NEW MERCAPTO ESTERS AS INTERMEDIATES FOR PVC STABILIZERS

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INTRODUCTION

The recent introduction of antimony mercaptides as PVC heat stabilizers is most timely in view of recent developments in the PVC field.

First, the use of twin and multiple screw extruders for PVC pipes and other rigid forms permits the use of low levels of stabilizers on the order of 0.4% and this low level is favorable for antimony stabilizers which otherwise would have many drawbacks at high concentration levels (203%).

Secondly, the erratic price of tin which recently reached approximately $8.00/lb. with forecasts of ever higher prices made antimony an attractive metal as its price of approximately $2.00/lb. has been very stable.

Third, the final approval by N.S.F. of antimony mercaptide stabilizers at a limit of 0.4% stimulated their use for PVC pipes.

One myst remember that the antimony stabilizers on the market are basically the same as first introduced in 1954 by Weinberg et al. At the time they had a short shelf life and usually in a few weeks they precipitated. This phenomenon is caused by their sensitivity to air and moisture. Antimony stabilizers are also sensitive to light and transfer to black liquid quite rapidly. Probably the following scheme summarizes this change:

1 J. E. Kresta (ed.), Polymer Additives
© Plenum Press, New York 1984
(1) \( \text{Sb(10TG)₃} \stackrel{\text{UV} + O_2}{\rightarrow} \text{Sb₂O₃ (white precipitate)} \)

(2) \( \text{Sb(10TG)₃} \stackrel{\text{UV} + N_2}{\rightarrow} \text{Sb₂S₃ (black sulfide)} \)

Recently Dieckman² in a U.S. patent claimed that the early color heat performance of antimony organic sulfur containing compounds was significantly improved if they were combined with ortho-dihydric phenols. Improvements in the long term heat stability also are achievable, according to the patent, and in addition, the compositions are asserted to be liquids which are shelf-stable at ambient temperatures. Dieckman points out that liquid antimony stabilizer compositions tend to deteriorate on standing, as observed by the formation and/or precipitation of solids in the liquid compounds forming heterogeneous liquids, which increase the problems of measuring and mixing the antimony compounds into vinyl halide resins for stabilization. This problem, it is asserted, is overcome by incorporating the ortho-dihydric phenols with the liquid antimony stabilizer. In these combinations, metal carboxylates, and particularly calcium stearate, can also be incorporated to achieve the advantages of the previously issued Dieckman patent.

A number of patents have suggested the use of antimony compounds, particularly sulfur-containing compounds such as the antimony mercaptides. These include U.S. Patents 2,680,726; 2,684,956; 3,340,285; 3,999,220; 3,466,261; and 3,530,158. These patents disclose various types of organic sulfur-containing antimony compounds, but none have been adequate in inhibiting the development of an early yellow discoloration.

German Patent 1,114,808 to Deutsche Advance proposed antimony compounds of the formula:

\[
(XS)_2\text{SbS(CH}_2\text{x})_x\text{COO-A-COO(CH}_2\text{x})_x\text{SSb(SX)}_2
\]

where \( x \) is an integer from 1 to 4, \( A \) an alkylene residue of up to ten carbon atoms, with or without \( \text{OH} \) groups, or merely \(-\)a bond, and \( SX \) is the residue (having from eight to eighteen carbon atoms) of an aliphatic of aromatic mercaptan, or of an ester of a thioalcohol of thio acid, as stabilizers for polyvinyl halide resins.

Chemische Werke Barlocher British Patent 1,194,414, published June 10, 1970, suggested antimony compounds of the formula:

\[
(R^1)\text{Sn-S-CH}_2\text{-COO-CH}_2\text{-CH}_2\text{-OOC-CH}_2\text{-S-Sb-S-R}^3\text{S-R}^4
\]

\[
(R^2)_2\text{Sn-S-CH}_2\text{-COO-CH}_2\text{-CH}_2\text{-OOC-CH}_2\text{-S-Sb-S-R}^3\text{S-R}^4
\]