

# Polycarboxylates in Soda Ash Detergents<sup>1</sup>

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Calcium carbonate deposition on cotton fabric from soda ash-based detergents containing polycarboxylates is measured and related to polymer composition and molecular weight, under varying conditions of temperature, water hardness and detergent composition. Deposition effects on fabric are compared with threshold inhibition effects and calcium binding capacities of the polymers.

Polyacrylic acids with molecular weights of 2000–5000 are most effective in preventing calcium carbonate deposition on fabric. A 1.5:1 acrylic acid:maleic acid copolymer is more effective than polyacrylic acid. Detergents with LAS left somewhat higher calcium carbonate deposits than detergents with a nonionic surfactant.

Prevention of visible calcium carbonate precipitation in the absence of fabric ("threshold effects") appears at polymer levels considerably lower than those necessary to prevent calcium carbonate deposition on fabric. Deposition on fabric can be prevented at levels of polymer much less than that necessary to bind most of the calcium ions, as determined by the calcium binding capacity.

In the continuing effort to reduce or replace phosphates as builders in laundry detergents, the use of sodium carbonate should be more thoroughly explored. Sodium carbonate is environmentally acceptable and is an effective builder in that it removes calcium ions from solution and provides alkalinity, both functions necessary to improve the detergent action of the surfactants in the detergent (1,2). However, the resulting precipitated calcium carbonate deposits on the fabric, especially on cotton, and leaves the laundered clothes with a very harsh hand. The deposited calcium carbonate tends to carry soil with it to the fabric surface, increasing soil redeposition and causing greying. Soda ash also lacks the dispersing or peptizing action of the phosphate builders.

Polycarboxylates have been suggested as builders due to their calcium sequestering properties (3–6). Other benefits, including lime soap dispersancy and calcium carbonate deposit inhibition, have been shown (4).

Taking into account the calcium binding properties and the antiprecipitation effects of polycarboxylates including polyacrylic acid and copolymers of maleic and acrylic acid, the objective of the present work was to outline formulations and conditions that effectively reduce the deposition of the precipitated calcium carbonate in soda ash built detergents, thus lending some direction to the formulation of soda ash based detergents which do not cause harshness buildup or greying in the laundered fabric.

## EXPERIMENTAL

Polymers used in this study were commercial and experimental samples from Alco Chemical Corp., Chattanooga, Tennessee.

Calcium binding capacities were determined by a Procter and Gamble method (7).

Threshold effects were determined by the following method: Three hundred ppm hard water at a 4:1 molar ratio of  $\text{Ca}^{+2}$  to  $\text{Mg}^{+2}$  was prepared by dissolving 0.326 g of  $\text{CaSO}_4$  and 0.148 g of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ /l of distilled water. Then 250, 200, and 150 ppm hard water were prepared in a similar manner. Stock solutions of the polymers were prepared as 1% solutions of their sodium salts in distilled water. A stock solution of sodium carbonate was prepared by dissolving 10 g of sodium carbonate in distilled water and diluting to 100 ml.

To test, 300 ml of hard water in a 400-ml beaker was heated in a water bath to  $50 \pm 1$  C, and 0.45 ml of 1% polymer solution was added, followed by 2.34 ml of 10% sodium carbonate. This is equivalent to adding 0.15% of a detergent containing 1% polymer and 52% sodium carbonate. If a visible calcium carbonate precipitate formed in less than 30 min the experiment was repeated at twice the level of polymer, until the polymer level was sufficient to prevent the appearance of a visible precipitate. Results are reported as the level of polymer in the detergent necessary to prevent visible precipitation of calcium carbonate, e.g., 1%, 2%, 4%, etc. If 8% polymer (in the detergent) was still insufficient, the results were reported as ">8%."

