Formulation of Transparent Melt and Pour Soaps Without Petroleum Derivatives

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Transparent melt and pour soaps are not considered to be natural according to the soap-making industry because they are synthesized with petroleum based products. These non-natural products include: propylene glycol, detergent (sodium laureth sulfate/bio-terge), and triethanolamine (TEA). There is a market for all-natural transparent melt and pour soap, and a procedure for synthesizing this soap has been the goal of this research. This research revolves around the understanding of industrial standard transparent melt and pour soaps, and finding modifications of these procedures to create a natural soap as defined by the soap industry.

INTRODUCTION

Many different soaps were investigated in this research with the main focus being on transparent melt and pour soap, cold-process soap, and transparent soaps from fatty acids. The cold-process soaps are synthesized from the saponification reaction of oils, mainly coconut and castor oils, and a mixture of lye. The saponification reaction is regarded as auto-catalytic because the soap produced is capable of dissolving lye and it is also capable of dispersing neutral fatty oils into a colloidal suspension (Palmqvist *et al.*, 1959). The saponification reaction that forms these cold-process soaps involves the reaction of the glycerol knuckle of the oil with the sodium hydroxide and water. The glycerol knuckle is composed of three soap molecules, a sodium head, and a hydroxide ion, and once saponified these components form the “soap” (Gammon, 2011). These cold-process soaps are opaque and do not allow light to shine through them as a result of the soap reflecting light at different angles. Rousseau explains that the influence of the structure of fat-crystal networks results in a rheological behavior and when the crystals are fully formed they are anisotropic and do not allow light to pass through (Rosseau *et al.*, 1998).

The other facet of this research was the formulation of transparent melt and pour soaps. The industry definition of transparent soap is the soap must be transparent enough to read 14-point Times New Roman font through a quarter inch thick piece of the soap. As explained by Evans, in making a bar of transparent soap it is necessary to figure closely, or, better, to know from practice, the proportions of the materials to use, since there is no chance to rework the soap when once made (Evans, 1937). Transparent soaps are synthesized using the “semi-boiled” process with the complete mixing and hardening of the transparent soap taking no more than a few hours to complete. These soaps, unlike cold-process soaps, are isotropic which allow light to pass uniformly through the same plane in the soap and therefore the light is not reflected by fatty acid crystal and this causes transparency in the soap. In commercial transparent soaps there usually present one or more substances which appear to act as retarders, preventing the formation of crystals. Mabrouk notes that to reduce the formation of fibrous crystals in the making of transparent soap, castor oil, ethanol, glycerin, and sugar are added to the hot soap solution (Mabrouk, 2005). Richardson backed this research up with his substance list that included: glycerol, ethyl and methyl alcohols, cane sugar or sorbitol, and alkali-metals salts of rosin (Richardson, 1908). As discovered in experimentation some of these substances maintain the transparency of the soap by acting as powerful solvents, while the other substances just simply acted as retarders of crystallization in the soap making process. Richardson noted the main process of synthesizing transparent soap is adding to a soap solution substances which will form a jelly and retard crystallization, causing transparency (Richardson, 1908). The melt and pour ability of the soap has the characteristic of either being isotropic or anisotropic, but the defining characteristic of melt and pour soaps are their ability to be produced, cooled, melted, and re-cooled to attain the same bar of soap that was originally produced. Initial understandings of the aforementioned characteristics of transparency and meltability were obtained and the research then focused on the actual bars of transparent melt and pour soaps. These transparent melt and pour soaps are able to be synthesized with transparent and melting abilities with the addition of petroleum derivatives, noticeably the addition of propylene glycol, a detergent (sodium laureth sulfate or bio-terge), and triethanolamine. These petroleum derivatives act to retard the growth of crystals in the soap and also give the bars their ability to be melt and pour soaps. This research focused on synthesizing a bar of transparent melt and pour soap without the use of the aforementioned petroleum derivatives. Industry standards define any soap that is produced with the use of petroleum derivatives as not “all-natural”, so the research focused on creating and producing a bar of transparent melt and pour soap that basically "all-natural."

