Research article

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The Investigation of Squeaky Feeling of Soap on the Skin

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ABSTRACT

The bar soap is one of the mostly used cleaning agents for centuries. After use of bar soap, there are some residues that cause a squeaky feeling which is favorable for some consumers because it reminds the feeling of cleanliness. However, some consumers do not like it. In this study, the reasons why the squeaky feeling is occurred after using the bar soaps were investigated. Through the ex vivo and in vivo tests, it was found that the residues on the skin were found due to magnesium and sodium salts of bar soap and magnesium and sodium ions in hard water. These result in the squeak and the amount of these salts and ions are affected by various parameters.

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Introduction

Although the bar soap is the oldest washing vehicle, the interaction of soap and kin has not been investigated sufficiently. It is observed that the squeaky feeling due to dryness and tension on the skin evokes the cleanliness, while some consumers do not prefer this. There are some arguments which propose that the soap removes the skin fat and dry the skin; and the residuals on the skin after soap use cause the squeaky feeling.

The external layer of skin stratum corneum is composed of proteins (65-75%), lipids (10-15%) and water (15%) and renewed by epidermis continuously [1, 2]. The capacity of skin barrier is related to the intracellular lipid molecular structure of stratum corneum [3].

When calcium and magnesium ions in bar soap contact with water, metal soap is formed. The solubility of the metal soap in water is very low so that it is hard to remove them from medium. Metal soap may remain between Stratum corneum layers [4,5].

Water hardness is a term used to describe the number of polyvalent ions found in water, especially the amount of calcium and magnesium. Calcium and magnesium bicarbonate salts $Ca(HCO_3)_2$ ve $Mg(HCO_3)_2$ cause "temporary hardness" or "carbonate hardness", while

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chlorine, sulfate, nitrate, phosphate and silicate salts of calcium and magnesium cause "permanent hardness". Hard water and soap can form a film called soap residue (white precipitate). The main component of these residues is calcium stearate from sodium stearate (soap) as in the following reaction [8].

The interaction of soaps and other surfactants with skin proteins cause skin barrier damage, redness, itching, the decrease in water holding capacity, penetration of surfactants and metal soaps into deeper layers of Stratum corneum because of protein swelling [6].

$$2C_{17}H_{35}COO^{-}{}_{(aq)} + Ca^{2+}{}_{(aq)} \rightarrow (C_{17}H_{35}COO)_2Ca_{(s)}$$

Studies have reported that the presence of calcium and magnesium salts in water increases the squeaky feeling on the skin (US 2013/0210696 A1) [9]. In another study, the squeaky feeling during rinsing was investigated by controlling the interaction between surfactant and cations. As a result, it has been found that the squeaky feeling in rinsing increases with the increase in water hardness (EP 1767186 A2) [10]. Similarly, in other studies, it has been reported that soap containing at least one anionic surfactant that can dissolve even in very soft water medium and a salt containing at least one multivalent cation is required for the formation of the squeaky feeling. The salt in the environment collapses on the skin surface with the surfactant and causes squeak (US 2013/0310296 A1) [11]. In addition, the degree of squeak can be increased by adding alkaline earth metal carbonates (calcium carbonate and magnesium carbonate) to soap-based products (US4557853) [12].

In the study of Conopco INC, D/B/A Unilever's patent number 2013/0210696 A1 published in 2012, tests were carried out with the Tribometer UMT device to increase the squeaky feeling left by cleaning compositions with calcium and magnesium salts and different surfactants. The friction test was performed by preparing solutions with certain concentrations with the solution, and it was observed that normal soap and synthetic surfactants had different levels of squeak as a result of the residues left on the skin at different rates.

In Patent no. 1767186A2 explains the compositions which give the increase in squeak during rinsing. The invention is also focused on the relationship between counter-ion and surfactant.

Specifically, it was found that increasing the precipitation of the counter ion surfactant complex helps reduce the micelle concentration of the surfactant, increase the surface tension, and increase the squeak.

In this study, the squeaky feeling after use of soap is investigated by using different tests for Evyap soaps which are produced as alkali soap by the saponification reaction.

Materials and Methods

In the study, two bar soap formulation were used with different fatty acid compositions as depicted in Table 1.

Table 1. Fatty acid compositions for bar soap formulations

Fatty acids	Toilet	Combo Soap
C12 (%)	10.45	3.14
C14 (%)	3.92	1.18
C16 (%)	40.97	12.30
C18 (%)	5.45	1.72
C18:1 (%)	27.93	8.34
C18:2 (%)	5.45	0.27
Glycerin (%)	0.90	0.31

Solution tests

A test was carried out to observe the interaction of soaps with different chemical structures with hard water. 2.3 gr $CaCl_2$/L was added to pure water and 15 FR hardness water was obtained. After adding 0.4 g of each bar soap formulation into hard water solution and they were mixed during two minutes and the water hardness values were measured again.