*Calcium carbonate deposition on cotton fabric.* This was determined as follows: Equipment and supplies included 500-ml wide mouth polyethylene bottles with tight unbreakable lids; a roller mixer designed to tumble bottles end to end at 60 to 80 rpm; water at the desired hardness (570 ml/cycle/test to wash and rinse), prepared as described above, and one 9" × 9" cotton percale sheeting swatch/test. Reagents for titrating calcium were standard 0.005 M EDTA, 5% and 1% acetic acid, 15% ammonia and Erichrome Black T indicator. Detergent was 52% sodium carbonate, 7.5% sodium silicate, 2.4:1, 30% sodium sulfate, 5% surfactant, polymer as indicated and 0.5% CMC.

*Procedure.* The cotton swatch for each test is marked with permanent ink and placed in a wide-mouthed plastic bottle. Three hundred ml of water at the temperature level and hardness appropriate to the conditions desired are added to each of the bottles, and 4.5 ml of a 10% solution or dispersion of detergent is added. (This is 0.15% detergent in the wash liquor.) The bottles are capped, inverted 10 times, and placed in the roller mixer. They are tumbled end to end at 60 to 80 rpm for 20 min. They are removed from the mixer, uncapped and the water drained, reserving about 30 ml of the wash water with the swatches. (This is the approximate amount of water that remains with the swatches when they are drained and not wrung.) Two hundred seventy ml of rinse water of the appropriate hardness and temperature are added to the wet

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swatches in the bottle, and the bottles are recapped and rolled for five min. The swatches are then removed, wrung to 100% moisture pick-up and air dried. The procedure is repeated for a total of five cycles.

After five cycles the harshness of the cotton percale swatches is evaluated by a trained observer and reported on any convenient scale.

*Determination of calcium carbonate deposition on the cotton percale swatch.* A sample of the swatch weighing from 0.5 to one g is weighed to the nearest 0.001 g. The sample is placed in a beaker, 20 ml of 5% acetic acid are added, and the beaker and contents are held at 80–90 C for one hr. The liquid is decanted and the swatch sample is rinsed twice with five ml of 1% acetic acid, combining all of the washings. The pH of the washings is brought to 10 with 15% ammonia, and then titrated with standard 0.005 M EDTA, using either a calcium specific ion electrode or a colorimetric (Erichrome Black T) endpoint. The results are reported as percent calcium carbonate in the swatch.

## RESULTS AND DISCUSSION

Polycarboxylates have been shown to perform at least three functions relating to their use in laundry detergents.

*Crystal growth inhibitors.* They act as crystal growth inhibitors for calcium precipitates, especially calcium carbonate. This is a well known but not completely understood phenomenon. We chose to demonstrate crystal growth inhibition in the context of the concentration of polymer needed to prevent the appearance of a calcium carbonate precipitate in a solution of detergent built with soda ash under laundry conditions. The results are shown in Figure 1.

At 25 C in 300 ppm hard water, all of the polycarboxylates prevented visible precipitation at a level of 2% or less on the weight of the detergent. The data shown

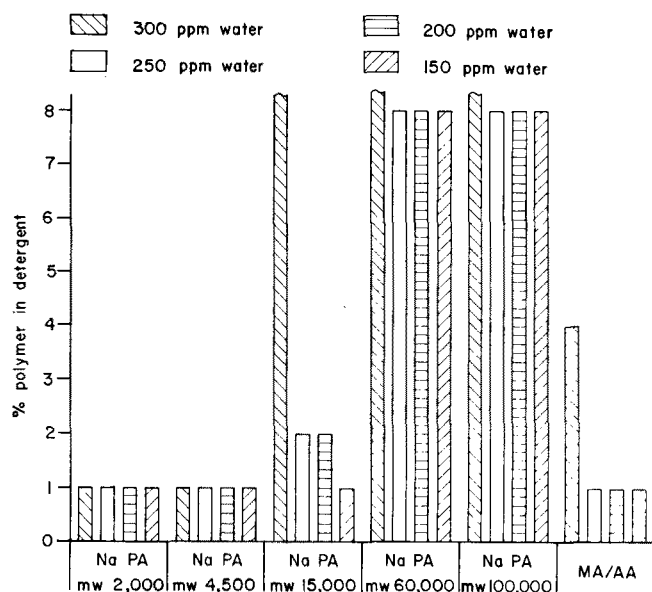


FIG. 1. Level of polymer in a detergent containing 52% soda ash necessary to prevent visible precipitation of  $\text{CaCO}_3$  at 50 C. Detergent level is 0.15%.