METHODS

To make Coconut Oil Cold-Process soap a batch of lye of equal weights of NaOH and De-ionized H2O is needed by weighing and mixing ingredients together in 125ml pp labeled bottle, 50 g of NaOH and 50g of H2O were used. As the lye mixture is reacting the cap of the bottle is preferably removed to prevent pressure build up from the heat emitted from the lye reaction. Preheat oven to 60OC. Weight out the Coconut oil: 100.00 g into a 500ml pp bottle; heat bottle in microwave to liquefy the oil. Weigh 35.2g Lye into the 500ml pp soap bottle with the Coconut oil and mix the two together vigorously until the mixture is thick. Pour mixture into a mold and let heat for 4 hours in oven. After 4 hours remove and let soap cool and harden.

To make Crystal Clear Melt and Pour Soap Base; Fioravanti's Method: create lye solution by mixing 3.03g NaOH and 3.03g DI H2O in 125ml pp labeled bottle. Measure 18.8g Propylene glycol, 6.28g Vegetable glycerin, 17.11g 70% Sorbitol solution, 30.25g Sodium laureth sulfate into 250ml beaker on hot plate with stir bar and heat mixture to 60OC. Once this heat is attained add 13.00g Stearic acid and 6.06g Myristic acid and heat mixture to 68OC. When at temperature slowly add the 50:50 lye solution and mix for 20 minutes while continuously stopping and starting stirring until mixture becomes transparent. Let solution sit for 1 hour at 68OC. After 1 hour slowly add 2.59g Triethanolamine (TEA). Let soap solution cool to 62-64OC and pour into soap mold, let cool and harden.

For Gammon's Method Soap: create lye solution of 2.96g DI H2O and 2.96g NaOH in 125ml pp labeled bottle. Measure 37.15g Vegetable glycerin, 19.53g 70% Sorbitol solution, and 29.75g Bio-terg into 250ml beaker on hot plate with stir bar and heat to 60OC. Once at temperature add 13.00g Stearic acid and 6.06g Myristic acid to solution and heat to 68OC. When at temperature slowly add 50:50 lye solution and mix for 20 minutes while continuously stopping and stirring until mixture becomes transparent. Let solution sit for 1 hour at 68OC. After 1 hour slowly add .99g Myristic Acid and 2.59g Triethanolamine (TEA). Let soap solution cool to 62-64OC and pour into soap mold, let cool and harden. *Note, this method is the procedure that was further modified and this will be differentiated in the results section.

Ingredients	Percentages (%)
Propylene Glycol	18.80%
Glycerol (Vegetable Glycerin)	6.27%
70% Sorbitol Solution	17.09%
Bio-terg/Sodium Laureth Sulfate	30.23%
Stearic Acid	12.99%
Myristic Acid	6.05%
Lye (50% NaOH)	6.05%
Triethanolamine	2.49%

Figure 1. Melt and Pour soaps with different alkali bases. The bar in this experiment used the same procedure as in the first two bars of transparent soaps, but this procedure used SLES instead of the sodium laurel sulfate.

RESULTS AND DISCUSSION

The first experimentation with transparent melt and pour soaps used the Fioravanti procedure and the results were not ideal on the first bar. The procedure called for 30.25g of sodium laureth sulfate (SLES), but sodium laurel sulfate was substituted in place of the SLES due to lack of SLES at time of experimentation. The bar lacked consistency and transparency, and it never hardened properly. It maintained a thick, gooey consistency and this was hypothesized to form this way because of the use of sodium laurel sulfate instead of SLES. Sodium laurel sulfate is a dry detergent and is very powdery, upon mixing this detergent in with the other substances the detergent did not fully dissolve into the solution causing the bar to be opaque throughout the whole process. Another trouble that occurred during this process was temperature control, where the hot plate never set the solution at a consistent temperature. Overheating occurred during this experiment and another hypothesis was formed that this could have caused the lack of hardness and consistency in the bar. Another experiment was ran using the same materials and chemicals but with a different method of heating the solution. A round bottom flask and heating mantle were used in this experiment to provide a more thorough heat to the solution. The solution was mixed and left to cool in a mold and a very white opaque bar of soap was formed. This bar was unsatisfactory as well due to the lack of transparency but it was determined from this experiment that the lack of hardness in the first bar was due to the lack of temperature control throughout the solution. The use of sodium laurel sulfate was deemed to be the factor controlling the transparency of the first two bars made and experimentation with sodium laurel sulfate ended with this bar of soap.

