Zinc stearate from galvanizing waste materials and its use as thermal stabilizer in PVC industries

F. K. Rony¹, S. K. Ray¹, A. Hoque¹, Asaduzzaman², S. Sultana¹, H. P. Nur¹* and S. T. A. Islam²

¹BCSIR Laboratories Dhaka, Bangladesh Council of Scientific and Industrial Research, Dhanmondi, Dhaka-1205, Bangladesh.
²Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka-1000, Bangladesh.

Abstract

Galvanizing industries of Bangladesh produce profuse amount of environmentally hazardous solid waste materials like zinc dross which contains significant amount of valuable zinc and harmful heavy lead. Zinc was extracted as zinc chloride (ZnCl₂) from zinc dross. Zinc stearate (ZnSt₂) samples were prepared by precipitation method from stearic acid, sodium hydroxide and ZnCl₂ by varying the amount of the reagents and product yield found within the range 96.06-99.18%. Characteristic peaks of ZnSt₂ were investigated by Fourier Transform Infrared Spectroscopy (FTIR). Differential Scanning Calorimeter (DSC) onset curve assigned accurate melting point within the range 122.84-124.03°C. Surface morphology of ZnSt₂ was observed by Scanning Electron Microscope (SEM) and products had semi-crystalline structure. Thermal stability of ZnSt₂ was evaluated by Thermo-gravimetric Analyzer (TGA) that complied with literature. A combination of ZnSt₂ and Calcium stearate (CaSt₂) at 1:1 ratio was used as thermal stabilizer in the powder commercial grade PVC resin and performed better thermal stability. The dehydrochlorination temperature of PVC with mixed stearates was 344.67±1.04°C for 10% (w/w) loading whereas for PVC, PVC with 10% (w/w) ZnSt₂ and PVC with 10% (w/w) CaSt₂, it was 269.83±1.04°C, 317.33±1.26°C and 323.33±2.08°C respectively.

Keywords: Zinc dross; Zinc stearate; PVC; Thermal stabilizer; Dehydrochlorination

Introduction

Galvanization is a process of applying a protective thin layer of zinc coating to steel or iron in order to prevent corrosion and increase the attractiveness of commodity. In hot-dip galvanizing processes lead is used to reduce the surface tension of zinc, improve the fluidity of the bath, enhance drainage properties and thus limit excess zinc on the dipped product (Asgari et al., 2007). The galvanizing industries are produced some wastes such as zinc dross which contains significant amount of heavy metals and also has tremendous health and environmental risk for human, animal and plant.

Zinc exhibits both the deficient or toxic effect on animal and plant. Zinc diet deficiency causes detrimental impact on growth, neuronal development and immunity but overdose zinc affects on health (Plum et al., 2010).

Inhalation of zinc containing smoke, generally originated from galvanization industry, affects respiratory system like chest pain, cough, bronchiolar leukocytes and dyspnea (Prasad, 2008). Zinc can interrupt the activity in soil as it negatively influences the micro-organisms and earthworms. It also slows down the breakdown of organic matter and increase the pH of water. On the other hand, heavy metal lead inimical affect almost all organs and systems in human body including the heart, bones, intestines, kidneys, nervous, immune and reproductive systems (Rossi, 2008). Recycling or recovery of valuable materials from the zinc dross waste is economically rewarding and also minimizing environmental pollutions.

Zinc chloride is produced by hydrochloric acid (HCl) leaching from zinc dross. In presence of hot concentrated HCl,
The desired water insoluble ZnSt₂ is subsequently produced (equation 4). The solubility product of ZnCl₂ is 127 mol⁻³L⁻³ and PbCl₂ is 1.6×10⁻⁵ mol⁻³L⁻³ at 25°C (Hahne and Kroontje, 1973). As the solubility of ZnCl₂ is million times greater than lead chloride, PbCl₂ precipitates easily at room temperature. The Fe²⁺ can be oxidized to Fe³⁺ with oxidizing agent and easily be separated as Fe(OH)₃. The residual solution is the aqueous solution of zinc chloride which can be dried or directly used for the preparation of ZnSt₂.

