of long chain polyene is very fast and the sheet looked brown in 50 min and the color darkens. Addition of CaSt_2 to PVC (Exp. No. 3) shows that polyene formation grows from 0 to 40 min slowly and then steadily upto 150 min and after 160 min it grows very fast (Fig. 8). The addition of hydroaltalcite (Mg-Al-CO_3) (Exp. No.8) shows slow formation of polyene. When the sheet was heated upto 280 min, polyene formation was slow and steady. This observation was supported by HCl evolution too. The addition of $\text{CaSt}_2 + \text{Mg-Al-CO}_3$ into PVC

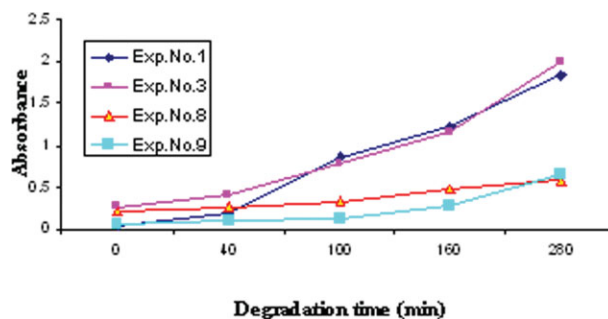


Figure 8 Plot of Absorbance versus degradation time (min) in presence of stabilizer system using UV-visible spectrophotometer at λ_{max} 400 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

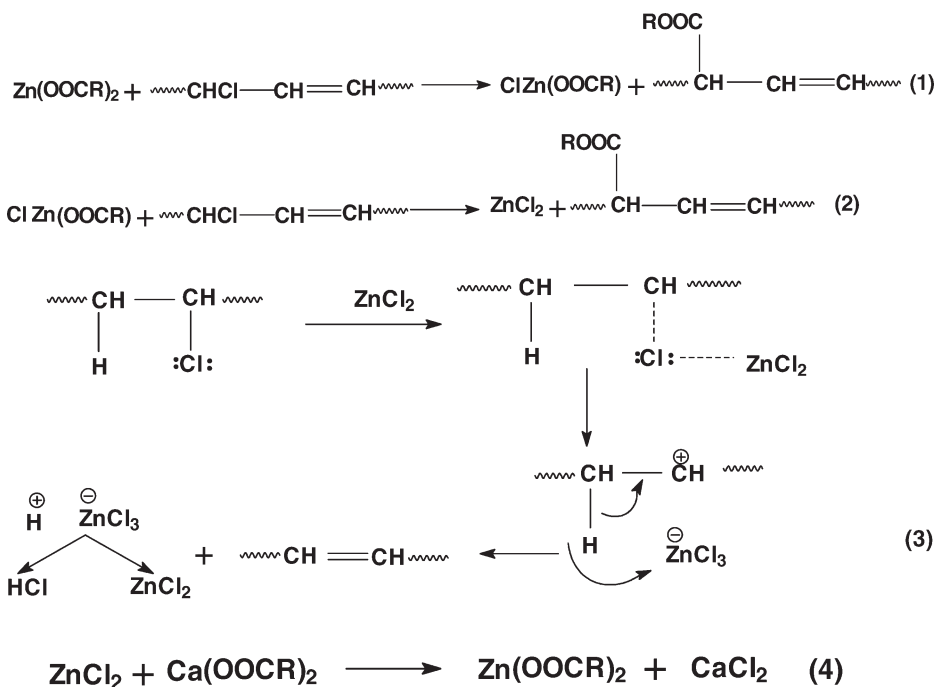
(Exp. No.9) shows that average size polyene ($n = 6-7$) formation was very slow during 0–100 min. It is much slower when compared with blank PVC.