Another experiment that was conducted was the creation of three melt and pour soaps with differing alkali bases; sodium hydroxide (NaOH), potassium hydroxide (KOH), and ammonia hydroxide (NH4OH). Calculations were done to determine equal molar parts of all three alkali bases and weights were then determined to experiment with. The first bar in this experiment was the same procedure as used in the first two bars of transparent soaps but this procedure used SLES instead of the sodium laurel sulfate, Table 1 shows the percentages of materials used to produce this bar. Upon hardening this bar was again opaque and white in color but unlike the previous two bars synthesized it was very smooth and no foam was formed on top of the bar. This bar was cut into three different sections and experiments were ran on all three of these sections. The first section was left as a control and no changes were made to it. The second section was re-melted and left to re-harden in a petri dish. When this section was melted down it became transparent as a liquid but upon re-hardening the bar slowly started turning opaque at the edges and finally turning fully opaque in only a few minutes after it was melted down. It was determined that just melting and re-hardening the bar of soap doesn't cause the bar to become transparent. The third section was re-melted down and 1% TEA by mass weight was added to this section to possibly add clarity to the opaque bar. After mixing and re-hardening a thin bar of transparent melt and pour soap was produced. The initial hypothesis held that adding more TEA to the soap would always produce a more transparent bar of soap. This idea was held up in Zhu's work in which is stated that triethanolamine is used widely in soaps to replace alkali bases like sodium hydroxide, triethanolamine is itself a weak alkali base, to neutralize fatty acids and create an anionic surfactant with a quaternary ammonium counterion (Zhu *et al.*, 2005). This previous research further assisted this research in determining that the TEA was acting as a weak alkali base in the transparent melt and pour soap to further break down the fatty acid crystals that cause the soap to become opaque. The second bar in this experiment was synthesized with potassium hydroxide (KOH) instead of sodium hydroxide (NaOH). When synthesized this bar of soap didn't actually form a hard and transparent bar, but remained a white and opaque liquid. This is to be expected of potassium hydroxide soap, seeing as most liquid soaps in the industry today are synthesized with potassium hydroxide. Further experiments were ran on this soap mostly to see if putting the soap into a vacuum oven to evaporate the H2O off the soap would make the soap become either transparent or hard. After the bar was put into the vacuum oven and the H2O was vacuumed off, the soap neither hardened nor did it become transparent. This concluded the experimentation with potassium hydroxide soap. The third bar of soap synthesized in this experiment was a bar of ammonia hydroxide (NH4OH) soap. This bar mixed well in the beaker with the rest of the ingredients and upon pouring the soap was fully transparent. Upon hardening the soap never fully hardened and it was not transparent either but a very opaque white color. It was determined from these experiments that substituting potassium hydroxide and ammonia hydroxide for sodium hydroxide is not a viable option for synthesizing transparent melt and pour soap.

No progress was achieved in the early stages of experimentation so Gammon's method of producing transparent melt and pour soap without propylene glycol was followed to determine if same results could be duplicated. In this experimentation 29.75g of sodium laureth sulfate was used in the mixing process instead of 29.75g of bio-terg,

Ingredients	Percentages (%)
Glycerol (Vegetable Glycerin)	32.58%
70% Sorbitol Solution	17.13%
Bio-terg/Sodium Laureth Sulfate	26.09%
Stearic Acid	11.40%
Myristic Acid	5.31%
Lye (50% NaOH)	5.21%
Triethanolamine	2.27%

Fig2. Table 2 shows the percentages used in calculating the weights for this procedure.