The effect of chelating agent on lime soap formation

The effect of chelating agent on lime soap formation was investigated by adding 1 gr Tetrasodium EDTA solution to 1% bar soap solutions dissolved in 15 FR water.

Testing on hydrophilic and hydrophobic silica surfaces

Internal tests were conducted to understand and examine the soap-skin interaction in more detail using hydrophilic and hydrophobic silica model surfaces. Stratum corneum is expected to show moderate surface energy like hydrophobic surface to see the effect of surface energy on the interaction of soap or lime soap with the surface.

Four different simulation methods were applied to prepare the silica surfaces. In first, silica surface was immersed into 5 ml of 0.1 w/w % Toilet soap dried with nitrogen. In second, silica surface was dipped in soap and then ultra pure water and dried with nitrogen. In third, surface layer was dipped in soap, then 40FR water and dried with N_2. In fourth, surface layer was dipped in soap, then adding $CaCl_2$ / $MgSO_4$ solution, then immersed in 40FR water and dried with N_2.

The effect of water hardness on residue on the skin - fluorescent dye test

Fluorescent dye has been used to visualize soap residues on the skin after washing and rinsing. The fluorescent dye has the tendency to bind with soap and can be homogeneously dispersed in soap-water solution. This method was tested by Wortzman M. (1986) [13] to evaluate the rinsing properties of 18 common soaps.

With reference to this method, a test was conducted on 10 panelists with the following parameters;

- 20 gr Toilet 1 soap was dissolved in 0 FR (Pure Water) and 60 FR hardness water.
- 0.05 gr Fluorescent dye (307027 Uranine-U, Sensient) was dissolved in soap solution
- A 5 cm diameter cloth moistened with a soap solution containing dye was applied to the panelists for 15 seconds
- The area where dyed with soap solution applied was rinsed with 250 ml tap water.
- Residue was photographed under UV light.
- Left arm was rinsed with 60 FR hard water, right arm was rinsed with pure water (0FR).

Result and Discussion

Interaction of soap's chemical structure with ions in water

It was observed that the water hardness decreased from 15 FR to 14.3 FR for Combo soap 9.8 for Toilet soap. It can be said that the carboxylate groups released by the dissolution of the sodium salts in the two soaps bond with the Ca2 + ion and form a calcium salt, and this ratio is higher in Toilet 1 soap compared to Combo Soap as in Figure 1.

Fig 1 Interaction of soaps with ions in Water

The reason why the decrease of water hardness is high in toilet 1 soap is that its content is completely composed of sodium salts and the high rate of carboxylate group released by dissolving in water, bonds with Ca^{2+}; The reason why this ratio is low in mixed soap is that it contains very little sodium salt soap.

The effect of chelating agent on lime soap formation

In Figure 2, Solution A represents 1% Toilet 1 solution dissolved in 15 FR hard water, B indicates 1 g Tetrasodium EDTA solution added on 1% soap solution dissolved in 15 FR water. It was observed that after the soap dissolved, white precipitates formed in the water as in Solution A. When 1 gr Tetrasodium EDTA was added into the prepared solution, it was seen that the water became clear as in Solution B. It has been observed that Tetrasodium EDTA retains metal ions and therefore did not precipitate, resulting in clearer water compared to hard water with only soap added.

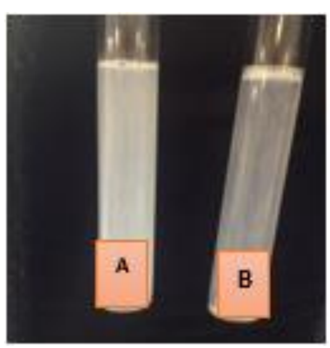

Fig 2 The effect of Tetrasodium EDTA on the precipitation of soap in hard water

Testing on hydrophilic and hydrophobic silica surfaces

The adsorption of precipitate on five hydrophilic silica surfaces was tested. The images in Figure 3 were obtained after the soap solution was applied to the surface. The dotted lines indicate the regions where sediment adsorption was observed, while the solid lines indicate the regions where adsorption was observed due to drying effects.

In Figure 3A, it was observed that when Toilet soap with 0.1% by mass is applied and dried with N_2, it formed a layer and remains on the surface after drying. In Figure 3B, it was observed that the layer formed quickly disappeared when MilliQ ultra pure water was rinsed with water due to the weak bond between the surface and soap. In Figure 3C and 3D, sediment adsorption was observed on the surface after rinsing with 40 FR water. Immediately after the addition of divalent Ca^{2+} and Mg^{2+} ionic electrolyte, the adsorption of the precipitates to the hydrophilic surface was observed. Adsorbed precipitates were low soluble Ca^{2+} and Mg^{2+} salts (lime soap). Electrons alone were observed to attach to the surface.

