Designing a Non-Soap Cleansing Bar

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Dove® Beauty Bar was developed by Lever Brothers Co., a subsidiary of Unilever in the United States, in the 1950's. It has had an unusual product lifecycle in that it had a minor share of the US soap market for over 25 years, after which it suddenly underwent a major expansion of market share, becoming the largest selling cleansing bar in the US (as measured by dollar sales). While the Dove® formulation has undergone relatively minor changes since its launch in the US in 1955, the marketing concept has seen major changes. Today's Dove® is marketed on a platform of extreme mildness to skin as evidenced by its neutral pH. However, the original problem definition had a very different focus.

The original product design problem was to formulate a non-soap cleansing bar that did not leave a bathtub ring. While the need to prevent bathtub rings may not seem significant today, most consumers in the 1950's still took baths and typically scoured their bathtubs to remove any residue of soap scum. Preventing the formation of a bathtub ring would therefore have saved significant labor. By this time synthetic (non-soap) detergents had already been commercialized for laundry applications, and these proved superior to soap in that they worked well in hard water. This suggested that a cleansing bar containing synthetic detergents would similarly be insensitive to water hardness, and therefore not form a bathtub ring. Such non-scumming toilet soaps had already been introduced to the market. However, the properties of these bars were considered deficient to ordinary toilet soap bars, either being significantly harsher to skin than ordinary soap, deficient in lather, or else having a draggy feel when wet. Hence, a need existed for a non-scumming cleansing bar with general use properties at least comparable to ordinary soap bars.

Dove® was launched in 1955 reaching a US market share of almost 3% by tonnage sold. This presentation will review the set of product and process attributes that were identified as critical to a successful launch for Dove®, the laboratory techniques that were used to assess these properties, and the experimental program that identified the actual composition.

Product Design Problem

As noted above, the original product design problem was to formulate a cleansing bar that did not leave a bathtub ring. In addition to this primary attribute, however, the product had to be generally recognizable as a high quality personal cleansing bar if it was to be a success in the consumer marketplace. This implies a set of secondary product properties, which can be broadly interpreted as the absence of gross negatives compared to ordinary soap bars. Among the important properties were sufficient bar firmness, creamy lather, no unpleasant odors or colors, absence of cracking of the bar during repeated wet/dry cycles, and mildness to skin.

In addition to these product attributes, the bar needed to be manufactured on a standard soap production line without the need for significant capital investment. A standard soap making production line of the time, which would also be perfectly acceptable today, included steam-jacketed mixing equipment, a chill roll (chilled roll mill with fixed blade) to solidify and form flake, a single stage extruder to produce noodles, a mixer for blending fragrance with the solid noodles, a three-roll mill for micromixing, a dual stage vacuum extruder (known in the soap industry as a plodder) to form solid billets, and a soap stamping press to form the final bar.

While there was a growing number of non-soap detergents that either were already commercialized (as for use in laundry applications) or else had viable commercial potential, it was decided early on to limit the compositional search space to compositions using sodium acyl isethionates (SAI) as the primary surfactant. This decision was based on an early assessment of a prototype bar comprised of SAI, stearic acid and lactic acid, for which Unilever had acquired patent rights. Although the prototype bar was non-scumming and milder than ordinary soap bars, it was deficient in lather, subject to rancidity and poor color, and developed severe cracks after normal cycles of wetting and drying in a soap dish. These problems would all need to be resolved for the bar to be acceptable to consumers.

The composition of choice would therefore contain SAI as the primary surfactant, a binder to ensure sufficient bar cohesiveness, and various other ingredients to modify bar properties as needed. While a decision had been made to use SAI as the primary surfactant, the specific blend choice of SAI was subject to selection. SAI has the general chemical formula:

$$RCOOCH_2CH_2SO_3Na$$

where R represents an alkyl chain. At the time these were made commercially by the anhydrous reaction of an acyl chloride (fatty acid chloride) with sodium isethionate:

$$RCOCl + HOCH_2CH_2SO_3Na \rightarrow RCOOCH_2CH_2SO_3Na + HCl$$

acyl chloride sodium isethionate sodium acyl isethionate hydrogen chloride

Hence, freedom to select the specific blend of SAI corresponded with the choice of acyl chloride (or, in turn, its source fatty acid) used in the manufacture of the SAI.

