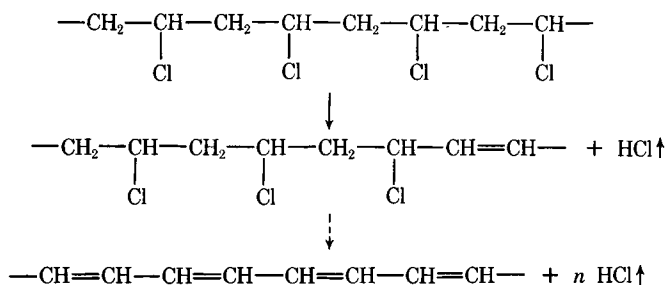


## Thermal Stabilization of Polyvinyl Chloride by Group II Metal Laurates<sup>1,2</sup>

RUDOLPH D. DEANIN, HOWARD H. REYNOLDS, and YURDAGUL  
OZCAYIR, *Departments of Chemical Engineering and Plastics Technology,  
Lowell Technological Institute, Lowell, Massachusetts 01854*

Polyvinyl chloride is one of the most important commercial plastics, especially in the plasticized flexible form. Its main drawback is its sensitivity to thermal degradation, which causes loss of HCl and results in conjugated unsaturation,

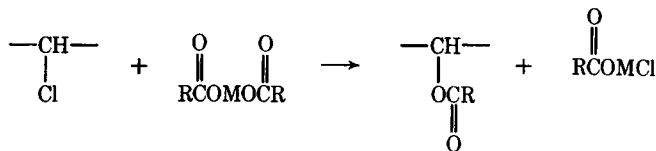


producing increasing discoloration as the length of this conjugation increases.<sup>3</sup> In commercial practice, such thermal degradation is retarded by the addition of certain selected "stabilizers."<sup>4</sup>

The commonest stabilizer system in commercial practice is a synergistic mixture containing at least 4-5 ingredients:

Barium soap  
Cadmium soap  
± Zinc soap  
Epoxidized fatty ester  
Organic phosphite ester

For food and drug applications, barium and cadmium soaps are replaced by calcium soap to avoid toxicity. The metal soaps are generally naphthenates, octoates, laurates, stearates, or phenates. Various mechanisms have been proposed to explain the stabilizing action of these metal soaps; the leading current theory involves replacement of chlorine atoms on the polymer chain by ester groups from the soap.<sup>5-6</sup>



For further understanding of the stabilizing mechanism, it should be noted that all the above metals are in Group II of the Periodic System, and that a more thorough study of stabilization by Group II metal soaps should help to clarify the situation; in the present work, the laurates were used for this purpose. In addition, present qualitative methods of describing thermal stability should be replaced by more quantitative techniques; in the present work, the Gardner Color Scale was used to provide such quantitative measurement. These were the two objectives of the present study.

Experimental compositions were made up containing 100 parts Goodrich Geon 101-EP polyvinyl chloride, 50 parts di(2-ethylhexyl)phthalate, and selected thermal stabilizers. These were milled 5 min at 154°C and molded 2 min at 149°C to produce clear colorless 60-mil sheets for heat aging. These sheets were cut into 1-in. squares, supported on aluminum foil, aged in constant-temperature circulating-air ovens, and samples were removed periodically to record the increasing discoloration of the materials. The colors of these aged samples were compared with Gardner Color Scale standards (ASTM D1544-58T) and assigned color numbers according to their positions on this standard scale. Rates of discoloration were finally plotted against time.

Unstabilized polyvinyl chloride discolored gradually and steadily during 150°C aging (Fig. 1). Magnesium, calcium, and strontium laurates alone were too ineffective to produce any major improvement in thermal stability; barium laurate was more helpful in retarding the rate of gradual discoloration. Mercuric, cadmium, and zinc laurates produced increasingly powerful initial stabilization, but were all followed by increasingly catastrophic failure.

When relative rates of discoloration were plotted against the atomic numbers of the metals in the periodic table, it was immediately evident that color stability with Group II-A metals increased with increasing atomic number (Fig. 2). Initial stabilizing efficiency of the Group II-B metals was inverse to atomic number, but their effective lifetime to catastrophic failure increased directly with increasing atomic number.