Both of these detergents are liquid so it was determined that no complications should occur in the mixing process. A bar of soap was synthesized using this procedure with the only one problem occurring. During the mixing process the stearic and myristic acids became very hard to dissolve into the rest of the solution, but after increasing the heat of the solution they dissolved fairly easily. The hardened bar appeared yellow in color but was very transparent, especially when cut into a quarter inch thick slab. The bar was fairly hard but still had rubberlike qualities to it, and it produced a nice thick lather that left the hands feeling very moist and soft. This was the first actual bar of transparent melt and pour soap that was synthesized in the research but it still had two petroleum derivatives that were used in the mixing process. Another experiment was conducted using Gammon's method but the sodium laureth sulfate was substituted with an "all natural" detergent in sulfated castor oil. A bar was synthesized with no problems and while mixing on the hot plate the solution was a very dark yellow color but still transparent. Upon pouring the soap into a mold the bar never fully hardened and it maintained a thick and mushy consistency. It was determined that sulfated castor oil is not a viable replacement for detergents like sodium laureth sulfate and bio-terge, because it doesn't maintain the transparency or the consistency of an industry standard bar of soap.

Then using slight deviations to Gammon's method an attempt was made to create transparent melt and pour soap with extra soap molecules substituted for the detergent. The solution was clear while still in its liquid sate. This resulted in many opaque melt and pour soaps that still used triethanolamine in them. It was shown that the soaps with only stearic acid were more transparent, but took more time and heat to melt into solution. For bars with myristic acid were not transparent but would melt rapidly. It was determined that a combination of the two produced the bar with the best of both being mostly transparent and more easily melted. Some were mostly transparent but lost transparency over time. It was also shown that it was possible to substitute the fatty acid for the detergent and produce a melting soap if the right solvents and crystal retarders were used. It proved to be a somewhat corrects answer to the question of making the natural melt and pour using only soap.

After some success in mini experiments performed the process switched to using soaps from fatty acids dissolved solely in glycerol in order to make soaps. There is a suggestion that novel surfactant derivatives from unsaturated fatty acids may have comparable properties to petroleum based surfactants10. This met with some success as soaps made using stearic, and myristic acid were made using this method. However it was shown that they were not quite as good, as the single fatty acids alone were hard to dissolve into solution and resulted in large clumps of non dissolved soaps and fatty acids being present. While mostly melting they were unable to fully go into a solution. The combinations of the fatty acids however were much easier to get into a solution and were transparent in liquid solution. They had no leftover non dissolved fatty acids or soap in them, and had a mostly translucent look to them which unfortunately faded over time. It was also determined that all of the soaps had started to absorb water from the atmosphere creating a form of oily sweat like substance which after running an infrared spectra on the "sweat" the spectra showed the "sweat" was a mixture of glycerol dissolved in water. It was through this though that a sixteen hundred gram batch was made that was mostly transparent though clouded after aging for a period of time.