Problem Solution Strategy

In the 1950's there was a complete absence of models to describe the behavior of cleansing bars, and hence design problems were tackled by a completely experimental methodology. Numerous compositions were explored, starting with the initial prototype bar. Once a compositions was selected, a batch would be made at pilot scale (~15 kg) to produce prototype bars, and a set of attributes would be assessed. Based on the results, additional compositions would be proposed, some identified through scientific intuition, others through a comprehensive search of compositional possibilities.

Rather than assess all attributes for each prototype, a subset of properties was selected for use as a screening process, including lather volume, odor stability, bar firmness and processability. (Protocols for screening tests that are broadly equivalent to those implemented by the Unilever product scientists during the development of Dove® have been published elsewhere.) These tests were relatively easy to perform, and served to rapidly eliminate unsuitable compositions. Only if a prototype passed all screening tests would it be subject to the remaining property assessments, including such properties as mildness.

Problem Solution

First and foremost among the deficiencies of the original prototype was the poor bar lather. It had been observed that a 10% aqueous solution of the prototype bar had a pH of 3, whereas a 10% aqueous solution of ordinary soaps has a pH of 10. This acidity resulted from the presence of both lactic acid and residual hydrogen chloride, which was a by-product in the manufacture of SAI.

Suspecting a connection with the poor lathering properties of the prototype, the pH of the prototype was raised from 3 to 7 by elimination of lactic acid and the addition of caustic solution, sodium carbonate, or sodium stearate.

While raising the pH gave some improvements in lather, more improvement was needed. Various co-surfactants, including alkyl sulfates, alkyl aryl sulfonates, and fatty acid taurides were effective in improving the speed of lather when present at levels of around 5%. Cost considerations led to choosing an alkyl aryl sulfonate, particularly sodium dodecyl benzene sulfonate, as it was already widely used in the formulation of laundry detergents.

Odor and color instability was traced to the choice of SAI. The original prototype composition used an SAI blend made from 80% coconut fatty acid and 20% tallow fatty acid. This mixture, however, was subject to rancidity. Hydrogenating the fatty acids before making the SAI brought considerable improvement in odor and color stability, but at the expense of lather in cold water. Use of potassium acyl isethionates, while improving lather, resulted in unacceptably soft bars. It was finally determined that the best compromise lay in partially hydrogenating the coconut fatty acid while simultaneously eliminating tallow fatty acid completely. Thus partially hydrogenated sodium cocoyl isethionate (SCI) was selected as the SAI of choice.

Binders are included in synthetic detergent bars for cohesion and to plasticize the formulation during the manufacturing operations of milling, extrusion and stamping. The original prototype was observed to crack excessively from repeated cycles of moisture adsorption and drying, and this was believed due to the use of stearic acid as the binder. Hence the experimental program examined the effect of using various commercial grades of fatty acids, soaps, and/or water soluble polymers as binders. A combination of long chain fatty acid and sodium soap allowed the formula to have the desired plasticity and low level of cracking, without losing processibility or mildness. The appropriate fatty acid level was established as 25-30% and the optimum level of sodium soap was established as 5-10%. For economic reasons, the long chain fatty acid that was selected was “triple-pressed stearic acid”, which is actually a eutectic mixture of 55% palmitic and 45% stearic acids. The sodium soap that was selected for use was ordinary toilet soap, made from a blend of 80% tallow and 20% coconut oil.

It was also observed that the pH of the finished bar was critical in controlling the amount of water absorbed by the bar and hence any subsequent cracking. It was found that when the pH was appreciably above 7, water absorption became excessive.

Water content is critical to the extrusion and stamping operations. Excessive water yields a very soft, sticky solid that is difficult to stamp and handle during packaging. On the other hand, low water content can yield a product with poor cohesivity**.** Too low a water content can also increase product viscosity during extrusion, raising the viscous dissipation of energy and thereby raising the product temperature to a point where the material becomes difficult to stamp. A target water level of 4-6% permitted the final extrusion to occur at a temperature of around 40° C, yielding a material that could be handled by the soap stamping and packaging equipment.

A penultimate prototype was tested by a large consumer panel of several hundred people to validate its comparative acceptability versus a competitor non-scumming soap bar and a typical tallow/coconut soap bar. All prototypes were unbranded and given to consumers in the same shape. The new Dove® prototype performed better than the other products on most consumer perceivable measures. Minor modifications were made to the formula to correct some undesirable characteristics before introducing the product to market.