If the mechanism of stabilization involved the free radical<sup>7</sup> replacement of chlorine atoms by ester groups on the polymer molecule, then it is reasonable that the less electropositive transition metals of Group II-B should form less ionic, more covalent laurates,



and participate more freely in such reactions, and that the Group II-B metals of lowest atomic number and least electro-positivity should be most reactive. Such high reactivity would produce high initial stabilization,

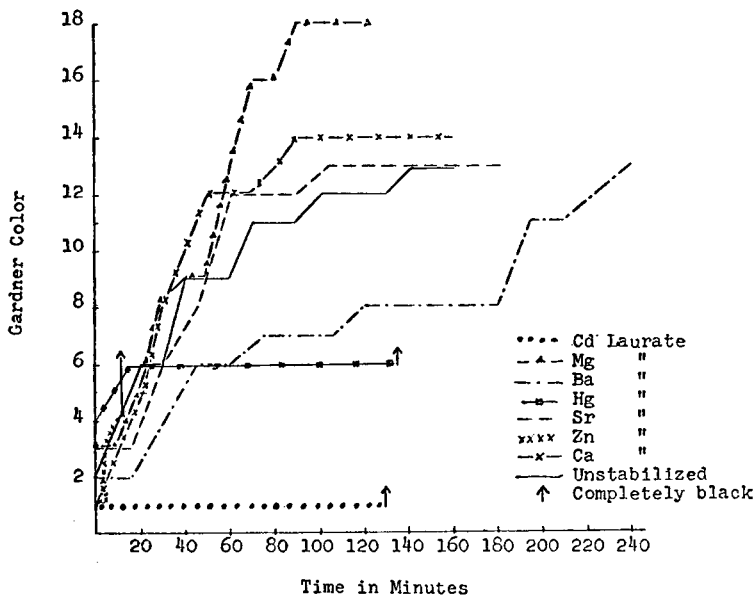


Fig. 1. Polyvinyl chloride + 2 PHR metal laurates. Gardner color versus time at 150°C.

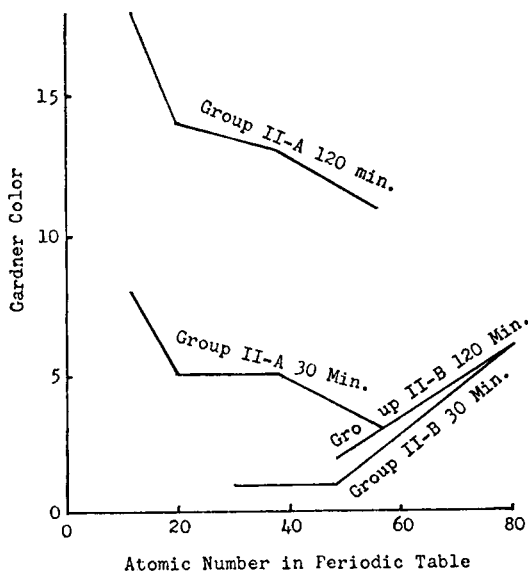


Fig. 2. Polyvinyl chloride + 5 PHR metal laurates. Gardner color versus atomic number: 30 and 120 min at 150°C.

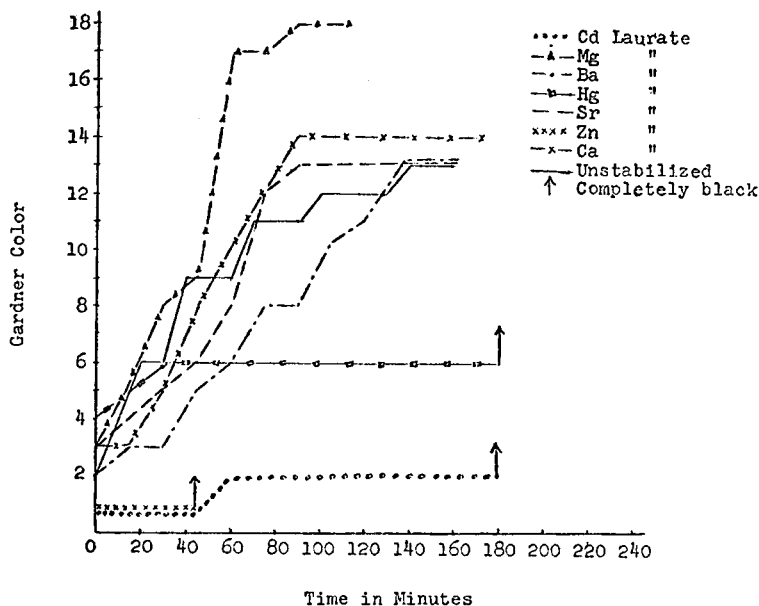


Fig. 3. Polyvinyl chloride + 5 PHR metal laurates. Gardner color versus time at 150°C.

until the stabilizer was completely exhausted, after which catastrophic failure would occur. This is exactly what was observed with the Group II-B metal laurates, especially at lowest atomic number.