After the experiment with the substituted sulfated castor oil using Gammon's method failed a few side experiments were conducted to determine how well the substances used in the formation of the soap acted as solvents. Duckbars Delight multi-oil cold-process soap was used in this experimentation, with it being made up of 28.8g 50:50 lye solution and 39g Olive oil, 28g Coconut oil, 28g Palm oil, and 5g Castor oil. A few pieces of Duckbars Delight soap was shaved off of the bar into three different flasks containing sulfated castor oil, 70% sorbitol solution, and glycerol (vegetable glycerin). There were no measurements or weights taken with this experiment. These flasks were put into the microwave and left in for 15 second intervals to see how well the cold-process soap dissolved in these substances. The sulfated castor oil did not readily dissolve the pieces of the cold-process soap even after staying in the microwave for a few minutes. This flask was put in the incubator and after several days the cold-process soap had slowly dissolved, but not fully. Experimentation determined that the sulfated castor oil was not a very good solvent and it was not used in anymore experiments. The 70% sorbitol solution started to dissolve the cold-process soap but after 45 seconds in the microwave the cold-process soap started to bubble furiously and then the solution started to harden even while being heated. Considering that sorbitol is a hexahyrdric alcohol with a straight chain of six carbon atoms and six hydroxyl groups and is readily soluble in water, it was determined that the sorbitol was reacting with the excess water in the cold-process soap and was not actually mixing but boiling while being heated together9. The last solvent used was the glycerol and after spending a few minutes in the microwave being heated up the cold-process was fully dissolved in the glycerol with a yellow/brown color and the solution was transparent, but also still a liquid at this time. This flask was left in the work hood overnight to harden and upon inspection the next day the solution had hardened in the flask into a transparent bar of soap. This soap was heated in the microwave and re-melted and poured into a soap mold. Once the soap hardened into an actual bar the soap was inspected and it was still transparent and meltable, but most importantly it was created without the use of petroleum derivatives. The only ingredients in this bar of transparent melt and pour soap were glycerol and cold-process soap, which are both made with industry standard “all-natural” ingredients. There were a few setbacks to this bar of soap. The soap “sweated” off excess glycerol or H2O, at the time of synthesis it was not truly known what exactly the bar was sweating off, but the bar sweated excessively. Another drawback to this bar of soap was that it wasn’t very hard but it was more rubbery and after sitting out in the open air for a few days the bar started to decompose into pools of glycerol and H2O. The initial hypothesis formed was that the bar of soap either was synthesized with too much glycerol in it or that the glycerol hydroxyl knuckles were sucking H2O from the atmosphere and forming a mixture of water and glycerol to form on the bar.

A modified procedure for making transparent melt and pour soap had been achieved but with two major setbacks. Experimentation was then conducted in trying to alleviate the two problems from the bar of soap. Multiple experiments were conducted using different batches of cold-process soap including another batch of Duckbars Delight, Coconut oil, and Palm oil soaps. These experiments consisted of having a fixed amount of 50g glycerol in three different beakers on hot plates with 25g, 35g, and 45g of cold-process soap dissolved in each beaker, respectively. From this experimentation it was determined that the only viable soap to use was the cold-process Coconut oil soap dissolved in the 50g of glycerol. The Duckbars Delight and Palm oil cold-process soaps dissolved in the 50g of glycerol never became transparent or very hard and these two bars sweated excessively compared to the Coconut oil soap dissolved in glycerol. The best bar of soap made using this modified method was the 25g of cold-process Coconut oil dissolved in 50g of glycerol. This bar hardened into a very transparent bar with a yellow color to it, it was also very hard and did not sweat excessively like previously noted with other bars of soap synthesized with different cold-process soaps. The lathering abilities of this soap were tested and positive results were found, the soap produced a very rich and thick lather like expected. This 25g Coconut oil dissolved in 50g glycerol soap was cut into four different sections, with one being left as a control section to compare results too. The first section had TEA added by 1% mass weight and this section hardened it was more transparent then before but it was very rubbery *(This could be due to the fact that the bar was very thin to begin with). The second section had 70% sorbitol solution added by 1% mass weight. When this section hardened it was very transparent like the TEA section but this section was considerably harder than the TEA section. The third section was put in the microwave and re-melted and re-hardened but showed no changes in consistency or sweating ability.

After determining that the cold-process Coconut oil soap was the best to use in glycerol an experiment was conducted where six bars were produced with a fixed amount of 50g of glycerol and 25g, 35g, and 45g added to the glycerol, respectively. The difference with these soaps was that three had TEA added by 1% mass weight.

Ingredients	Percentages (%)
Glycerol (Vegetable Glycerin)	66.0%
Coconut Oil	25.1%
Lye (50% NaOH)	7.9%
Triethanolamine	1 %

Fig3. Table 3 shows the percentages used in the calculation of these bars.