Mechanistic overview

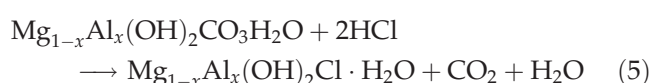
The above findings clearly reveals that color stability and HCl evolution are not directly related, shorter the induction period (T_s) when no detectable HCl is liberated the more is the color stability, but when HCl evolution rate is slow, blackening time of PVC samples increased considerably. Results show that hydrotalcite scavenge HCl from system very fast and do not allow HCl to catalyze further dehydrochlorination and hence the blackening time got increased. It is also evident by UV-visible studies that an average sized polyene gives pale yellow color, whereas red or brown color was developed due to long range polyene ($n = 10-14$) sequences. Hence, the HCl evolution depends on the rate of dehydrochlorination, but color depends on the kind of polyene formed.

Because the stearates showed longer induction period as well as slow rate of dehydrochlorination,

that is, all the stearate are comparable to hydrotalcite. It has been reported by researchers^{25,26} that soap stabilizers mainly work by displacement of labile chlorine (tertiary and allylic chlorine) atoms on the PVC chain by more stable ester moiety and this will occur at the early stages of degradation before the loss of any HCl gas, that is, consumption of soap stabilizers during the early stage of degradation was very fast, which is shown by larger induction period. Cleavage of the ester bond required higher activation energy than the cleavage of the C–Cl bond. Because of this reason, the release of HCl from stabilized PVC decreased. After termination state, the ester group splits off from the chain and the stearic acid content increased rapidly. Stearic acid then catalyzes the continuing elimination of HCl thus contributing to the increase in the dehydrochlorination rate after induction period thus polymer turns black. The synergistic effect of $ZnSt_2$ and $CaSt_2$ has been attributed to a fast exchange reaction between $ZnSt_2$ and $CaSt_2$, where the active $ZnSt_2$ was regenerated and the undesirable $ZnCl_2$ was consumed. This assumption can be represented by following mechanism.^{27,28}

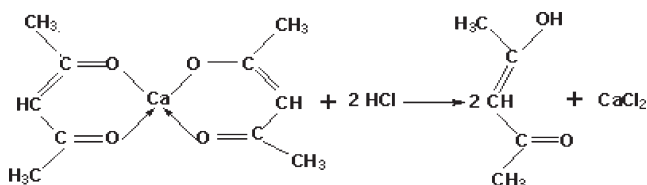


In this way alkaline earth carboxylate removes the potentially destructive effect of the covalent metal chlorides. Hydrotalcite are slow HCl scavengers resulting scavenging duration very long. The ion-exchange mechanism¹⁴ was suggested for their stabilizing efficiency.



Although we have suggested that besides ion-exchange, adsorption is a key factor for augmenting the stabilizing efficiency in hydrotalcites.²⁹

The study of synergistic effect, the initial color has been found to improve markedly when acetylacetonate complex with long term stabilizers such as Mg-Al-CO₃ was used along with CaSt₂. It can be seen that when only CaSt₂ was used discoloration time was 40 min, with Mg-Al-CO₃ it was only 20 min, but when 0.5 phr Mg(acac)₂ was added, PVC remained white for a considerably increased duration, that is, 80 min. It clearly shows that Mg(acac)₂ complex behaves as short-term costabilizers and increased initial color stability. The acetylacetonates substitute allylic chlorides inhibiting the formation of long polyenes and hence no discoloration of the polymer.⁹



HCl is produced as a product of the reaction in larger quantity when all of the calcium stearate and metal acetylacetonate was consumed. This leads to blackening of the polymer. In Exp. No.10 when hydrotalcites Mg-Al-CO₃ is added, blackening time increased to 800 min. Thus it can be concluded that metal stearate and metal acetylacetonate act as short-term stabilizer while hydrotalcites act as long term stabilizer.

CONCLUSIONS

Above findings leads to the following conclusions

1. The stabilizers, with greater induction period and faster rate of dehydrochlorination, reveal that in such cases all the stabilizing properties are exhausted during the induction period.
2. The first category of stabilizer characterized by the greater efficiency [longer Ts (induction period during which no detectable amounts of HCl gas are liberated) and lower rate of dehydrochlorination] are hydrotalcites and metal stearates.
3. The second category of stabilizers characterized by the lower efficiency (shorter Ts and higher rate of dehydrochlorination) is metal β -diketones.
4. In case of costabilizers, metal acetylacetonate reacts at the very beginning and the later degradation is controlled by the metal stearates and hydrotalcite.
5. By scavenging HCl using hydrotalcite autocatalytic, degradation of PVC can be delayed.