On the other hand, the Group II-A metals are much more electropositive, so their laurates should be less susceptible to the free radical reaction, and give much weaker stabilizing effects but last much longer before complete failure; the experimental results confirm this judgment. Since the highest atomic number and greatest electropositivity of barium provided more stabilization than the other Group II-A metals, it would appear that here an ionic mechanism<sup>7</sup> may be involved. In commercial synergistic stabilizer systems, the combined use of Group II-A and II-B metal soaps may depend upon the combined effects of these two different mechanisms.

Stabilizer efficiency was generally rather insensitive to concentration (Fig. 3), suggesting that the stabilizing effects were primarily catalytic in nature.

In a brief study of possible synergism, each of the metal laurates was added to a complete commercial stabilizer system (Fig. 4). Since the commercial system was already complex and balanced, most of the additives had no significant effects; but additional cadmium laurate did improve it significantly, suggesting that commercial stabilizer efficiency could be improved in this way.

Since use of the Gardner Color Scale provided a quantitative measure of thermal discoloration, and color vs. time plots gave straight lines either directly or on log-log plots, it was possible further to calculate equations

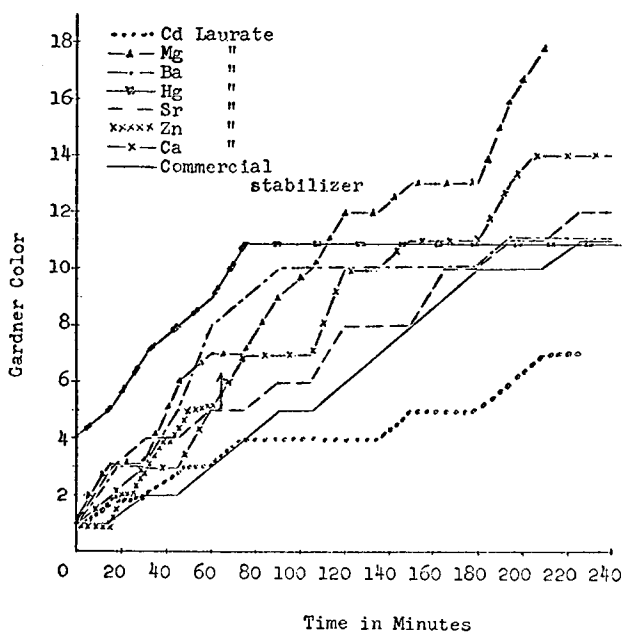


Fig. 4. Polyvinyl chloride + commercial stabilizer + metal laurates.\* Gardner color versus time at 170°C.

\* Commercial Stabilizer

Advance Solvents Advastab BC-206 Ba-Cd-Zn Soap	2 PHR
Rohm & Haas Paraplex G-62 Epoxidized Soy Oil	5
Metal Laurates	2

for the effects of stabilizers, concentrations, and times upon thermal stability.

Unstabilized color vs. time in minutes at 150°C	$C = 1.78 t^{0.40}$
2 PHR Ba Laurate, color vs. time in minutes at 150°C	$C = 0.59 t^{0.55}$
Commercial stabilizer, color vs. time in minutes at 170°C	$C = 0.7 + 0.046t$
Commercial stabilizer + 2 PHR Cd Laurate, color vs. time in minutes at 170°C	$C = 1.3 + 0.024t$
Blackening time in minutes at 150°C vs. Group II-B Metal Laurate in PHR	$t = 4 + 7.6 Zn$ $t = 90 + 18 Cd$ $t = 60 + 21 Hg$

While these were too dependent upon practical measurement units to have any great fundamental significance, they do indicate a direction which can be followed for more theoretical study.

Current studies are concerned with the use of these experimental methods for the analysis of synergistic interactions between the ingredients of the complete commercial stabilizer system.

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