\[
\text{Zn}(aq) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g) \quad (1)
\]

\[
\text{Pb}(aq) + 2\text{HCl}(aq) \rightarrow \text{PbCl}_2(aq) + \text{H}_2(g) \quad (2)
\]

Zinc stearate [Zn(C₁₈H₃₅O₂)] ester is one of the important hydrophobic ionic surfactants of metal soaps that is commercially important and finds applications in areas such as thermal stabilizer specially for polyvinyl chloride (PVC), synergic stabilizer for Ba/Cd and Pb stabilizer systems, gloss imparting agent in paint industry, metal release agent in rubber, polyurethane and polyester processing system, die release agent in powder metallurgy, lubricant in cosmetics to improve texture, waterproofing agents for plastics, acid scavenger and processing aid for certain polyolefin applications etc. (Akanni et al., 1992; Fang, 2009; Rahman et al., 2011).

ZnSt₂ soap is manufactured by using one of the three processes: double decomposition (precipitation process, reaction 3 and 4), direct reaction of carboxylic acid with metal oxides, hydroxides or carbonates and direct reaction of metals with molten fatty acids (Gönen et al., 2005). In precipitation process, the fatty acid is first saponified in relative large volume of heated water with an equimolar to a slight excess quantity of a strong alkali solution (NaOH) to form water soluble alkali stearate soap (reaction 3). The desired water insoluble ZnSt₂ is subsequently produced by adding metal salt solution (ZnCl₂) at a temperature below the boiling point of water under atmospheric pressure (equation 4).

\[
\text{C}_{17}\text{H}_{35}\text{COOH}^- + \text{NaOH}(aq) \rightarrow \text{C}_{17}\text{H}_{35}\text{COO}^- \text{Na}^+(aq) + \text{H}_2\text{O}(l) \quad (3)
\]

\[
2\text{C}_{17}\text{H}_{35}\text{COO}^- \text{Na}^+(aq) + \text{Zn}^2+2\text{Cl}^-(aq) \rightarrow \text{C}_{17}\text{H}_{35}\text{COO}_2\text{Zn}^{2+} + 2\text{Na}^+\text{Cl}^-(aq) \quad (4)
\]

Poly(vinyl chloride), PVC, is one of the common commodity plastic, and its production is the third largest, after polyethylene and polypropylene (Yoshioka et al., 2008). It is cost-effective, highly versatile and is used in many construction applications as water, sewage and drainage pipes, and a variety of extruded profiles (van Es et al., 2008). Though PVC is one of the most important commercial plastic materials but it is thermally unstable at processing temperature. Until the discovery of thermal stabilizers, PVC was not an industrially very useful polymer, as it could not be processed to useful articles without degradation at elevated temperatures (Folari and Sadiku, 2011).

Thermal degradation of PVC occurs by autocatalytic dehydrochlorination reaction (Zipper reaction, reaction 5) with the subsequent formation of conjugated double bonds (Moulay, 2010; Sánchez-Jiménez, et al., 2010; Šimón, 1992). After the loss of first HCl molecules, the subsequent unsaturated structure formed in a PVC chain is an allylic chlorine structure which stimulates the next loss of HCl molecule. The repeated process leads to the chain or zip dehydrochlorination. The process starts at the glass transition temperature (70 °C) by elimination of HCl which is the main volatile product up to 300 °C (Klaric et al., 2012). The elimination of HCl from polymer backbone leads discolouration of polymer polyene sequences of 5 to 25 double bonds (Tahira et al., 2014). Depending on the number of conjugated double bonds formed, it becomes yellow, orange, red, brown and finally black (Sabaa and Mohamed, 2007). The splitting off of HCl from the polymer backbone affects the physical, chemical and the mechanical properties of the PVC. It is well established that ZnSt₂ react with the allylic chlorine atoms (reaction 6) which leads the PVC esterification (Chen et al., 2014). Thus, the by-product of the stabilization reaction is ZnCl₂ which is strong Lewis acids and is powerful catalyst of the substitution reaction as well as the dehydrochlorination. It’s accumulation in the polymer matrix has a detrimental effect on PVC thermal stability (Chen et al., 2014; Hoang et al., 1976; Michel and Van Hoang, 1981). On the other hand, the previous stabilization reaction through the O-alkylation is not permanent because the unsaturated ester is able to react with HCl even at moderate temperature to generate again allylic chlorine atoms and carboxylic acid (Michel and Van Hoang, 1981). Calcium stearate (CaSt₂) not only absorbs HCl but also exchanges
ions with ZnCl₂ (Xu et al., 2014). In the ion exchange reaction, the active ZnSt₂ is generated and the undesirable ZnCl₂ is consumed (reaction 7). The accumulation of CaCl₂ in the polymer matrix has no adverse effect on the blackening and the cross-linking of the polymer. In consequences, the main role of the CaSt₂ is delay the accumulation of ZnCl₂ in the polymer matrix and to serve as a reserve to increase the lifetime of the ZnSt₂ (Hoang et al., 1976).