6. Although metal soaps react with polyenes, they are poor HCl acceptor. So the combination of good HCl acceptor such as synthetic hydrotalcites and polyene destructive compounds may be useful to inhibit the discoloration of PVC during its processing at 180°C.
7. A heavy metal (like Pb, Cd, Ba) and zinc free stabilizer system can be prepared by using a combination system through proper choice of β -diketone, metal stearate and hydrotalcite.

The authors are grateful to IUC Indore (India) for providing facilities to records spectra of EDX and XRD. We gratefully acknowledge the facilities extended by HPL Faridabad (India) in preparing sheets.

References

1. PVC poses new opportunities for compounders' p 172, Chem weekly February 7 2006 No. 25, Vol. LI, Sevak Publication Mumbai.
2. Kirk-Othmer, Encyclopedia of Chemical Technology, 4th edition; Wiley: New York, 1994, Vol. 12, p 1071.
3. Drewes, R.; Kolb, M.; Kuhn, K. J.; Sander, H.; Wehner, W. EP 677, 550, 1995.
4. Lutz, J. T. R. F., Jr.; Grossman, R. F. Polymer Modifiers and Additives; Marcel Dekker Inc.: New York, 2001.
5. Michell, E. W. J vinyl Technol 1986, 8, 55.
6. Iida, T.; Goto, K. J Appl Polym Sci 1980, 25, 887.
7. Iida, T.; Kawato, J.; Tanie, S.; Goto, K. J Appl Polym Sci 1989, 37, 1685.
8. Leistner, W. E.; Setzler, W. E. US Patent 2,564,646, 1951.
9. Benavides, R.; Edge, M.; Allen, N. S.; Telly, M. M. J Appl Polym sci 1998, 68, 1.
10. Albarino, R. V.; Otoka, E. P. J Appl Polym Sci 1972, 16, 61.
11. Mohamed, N. A.; Al Magribi, W. M. Polym Degrad Stab 2002, 78, 149.
12. Lerke, I.; Szymanski, W. J Appl Polym Sci 1977, 21, 2067.
13. Fisch, M. H.; Bacalogue, R. Plast Rubber Compos 1999, 28, 119.
14. Kalouskova, R.; Novotna, M.; Vymazal, Z. Polym Degrad Stab 2004, 85, 903.
15. Yun, S. K.; Pinnavaia, T. J. Chem Mater 1995, 7, 348.
16. Katsumi, I.; Takeo, K.; Ryoichi, O.; Shigeru, K. Chem Abstr 1978, 89, 7978 w.
17. Masayuki, N.; Zenichi, I.; Takuya, M. Chem Abstr 1978, 88, 91405 s.
18. Okada, M. WO Patent 000,02,838, 2000.
19. Cavani, F.; Trifiro, F.; Vaccari, A. Catal Today 1991, 11, 173.
20. Labajos, F. M.; Rives, V.; Ulibarri, M. A. J Mater Sci 1992, 27, 1546.
21. Hernandez-Moreno, M. J.; Ulibarri, M. A.; Rendon, J. L.; Serna, C. J. Phys Chem Miner 1985, 12, 34.
22. Houri, B.; Legroun, A.; Barroug, A.; Forano, C.; Besse, J. P. J Chim Phys 1999, 96, 455.
23. Bookin, A. S.; Drits, A. Clay Clay Miner 1993, 41, 551.
24. Chibwe, K.; Jones, W. J Chem Soc Chem Commun 1989, 926.
25. Tawfik, S. Y.; Asaad, J. N.; Sabaa, M. W. Polym Degrad Stab 2006, 91, 385.
26. Arkis, E.; Balkose, D. Polym Degrad Stab 2005, 88, 46.
27. Fish, M. H.; Bacaloglu, R. J Vinyl Add Tech 1995, 5, 205.
28. Stoeva, S.; Karaivanova, M.; Benev, D. J Appl Polym Sci 1992, 46, 119.
29. S. Gupta, Ph.D. Thesis, Jiwaji University, Gwalior (M.P.), India, 2006.