



## Physical Properties of Blends of Soap and Lime Soap Dispersants<sup>1</sup>

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### ABSTRACT

The mechanism of action of soap lime-soap dispersant (LSDA) combinations is based on a close association between these two components. In deionized water this association is mixed micellar. Surface tension curves confirm the presence of mixed micelles in deionized water and show a combination of optimum surface active properties (low critical micelle concentrations (CMC), high surface concentration and low surface tension above the CMC). Solubilization of high Krafft point soap by LSDA and of difficultly soluble LSDA by soap are related results of this association. Analysis of dispersions of mixtures of soap and LSDA in hard water shows that the dispersed particles are mixtures of soap and LSDA in the same proportion as they were originally added. These findings are inconsistent with the view that soap reacts separately with hard water ions and that the resulting lime soap is suspended by surface adsorption of LSDA. The suspended particles are responsible for surface active properties and detergency and do not permit deposits on the fabric like those found with soap alone.

### INTRODUCTION

Lime soap dispersing agents (LSDA) have long been known to improve the hard water performance of soap (1-3). As the need to reduce phosphate effluents as environmental pollutants in certain areas became apparent, this Laboratory undertook a systematic study of soap LSDA combinations as potential substitutes for phosphate-built detergent formulations. Tallow soap was formulated with an appropriate amount of various LSDA and alkaline builders to give products that washed as well in hard water as commercial products heavily built with sodium tripolyphosphate (4).

Although lime soap dispersing ability is not directly related to detergency (5), it is a prerequisite for hard water detergency and for absence of lime soap deposits on fabric (6). While the mode of action of the LSDA has not been elucidated completely as yet, a substantial amount of research has been carried out to give a clearer picture of what occurs when an LSDA is added to soap in water solution.

Early work at this Laboratory (7) suggested that soap could be combined with surfactants having bulky hydrophilic groups to form mixed micelle-like particles with better hard water stability than that of soap alone. An alternative consideration would be that soap and LSDA function separately. This would suggest that soap reacts with polyvalent ions to soften the water, leaving the LSDA

free to perform surface active functions such as detergency and dispersion of lime soap curd. If this type of dispersion were formed, the LSDA would be adsorbed on the surface of the particles only, and relatively small amounts of LSDA would be required.

In the discussion below, various observations on the physical nature of the soap/LSDA blends are brought together to show that the intimate association of soap and LSDA indeed exists.

### DISCUSSION

#### Mutual Solubilization

Lime soap dispersing agents which have high Krafft points or are insoluble in deionized water show considerable lowering of their Krafft points when combined with soap (8). Particularly striking mutual solubilization was observed with certain difficultly soluble amphoteric LSDA whose anionic and cationic sites are separated by only two methylene groups (9). Thus the strong ion/ion interactions which are believed to be responsible for their limited solubility are replaced by soap/LSDA interactions, and resultant mixtures have considerably lower Krafft points. Similar solubilization effects were observed when LSDAs were added to high Krafft point soaps such as sodium palmitate. If the soap and LSDA were to function independently, mutual solubilization would not be expected to take place.

#### Surface Tension Studies

Additional evidence for the close association between soap and LSDA is shown in the surface tension curves of their distilled water solutions (10). The presence of only one break in the surface tension curve of mixtures confirms that they form mixed micelles. The cited reference (10) also shows that mixtures of 10-50% LSDA with soap all have CMC values which are close to those of the LSDAs which have the lower values.

#### Analysis of Soap-LSDA Dispersions

Soap-LSDA dispersions in hard water were analyzed to determine if the intimate association of mixed micellar systems found in distilled water solution would apply to hard water dispersions (11). Such dispersions were found to be quite stable over a period of several years without sedimentation. While they could not be separated by conventional means, solid material could be separated by filtration through fine porosity polymer membranes (11).

Analysis of the membrane-separated solid matter showed that it contained all of the soap and LSDA, all of the  $\text{Ca}^{++}$  and most of the  $\text{Mg}^{++}$ , while the filtrate contained no surface active material. Regardless of the ratio of soap/LSDA used, their ratio in separated solids was the same as that of the starting mixture. This shows that surfactants were intimately mixed and suspensions were not stabilized

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by surface adsorption. The filtered solids were redispersed in water, and the resulting dispersion exhibited surface activity such as surface tension depression and detergency.

The effects of the soap/LSDA dispersions in hard water on washed fabric were studied. Analysis of the fabric and visual examination by scanning electron microscopy revealed that no deposits of organic matter containing  $\text{Ca}^{++}$  or  $\text{Mg}^{++}$  were formed (6). This shows that such dispersions are stable and, unlike soap by itself, do not form deposits on washed fabric.

Thus, all of the evidence cited indicates that the soap/LSDA blends are in close association with each other and function, for the most part, as if they were single surfactants rather than separate entities.

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