\[
\begin{align*}
\text{CH}_2\text{CHCl}-\text{CH}_2\text{CHCl} & \rightarrow \text{CH}2=\text{CH}=\text{CH}+2\text{HCl} \ldots \ldots (5) \\
2\text{CH}_3\text{CH}=\text{CH}-(\text{CH})\text{Cl}-\text{CH}_2\text{CH}_3 & + (\text{RCOO})_2\text{Zn} \\
\downarrow \\
2\text{CH}_3\text{CH}=\text{CH}-(\text{OOCR})-\text{CH}_2\text{CH}_3 & + \text{ZnCl}_2 \rightarrow \text{Zn}(\text{OOCR})_2^+\text{CaCl}_2 \ldots \ldots (6) \\
\text{ZnCl}_2+\text{Ca(OOCR)}_2 & \rightarrow \text{Zn(OOCR)}_2^+\text{CaCl}_2 \ldots \ldots (7)
\end{align*}
\]

The purpose of the research reported here was to extract economically valuable zinc and lead from galvanizing waste and to minimize the environmental pollutions. This study addresses the preparation and characterization of ZnSt₂ by using extracted ZnCl₂ and its potential application as thermal stabilizer of PVC resin.

Materials and methods

Materials

The zinc dross was collected from a galvanizing plant located at Chittagong, Bangladesh. The zinc dross contained 66.18% lead, 23.56% zinc and other insoluble impurities. Analytical grade stearic acid (Poole, England), hydrochloric acid (Merk, Germany), sodium hydroxide (Poole, England), hydrogen peroxide (Active fine chemicals, Bangladesh) were used in this research. The commercial grade PVC (LG Chem (Taiwan) Ltd) was collected from local market. Mineral (ash) content and volatile content (in house oven dried at 105°C) of PVC were 8.41% and 0.045% respectively.

Methods

Production of ZnCl₂ and PbCl₂

The zinc dross (10 g) was leached in HCl for 10 hrs at 100 °C temperature. The leached liquor was filtered at hot condition and concentrated to such a point that crystallization began on cooling. It was then filtered to separate PbCl₂. The pH of the solution was kept between 3.9-4.0 by adding ammonium hydroxide and HCl. The solution was diluted 100 ml and heated nearly to boil. Then the solution boiled two minutes with 0.4 ml H₂O₂ (30%) and followed by freezing in refrigerator for 3 days. Iron was precipitated as Fe(OH)₃ and ZnCl₂ solution was obtained after filtration. ZnCl₂ was investigated by atomic absorption spectroscopy (AAS) (AAnalyst 800, Perkin Elmer).

Preparation of ZnSt₂

Eight batches of ZnSt₂ were produced with reagents variation by precipitation process (Table I). The Batch 1 was produced by using analytical grade ZnCl₂ and other seven batches (Batch 2 to Batch 8) were synthesized from extracted ZnCl₂. The stearic acid (5 g) was added in 200 ml preheated water in a beaker and stirred on a hot plate magnetic stirrer at 60-70 °C temperature and 120 rpm. Then, NaOH solution was slowly mixed with melted stearic acid and heated until clear NaSt was produced. Zinc chloride solution was slowly added in the NaSt solution and heated at 80-90 °C for 30 mins to produce ZnSt₂. The final ZnSt₂ solution was filtered and washed with water. The wet ZnSt₂ was dried and stored.

