Correlation of Fat and Oil Quality with Soap Base Color

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It is often difficult to determine whether a particular lot of a fat or oil will produce a poor or "off" color in a soap. Even raw materials with acceptable color can lend unwanted yellow or orangey tones to the resultant soap base. Once saponification has occurred, the color is difficult to improve. In our research, two test methods have been combined to establish a novel way of predicting final soap base color from the starting oils and fats. With this information, we have been able to work with vendors to improve the color of our premium base.

Traditionally, the color of fats and oils has been used as an indicator for predicting the color of finished soap base. Typically, the color of incoming or processed material is measured by one of several methods: Lovibond, Gardner, or spectrophotometrically at 440 and 550 nm. Such measurements indicate the relative success of any refining, bleaching, or deodorizing steps prior to the soap-making process. These steps remove impurities, such as proteins, sterols, carotenoids, chlorophylls and colored compounds generated by the rendering process. However, there can be small amounts of a few colorless natural compounds, not affected by these purification processes, which become color bodies during saponification and contribute to the soap base color. These compounds are believed to be unsaturated ketones, which convert to polyhydrofuranes in the alkaline environment of a soap kettle.[1]

Logic suggests that a strong relationship exists between the color of a tallow and the soap made from that tallow. This is true when different grades of tallow are compared. A very high quality, odorless, white soap base has been formulated using edible fats and oils. During initial formulation of our premium base, the superior color and odor qualities of edible-grade tallow clearly gave a whiter base than various inedible grades commonly used. Nevertheless, this relationship does not hold true when various shipments of edible tallow are compared. Therefore, we needed a better understanding of why off colors developed, and how such problems could be predicted.

Research focused on the full-boiled kettle process, utilizing beef tallow, and coconut or palm kernel oil, as reported earlier.[2] An attempt was made to identify all factors which generate or eliminate color bodies. Beef tallow was the prime contributor to color generation; the color contributed by other oils was an order of magnitude less intense.

The Process

The full-boil kettle saponification process uses a countercurrent flow of lye against the fats and oils. This concentrates the soap in the neat phase, and the glycerin and color bodies by-products in the lye phase. Figure 1 is a simplified diagram outlining the flow of materials which contain color bodies. The saponification process is performed in large open top tanks called "kettles." A kettle could hold upwards of 100,000 pounds of material. A typical batch proceeds as follows:

1. The seats (a 40% soap solution remaining in the kettle at the end of a batch) from the prior batch are heated to

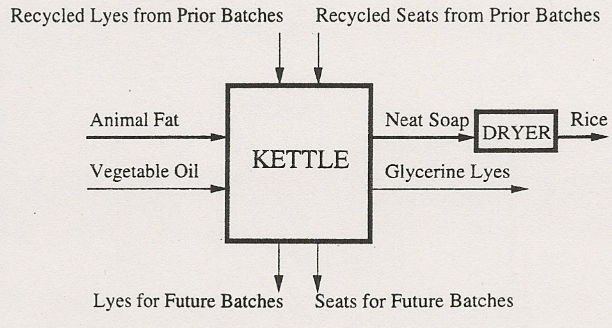

Figure 1. Color bodies mass balance of saponification

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boiling by injecting steam directly into the bottom of the kettle. The steam serves two purposes, to heat the kettle contents and to provide agitation.

2. The ingredients are loaded into the kettle in precise ratios to effect the saponification process. Those ingredients include animal fats and vegetable oils, caustic (50% NaOH in water), brine (26% NaCl in water), water, and recycled wash lyes from prior batches.
3. The saponified mixture is allowed to settle into two phases. The upper phase is called a curd, and will typically contain 60% soap. The lower phase is called a lye, which contains less than 1% soap, up to 20% glycerin and a large fraction of the color bodies. This resultant "glycerine lye" is removed from the kettle and further processed to concentrate and purify the glycerin.
4. One or more washings of the curd are performed to remove additional color, odor and glycerin. After each wash, the kettle is again allowed to settle, producing a curd and a lye. These lyes are recycled into future kettles in such a way that the lye generated from the first wash is used during the loading of a subsequent kettle. The lye generated from the second wash is used during the first wash of a subsequent kettle. The final washing of a kettle does not use any recycled materials. Therefore, the flow of lyes is "counter-current" to the flow of soap.
5. After the desired number of washes have been performed, the curd is "fitted." Here, water is added to the kettle to produce a smooth solution which, when left to settle again, produces two phases. In this case, however, the upper phase is the "neat" soap phase which is high in soap (>65%) and low in free alkali and salt, and the lower phase is the "seat" described in step 1. The neat soap is removed from the kettle, leaving the seat behind to start a new batch.
6. The neat soap must be dried from its present 30 to 31% moisture to 12 to 14% moisture, in order to be formed into bars. The soap is "superheated" and then allowed to "flash dry" so that the excess water leaves as steam. The resultant soap is then formed into small pellets which have the look and feel of rice. This "rice" is combined with fragrance, color, and other additives before being milled and pressed into a finished bar.