is for precipitation at 50 C and the water hardnesses shown. The molecular weight of the polymers is the most significant variable in the prevention of crystal growth of calcium carbonate, with the lower molecular weight polymers being the more effective and the higher molecular weight polymers being essentially ineffective. The maleic-acrylic copolymer had an average molecular weight of 20,000 and is somewhat more effective than a polyacrylate of similar molecular weight.

We found the same behavior with a system containing only soda ash and polymer as we found in a system containing a formulated soda ash detergent containing sodium silicate, sodium sulfate and nonionic surfactant and LAS. Thus, the other components of the detergent do not significantly modify the precipitation of calcium carbonate, nor do they interfere with the crystal growth inhibition properties of the polymers.

*Calcium ion sequestrants.* Polycarboxylates also function as calcium ion sequestrants (Fig. 2). The higher molecular weight polymers are the more effective calcium ion sequestrants, with the maleic-acrylic copolymer somewhat more effective than the same molecular weight acrylate homopolymer. The difference is rather small.

*Dispersants for particulate materials.* Polycarboxylates are also known to be effective dispersants for particulate materials, including laundry soil. Dispersing action is maximum with low molecular weight polycarboxylates at relatively high concentrations. Under the right conditions the polymers can compensate for this deficiency in the soda ash itself. This has been demonstrated in our laboratory as well as by others (4), but is beyond the scope of the present work. Under the opposite conditions, that is, high molecular weight polymers and low concentrations, polycarboxylates can act as flocculants; these conditions must be avoided.

If polycarboxylates were used in detergents at high enough levels to sequester all or a significant portion of the calcium ions in the wash liquor this obviously would prevent calcium deposits in the presence of soda ash. But under normal use conditions, sequestering a significant portion of the calcium ions would require the detergent

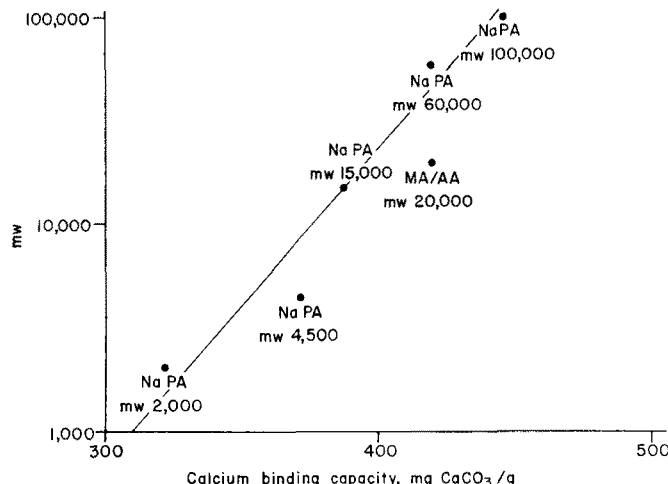


FIG. 2. Calcium binding capacity vs. polymer molecular weight.

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to be about 30% polymer, a level which is of course economically unacceptable, and would create severe formulating problems. Therefore, for laundry detergent applications the calcium sequestering ability of the polycarboxylates is not as important as are the crystal growth inhibition and dispersion properties of the polymers.