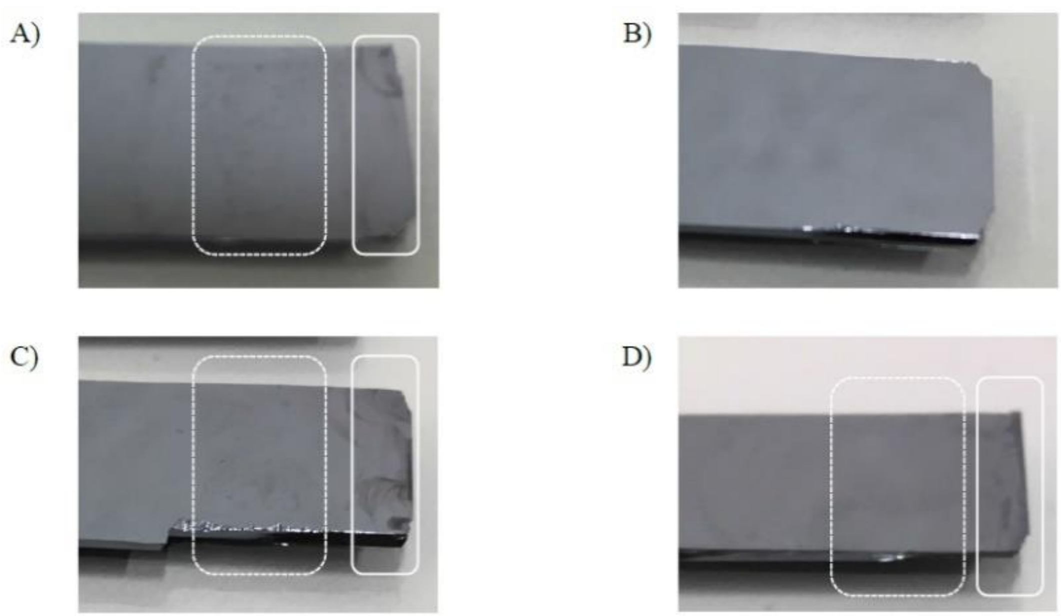

Fig 3 Images of hydrophilic model silica surfaces A) after immersion in soap and with N_2 After drying, B) first dipped in soap, then MilliQ water and set with N_2 C) first dipped in soap, then 40FR water and dried with N_2 D) first put in soap, then adding $CaCl_2$ / $MgSO_4$ solution, then immersed in 40FR water and dried with N_2

In the light of the studies and observations, soap and electrolytes alone do not hold on the surface for a long time, could be easily rinsed and leave no residue. However, it was concluded that Ca^{2+} and Mg^{2+} salts precipitated due to the electrolyte addition to the surface and did not move away.

After rinsing with 40 FR water and after electrolyte addition on hydrophilic and hydrophobic surfaces, soap residue and Ca^{2+} / Mg^{2+} salt deposits were formed in the same direction; but it was observed that the amount of precipitate formed after the addition of electrolyte on the hydrophobic surface was higher than the hydrophilic surface (Figure 4).

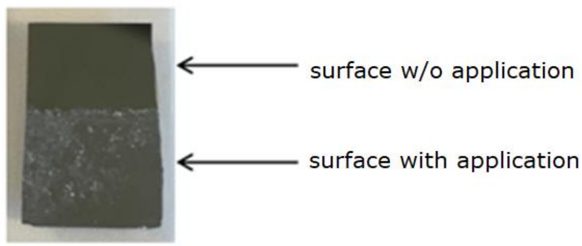

Fig 4 Hydrophobic Silica Model Surface - first immersion in soap, immediately after the addition of $CaCl_2$ / $MgSO_4$ solution, then immersion in 40FR water and drying with N_2

The upper surface of the Stratum Corneum is hydrophobic; more precipitation is observed on the hydrophobic silica surface than on the hydrophilic surface. After washing and rinsing with hard water, it was concluded that Ca^{2+}/Mg^{2+} salt precipitates in water could adhere to the skin.

Once bar soap contact with hard water, metal soap which main component is calcium stearate and magnesium stearate, is formed. The solubility of calcium and magnesium salts in water are very low so that it is hard to remove them from medium [4,8]. Due to presence of calcium and magnesium salts in water increases the squeaky feeling on the skin. Hence, It can be concluded that squeaky feeling in rinsing increases with the increase in water hardness [9,10,11].

Conclusion

In the study, it was concluded that when the surfactants formed as a result of the saponification reaction are dissolved in water. The free carboxyl groups compound with calcium and magnesium ions that determine the water hardness. When the soap is dissolved in water, the water hardness decreases, and Tetrasodium EDTA prevents the precipitation in the soap solution. In panel tests, when Toilet soap and Combo soap were compared, it is found that soap caused squeak in hard water and no squeak was felt in soft water. There was no difference in the mixture of soaps in two different water hardness. The simulation studies were performed by considering the structure of Stratum Corneum on hydrophobic and hydrophobic surfaces and the soap accumulation was higher on the hydrophobic silica surface similar to the structure of the Stratum Corneum. Based on these results, it is intensely emphasized that the squeaky feeling may occur due to the precipitation of ions in hard water as calcium / magnesium salt on the skin.

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