ZnSt₂ characterization

A Fourier transform infrared (FTIR) spectrophotometer (Model: IRPrestige-21, Shimadzu Corporation, Japan) was used to investigate the characteristics functional group peak of ZnSt₂. Approximately 2 mg of dried ZnSt₂ sample and

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Batch 3</th>
<th>Batch 4</th>
<th>Batch 5</th>
<th>Batch 6</th>
<th>Batch 7</th>
<th>Batch 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic acid</td>
<td>equimolar</td>
<td>equimolar</td>
<td>10% excess</td>
<td>5% excess</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>10% excess</td>
<td>5% excess</td>
<td>equimolar</td>
<td>equimolar</td>
</tr>
<tr>
<td>NaOH</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>equimolar</td>
<td>10% excess</td>
<td>5% excess</td>
</tr>
</tbody>
</table>
200 mg of potassium bromide (KBr) were blended and trituated with an agate mortar. The mixture was compacted using an IR hydrolaulic press at a pressure of 6 tons for 60 s. The spectra of ZnSt₂ samples (in the form of KBr discs) were obtained using the spectrophotometer with a wave number range of 4000-400 cm⁻¹. The melting point of ZnSt₂ was measured in melting point apparatus (Model- WRS-1B, Sunon Wealth Elec. Mech. Ind. Co. Ltd). The sample (1-2 mg) was taken in a capillary tube and placed in the apparatus. The melting point was observed with increasing temperature 1 °C/min.

Results and discussion

Analysis of ZnSt₂

The characteristic peaks of ZnSt₂ at 1540 and 1398 cm⁻¹ were observed in the FTIR spectrum. These bands are due to antisymmetric and symmetric carboxylate stretching bands (COO⁻ and COO⁻) respectively (Sakai & Umemura, 2002). The coordination of oxygen atom to zinc atom was in chelating form because the IR peak at 1540 cm⁻¹ was observed instead of IR peak at 1576 cm⁻¹ (Benavides et al., 1994).

Antisymmetric and symmetric methylene stretching, and methylene scissoring bands (CH₂, CH₂, and CH₂) were observed at about 2916, 2846, and 1458 cm⁻¹ respectively (Gönen et al., 2005). These bands are due to the alkyl chain in the ZnSt₂ structure. The absence of asymmetric stretching vibration of COO⁻ (Carboxylate of NaSt₂) around 1560 cm⁻¹ indicates that all NaSt₂ was converted into ZnSt₂. On the other hand, absence of C=O stretching around 1700 cm⁻¹ revealed that product was free from stearic acid.

EDX elemental compositions of ZnSt₂ were performed at three different points of the sample and average values of these results are reported in Table II. From the table, it is revealed that the composition of ZnSt₂ produced by analytical grade ZnCl₂ (Batch 1) and extracted ZnCl₂ (Batch 2) show similar results which assign the purity of extracted paper was placed on open part of the capillary tube. One drop of distilled water was used to wet the indicator paper which confirmed the sealing of the tube. The dehydrochlorination temperature was observed with initial temperature set up at 140 °C and 3 °C/min rise up.

Analysis of PVC

A thermo-gravimetric analyzer (TGA-50, Shimadzu, Japan) was used to determine the thermal behavior of ZnSt₂, PVC and ZnSt₂ loaded PVC. The sample (8-10 mg) was loaded in aluminum pan and heated from 30 to 600 °C at a heating rate of 10 °C per min. under 10 ml/min nitrogen gas flow. A Differential Scanning Calorimeter (DSC) (Model: DSC-60, Shimadzu Corp., Japan) was used to determine accurate melting point and phase transition of ZnSt₂. The sample (2-4 mg) was taken in aluminum pan and pellet was formed under pressure and heated from 30 to 200 °C at a heating rate of 10 °C per min. under 20 ml/min nitrogen gas flow.