The calcium deposits generated on cotton fabric under a number of conditions using a detergent containing 52% soda ash and 4% active sodium salt of the polymers are shown in Figure 3. In 100 ppm hard water at 25 C all of the polymers were able to completely prevent calcium carbonate deposition. In 200 ppm hard water at 25 C the polymers significantly reduced the deposits, and were somewhat more effective in detergents containing a nonionic surfactant, linear  $C_{12}$  to  $C_{15}$  alkyl alcohol condensed with nine moles of ethylene oxide (Neodol 25-9 from Shell Chemical Co.), than in detergents with LAS. In 200 ppm hard water at 50 C the calcium deposits were actually higher with the polymer present. We have observed this many times, and it seems to be a general phenomenon at high wash temperatures when the polymer is grossly inadequate. The reasons for this will be discussed later. The maleic-acrylic copolymer was much more effective than the acrylate homopolymers under all conditions (except the most severe). The lower molecular weight polycarboxylates were somewhat more effective than higher ones, with essentially no demonstrated differences between the 2000 and 4500 mol wt polymers.

Figure 4 shows calcium carbonate deposition vs level of polymer for a 4500 mol wt polyacrylate, and the 20,000 mol wt maleic-acrylic copolymer. Both polymers are somewhat more effective in nonionic detergents than in LAS detergents, and the maleic-acrylic copolymer is very effective at levels of 4% or higher under these conditions.

It is apparent from comparing the results from the calcium carbonate precipitation on cotton fabric with the results from the crystal growth inhibition experiments that the level of polymer necessary to prevent crystal growth in the absence of fabric does not directly relate to the prevention of calcium carbonate deposits on cotton fabric. Figure 1 shows that to prevent crystal growth in the absence of cotton fabric, weight ratios of polymer to precipitated calcium carbonate as low as 0.05 are effective, even at 50 C. However, to prevent precipitation on cotton fabric at 50 C a ratio of 0.3 is inadequate, while a ratio of 0.6 is fairly effective with polyacrylate, and much more effective with the maleic-acrylic copolymer (Fig. 5). At 25 C a ratio of 0.3 is quite effective and a ratio of 0.6 completely prevents deposition. This compares with a ratio of 2.5 to 3 for the complete sequestering of calcium ions, determined from the calcium binding capacity. From this we conclude that the surface of the cotton promotes crystal growth, thus necessitating a much higher level of polymer to prevent deposition than would be predicted from crystal growth inhibition experiments. To explain why the polymers appear to increase deposition on the fabric at high temperatures and high water hardness, we postulate that in the absence of polymer the calcium carbonate precipitation is so rapid and complete under these conditions that most of the precipitation occurs in the water and not at the fabric surface, and the precipitated calcium carbonate stays suspended in the water. The addition of an inadequate level of polymer prevents or slows

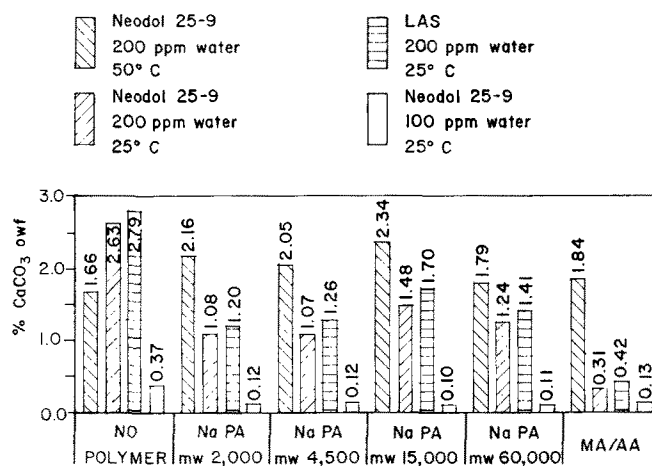


FIG. 3.  $\text{CaCO}_3$  deposition on cotton fabric. Polymer level in detergent is 4%; conditions as shown.