The other three had 70% sorbitol added by 2, 3, and 4% mass weight, respectively.

Ingredients	Percentages (%)
Glycerol (Vegetable Glycerin)	65.4%
Coconut Oil	24.8%
Lye (50% NaOH)	7.8%
70% Sorbitol Solution	2%

Fig4. Table 4 shows the percentages used in the calculation of these bars.

The best two bars that were formed in this experiment were the 25g of Coconut oil cold-process soap dissolved in 50g of glycerol with 1% TEA added and 25g of Coconut oil cold-process soap dissolved in 50g of glycerol with 2% sorbitol added. These bars were synthesized in a beaker on a hot plate set at a constant temperature of 205OC with a magnetic stir bar constantly stirring the mixture. This was determined to be the best method to synthesize the soap in the quickest and easiest fashion. The two bars were synthesized using the aforementioned method and then upon pouring they were kept in a desiccator to test the hypothesis that the atmosphere was producing the sweating that the other bars were showing. While staying in the dessicator these bars did not form any excess glycerol or H2O on their outer surface and they were both transparent to the point that 5-point font could be read fairly easily. These bars had their lathering abilities tested and they both lathered exceptionally well. These bars were cut in half and one half was left in the desiccator while the other half was left out open to the atmosphere, these bars were also coated in ethanol after the lathering test was administered. The bars outside the desiccator started to sweat in the areas where the ethanol had not been put on the bar, this lead to the discovery that covering the bars in ethanol retards the formation of the sweat crystals on the outer surface of the soap for about a day and a half. Another important discovery found in this experiment was that the use of 70% sorbitol solution had the same effect on the soap as the TEA had on the same soap. A reason that sorbitol might be considered a substitute for TEA in this instance is mentioned by Fedor in his report on sorbitol where he states that sorbitol is inert to dilute acids and alkalies (Fedor *et al.*, 1960). This is important for the research in the fact that it eliminates the use of all three petroleum derivatives that were causing these bars to not be "all-natural."

Formulation of an "all-natural" bar of soap was completed and the two setbacks had been solved but the two bars that alleviated these problems were kept in a desiccator and therefore weren't usable bars for the soap industry. A new procedure was formulated that included the use of cetyl alcohol to possibly stop the absorption of H2O molecules from the atmosphere. Twelve bars of soap were synthesized in this experiment using different weights of cetyl alcohol and sorbitol.

Preferred Weights	0g	0.6g	1.2g
0g	0g Sorb. 0g CA	0g Sorb. 0.62g CA	0g Sorb. 1.20g CA
0.6g	.63g Sorb. 0g CA	0.63g Sorb. 0.60g CA	0.62g Sorb 1.21g CA
1.2g	1.24g Sorb. 0g CA	1.25g Sorb. 0.62g CA	1.23g Sorb. 1.19g CA
1.8g	1.82g Sorb. 0g CA	1.82g Sorb. 0.59g CA	1.83g Sorb. 1.21g CA

Fig5. Table 5 *Cetyl Alcohol on horizontal axis, Sorbitol on vertical axis.

The initial soap was 150g of cold-process Coconut oil soap dissolved in 300g of glycerol. After experimentation was completed it was determined that cetyl alcohol by itself did not translate into a perfect bar of soap, as was believed to be the case. All of the bars produced in this experiment formed the "sweat" on the outer surface and the bars with more cetyl alcohol became less hard and less transparent as the weights went up. Cetyl alcohol could prove useful in further research with other substances mixed together with it but in this experimentation it proved to be useless in fixing the initial problems.

This concluded all experimentation done with this research and the initial goal of formulating a bar of transparent melt and pour soap without the use of petroleum derivatives was achieved. Although there are a few setbacks to the soap that was formulated from modified procedures further research will be undertaken to optimize these bars of "all-natural" soap. Experimentation was conducted into researching all the different aspects of soap making and deep understanding of the chemistry behind soap was formed.

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