Processing

While the final Dove® composition was processable at reasonable line speeds on a conventional soap processing line (roll mills, extruders, stampers), some equipment modifications were necessary. For example, whereas soap is normally mixed in large agitated tanks, the Dove® mixture had a much greater viscosity therefore required use of a steam-jacketed kneader mixer such as used to make bread dough, pastes or mastics.

Water level during processing provided an additional degree of freedom during design, as a higher level of water could be used as needed for viscosity modification during the early stages of processing, provided that any excess water could be removed in later stages of processing. It was found that if the batch was mixed in the temperature range of 95-115° C, if the water level dropped too low a low viscosity dispersion formed which inhibited good mixing, but keeping the mixture at a water level of 4-8% allowed a high viscosity emulsion to form, which facilitated adequate mixing. The hot batch could then be cooled by dropping material on a chill roll or passing material through a water cooled mill. Solid chips or ribbons were refined, i.e. extruded into noodles, then blended with perfume in a ribbon blade mixer, milled and refined again, and finally extruded into continuous logs, cut and stamped into the desired shape.

Nevertheless, stickiness of the final composition made stamping difficult. This problem was mitigated by spraying a die lubricant of 6% aqueous sodium chloride on the chilled die faces.

Discussion of Results

Selection of Partially Hydrogenated Sodium Cocoyl Isethionate (SCI)

The choice of alkyl chains used to prepare the SAI strongly impacts the bar lather, because the hydrophobicity of the surfactant is controlled by the molecular weight, degree of unsaturation, and branching of the chain. For example, it is known that an alkyl chain length of around C_{12} has the right hydrophobicity to balance off the hydrophilicity of the isethionate head group. Longer alkyl chain lengths lead to less water solubility; shorter alkyl chain lengths lead to less surface activity. Hence it is not surprising that the final choice of SCI is rich in C_{12} chains.

Odor and color stability problems were also related to the alkyl chains used for SAI. These could be traced to the oxidation of unsaturated carbons, such as are present in oleic acid, linoleic acid, and linolenic acid. Natural coconut fatty acid contains about 6% oleic acid, about 3% linoleic acid, and less than 1% linolenic acid. Tallow fatty acid contains nearly 44% oleic and about 6% of other unsaturates. Partial hydrogenation of the coconut fatty acid used in the manufacture of SCI served to eliminate linoleic and linolenic acids for improved odor stability, while not eliminating oleic acid, which is important for good lather.

Binder Selection

Prototypes formulated with SCI, foam booster, stearic acid as a binder, and water produced acceptable lather, appropriate bar feel, and good plasticity for processing but showed cracking on repeated cycles of moisture adsorption and drying. Adjustment of the pH, which effectively sets the ratio of soaps to fatty acids in the binder, was found to be the key variable controlling cracking. Long chain fatty acids are water insoluble, though short chain fatty acids can melt in hot water. However, a higher pH converts more of the fatty acid to soap, and short chain soaps are quite water soluble. These soluble soaps lead to increased water penetration and finally to cracking upon drying of the bar. At pH 7, an insoluble molecular complex of sodium soap and fatty acid is favored, inhibiting water penetration and thereby preventing cracking.

Choice of Co-Surfactant

Various detergents were examined for their effect on lather properties. It was observed that alkyl aryl sulfonates (like sodium dodecyl benzene sulfonate) and alkyl sulfates (like sodium lauryl sulfate) had the biggest impact as foam boosters. This is not surprising, as both surfactants have head groups with high charge density, which is important for achieving rapid and stable foam.

Conclusions

In principle, the iterative experimental approach one would take today is no different than the one pursued by the product developers at Lever Brothers Co. in the early 1950's, though possibly accumulated data about surfactants, fatty acids, and soaps in the public domain might make ingredient selection somewhat easier today. Also, the scale of the batch size used for early prototype evolution in the present might be reduced because instruments for material property assessment (relevant to both use properties and processing) allow for smaller sample sizes to be tested. Perhaps 100 grams to a few kilograms of material might be required for characterization studies in early prototyping.

Nevertheless, the composition that was identified has stood the test of time. Minor modifications have been made to make improvements in clinically assessed mildness without sacrificing lather**,** but the Dove® composition remains largely unchanged to this day.