Dehydrochlorination of PVC

The performance of stabilizer (ZnSt₂ and CaSt₂) in PVC was estimated by measuring dehydrochlorination temperature of PVC and thermogravimetric analysis. Test samples were prepared by adding metal stearate into powder PVC and mixed properly by an extruder (LME230, Alpha Group, USA). The dehydrochlorination temperature of PVC was measured by digital melting point apparatus (WRS-1B, supplier- Sunon Wealth Elec. Mech. Ind. Co. Ltd). Test samples (1-2 mg) were taken in a capillary tube. A strip of universal indicator

Morphological and elemental analysis of ZnSt₂ using SEM-EDX

The particle morphology and elemental composition of ZnSt₂ were investigated by using a high-resolution SEM-EDX (Model No. JOEL JSM-6490 LA, Joel Ltd. Japan) instrument at 3.0 nm and an accelerating voltage of 10 kV.

Effects of reagents on elemental composition of ZnSt₂

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TG and DSC analysis of ZnSt₂ and PVC

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ZnCl₂. All ZnSt₂ products have higher zinc content than theoretical value owing to the formation of coordination of O with Zn²⁺ ion rather than ionic form. The molar ratio of oxygen atom to zinc atom of ZnSt₂ is lower than the theoretical value confirmed the coordination of O atoms with Zn²⁺ ion which is consistent with FTIR observation.

Table II. EDX elemental analysis of ZnSt₂

<table>
<thead>
<tr>
<th>Elements</th>
<th>Theoretical value</th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Batch 3</th>
<th>Batch 4</th>
<th>Batch 5</th>
<th>Batch 6</th>
<th>Batch 7</th>
<th>Batch 8</th>
</tr>
</thead>
</table>
| C        | 68.43            | 69.10± | 69.11± | 68.62  | 68.54  | 67.63± | 67.74± | 69.41± | 69.39±1.194 2.15 ±0.99 1.22 1.46 0.90 2.21 14
| O        | 10.12            | 8.75±0.66 | 8.67±1.07 | 9.47±1.27 | 9.42±1.55 | 8.49±1.14 | 8.56±1.09 | 8.15±1.09 | 8.11±1.12 |
| Zn       | 10.34            | 11.6±1.29 | 11.13±1.39 | 10.82±0.30 | 10.95±0.59 | 12.79±1.27 | 12.61±1.52 | 11.35±1.12 | 11.41±1.46 |
| H (Theoretical value) | 11.09 11.09 11.09 11.09 11.09 11.09 11.09 11.09 11.09 |
| Molar ratio of O to Zn atom | 4 2.96 2.92 3.28 3.23 2.49 2.55 2.69 2.66 |

Effects of reagents on yield and phase transition temperature of ZnSt₂

The yield percentages and phase transition temperature (melting point) of different ZnSt₂ products are reported in the Table III. The yield percentages for excess reagents were higher than equivalent ratio because maximum conversion of limiting reagent was performed here. Maximum yield were found in Batch 3 and 4 because almost all stearic acid was combined with zinc. The melting points of ZnSt₂ were lower than reported value in the literature assigned the presence of other fatty acid soaps in ZnSt₂.

Morphological analysis of ZnSt₂

The crystal morphology of ZnSt₂ samples are presented in Fig. 2. From the figure it is clear that the particles of batch 3 product (ZnSt₂ produced from excess stearic acid) are large but the crystal is less sharp than the crystals of the other prod-
ucts of ZnSt$_2$ due to presence of unreacted stearic acid. The presence of excess stearic acid in reactor causes large agglomerated crystal growth. These observations are consistent with literature (Gönen et al., 2005). The products obtained from excess ZnCl$_2$ (Batch 5) and excess NaOH (Batch 7) showed smaller crystal than batch 3 product but larger than equivalent ratio (Batch 2) product. The particles of equivalent ZnSt$_2$ (batch 2) were more orderly packed and its crystal had sharper edges than other products.