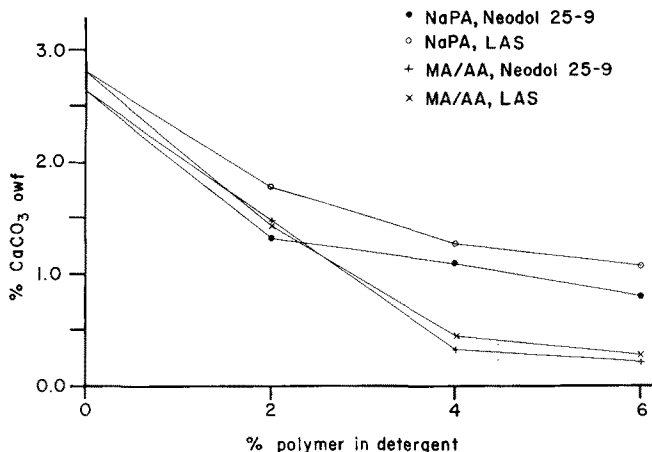


FIG. 4.  $\text{CaCO}_3$  deposition on cotton fabric vs level of polymer. Conditions: 200 ppm hard water. 25 C.

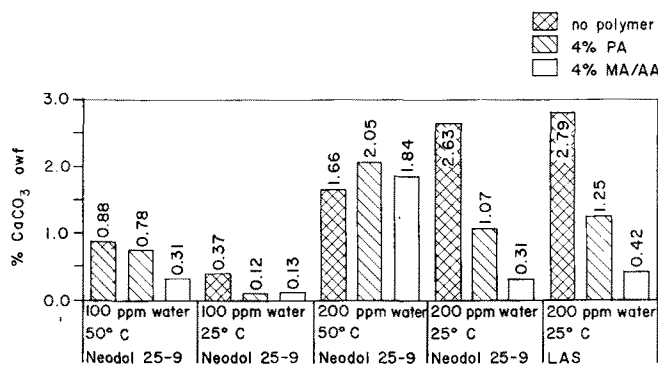


FIG. 5.  $\text{CaCO}_3$  deposition on cotton fabric, comparing polyacrylic acid and a maleic-acrylic copolymer.

the precipitation in the water phase but does not prevent crystal growth on the cotton surface.

The hand of the cotton fabric is predictably improved when the calcium deposits are reduced. We have found, however, that the polymers can in some instances reduce the harshness of the fabric without significantly reduc-

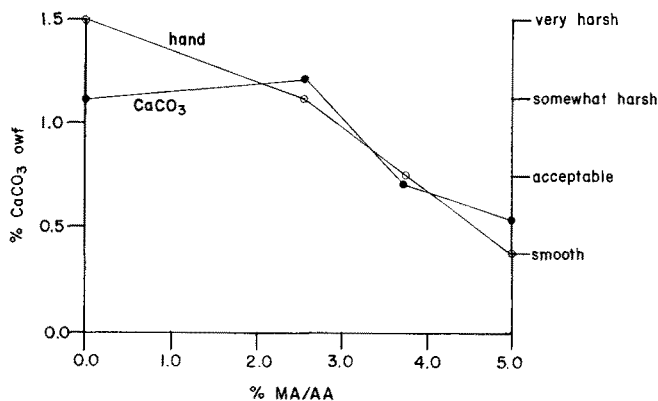


FIG. 6. CaCO<sub>3</sub> deposition on cotton fabric compared to hand improvement.

ing the amount of deposited calcium carbonate (Fig. 6). This is somewhat difficult to illustrate, but the results we have attempted to show are typical. The figure shows a notable improvement in hand on adding 2.5% of a maleic-acrylic copolymer, while there is actually an increase in the amount of deposited calcium carbonate. We attribute this to the ability of the polymers to modify the crystal growth of the calcium carbonate so that it is deposited as smaller, impalpable particles.

Polycarboxylates can at economical levels significantly reduce the deposition of calcium carbonate from soda ash based detergents and thus improve the hand and appearance of laundered fabric. Copolymers of maleic acid and acrylic acid are superior to homopolymers of acrylic acid for this application. They are highly effective in cold water washing, but become ineffective without further modification of the formulations at very high hardness levels in hot water washes. However, it has been estimated that 80% of the water in the U.S. is of less than 150 ppm hardness, and most home laundries use wash temperatures below 100 F. Thus, even with this rather simple approach, effective products could be provided to a broad market by using polycarboxylates with soda ash.

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