Thermal analysis of ZnSt$_2$

The DSC thermograms of ZnSt$_2$ are plotted in the Fig. 3. All products had a large sharp endothermic peak in the DSC thermogram owing to the melting of ZnSt$_2$. The melting tran

Table III. Effect of reagents on melting point and yield percentage of ZnSt$_2$

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>Melting point from melting point apparatus (ºC)</th>
<th>Melting point from DSC thermogram (ºC)</th>
<th>Limiting reagent for yield (%) calculation</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch 2</td>
<td>119-121</td>
<td>123.24</td>
<td>Stearic acid</td>
<td>96.06</td>
</tr>
<tr>
<td>Batch 3</td>
<td>116-120</td>
<td>122.84</td>
<td>ZnCl$_2$</td>
<td>99.18</td>
</tr>
<tr>
<td>Batch 4</td>
<td>119-123</td>
<td>-</td>
<td>ZnCl$_2$</td>
<td>98.08</td>
</tr>
<tr>
<td>Batch 5</td>
<td>119-123</td>
<td>124.03</td>
<td>Stearic acid</td>
<td>98.32</td>
</tr>
<tr>
<td>Batch 6</td>
<td>118-122</td>
<td>-</td>
<td>Stearic acid</td>
<td>97.85</td>
</tr>
<tr>
<td>Batch 7</td>
<td>118-122</td>
<td>123.24</td>
<td>Stearic acid</td>
<td>98.56</td>
</tr>
<tr>
<td>Batch 8</td>
<td>118-122</td>
<td>-</td>
<td>Stearic acid</td>
<td>98.34</td>
</tr>
</tbody>
</table>

Fig. 2. SEM micrograph of ZnSt$_2$ products (a) Batch 2 (b) Batch 3, (c) Batch 5 and (d) Batch 7

The TG thermogram of ZnSt$_2$, PVC and ZnSt$_2$ loaded PVC are shown in the Fig. 4 within the temperature range of 40 to 500 ºC. From the TG thermogram, the remaining mass of ZnSt$_2$ above 450 ºC is 12.2% whereas above this temperature no weight loss occured. The ZnSt$_2$ started to lose weight around 200ºC at which degradation starts. The remaining mass of ZnSt$_2$ at the end of thermal treatment could be oxide and carbonate of zinc metal (Akanni et al., 1992). The major decomposition products of ZnSt$_2$ might be carbon dioxide, alkanes, and ketones as gas products (Artok and Schobert, 2000).
Analysis of PVC thermal stabilizer

The dehydrochlorination temperature of ZnSt₂ and CaSt₂ loaded PVC are plotted in Fig. 5 (a). It was observed that incorporation of both metal stearates increases the dehydrochlorination temperature of PVC resin and with the addition of 10% ZnSt₂ and CaSt₂ it was increased from 269.83±1.04 °C to 317.33±1.26 °C and 323.33±2.08 °C respectively. Above 10% both stearates loading had slight effect on the dehydrochlorination temperature and are not
economic feasible. The thermogravimetric analysis of PVC and PVC with ZnSt$_2$ revealed the similar result which is showed in above Fig. 4. From TG thermogram (Fig. 4 b), it was observed that first weight loss of unstabilized PVC was found above 271 °C. This weight loss assigned the dehydrochlorination of PVC. On the other hand, the initial degradation temperature of stabilized PVC shifted to above 319 °C because of incorporation of 10% ZnSt$_2$. The combined ZnSt$_2$ and CaSt$_2$ was more effective thermal stabilizer than individual and plotted in the Fig. 5 (b) for 10% (w/w) mixed stearate loading. This zinc chloride was consumed by calcium chloride and regenerated ZnSt$_2$. The dehydrochlorination temperature of 10% (w/w) mixed stearates (50% ZnSt$_2$ + 50% CaSt$_2$) mixture was observed 344.67±1.04 °C.

Conclusion

It could be concluded that acid leaching was the chemically and economically feasible process for extraction of zinc and lead from zinc dross. The extracted aqueous ZnCl$_2$ was highly pure which could be directly used for the production of ZnSt$_2$. The high yield percentages of ZnSt$_2$ confirmed the fast and complete reaction rate. The variation of reagents had slightly affected on particle morphology, elemental composition of ZnSt$_2$, yield, thermal response and stabilizing efficiency of ZnSt$_2$ but best quality ZnSt$_2$ was obtained by equivalent reagents ratio. Both ZnSt$_2$ and CaSt$_2$ performed excellent thermal stabilizer for PVC. Upto 10% metal stearates or their mixture would performed optimum thermal stabilizer and above this percentage were not economically feasible.

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References


Asgari H, Torogheinejad M and Golozar M (2007), On texture, corrosion resistance and morphology of hot-dip


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