Detailed descriptions of how this process works are available in George and Woollatt.[2,3]

Taking the basic principle, "what goes in must come out," we performed a mass balance analysis on the color bodies flowing through the system. In a "steady state" process, the only contribution of color bodies to the system comes from incoming fats and oils, since color added by the lyes and seats from prior batches will approximately equal the color removed by lyes and seats for future batches. Therefore, we concluded that the total amount of color bodies present in the neat soap and glycerin lyes must equal the total color bodies in the animal fats and vegetable oils. Since the ratio of animal fats to vegetable oils is equal to or greater than 4:1, the principle source of color bodies is clearly the animal fats. Because the process is well defined, and is maintained at a steady state, the ratio of color bodies in the dried, "rice" (rice-like soap pellets) soap base to the color bodies in the glycerin lyes remains constant. The conclusion, then, is that there is a simple relationship, expressed as:

$$\text{Color of soap rice} = f(\text{Color bodies in animal fat}) \quad (1)$$

this relationship can be approximated as a linear function:

$$\text{Color of rice} = m \cdot (\text{Color bodies in animal fat}) + b \quad (2)$$

where m is a slope greater than zero and b is the y-intercept. The problem is now reduced to determining the parameters:

- Color bodies in animal fat, and
- Color of rice

from which m and b can be determined.

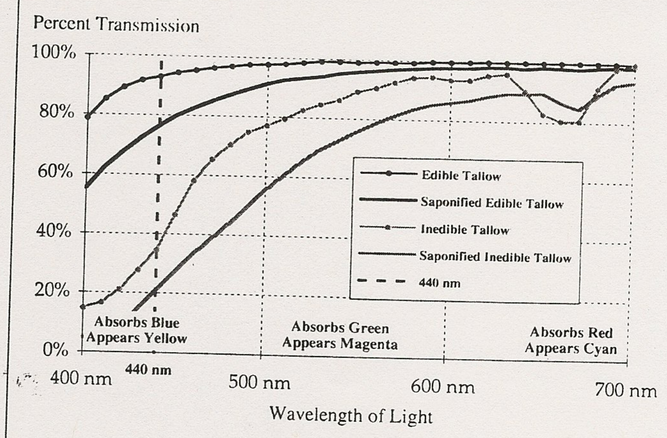

Figure 2. Transmission of visible light

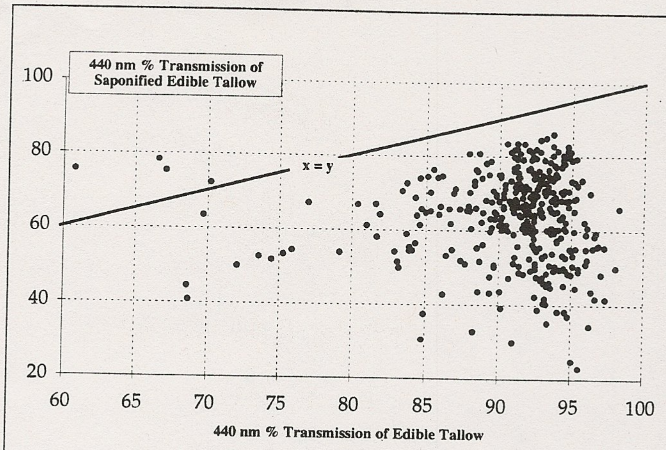

Figure 3. Relationship between the color of edible tallow and the color of saponified edible tallow

Color Bodies in Animal Fat

There are three widely used measuring scales for fat and oil color: Gardner, Lovibond Red and Yellow, and percent transmission at 440 and 550 nm. Both the Gardner and Lovibond scales are based on subjective color matching—the observer must compare the sample to a series of calibrated filters, and choose the "best" match to define the color of the sample. Results will vary with different observers. However, both these techniques can now be done using automated color-matching equipment, to eliminate observer variation.

Percent transmission is measured with a spectrophotometer, which yields an objective value for color. Transmission at both 440 nm (blue light) and 550 nm (green) is usually measured, since absorption of blue light gives yellow and absorption of green light gives magenta.

Liquid tallow is yellow, so it makes sense that the 440 nm blue light is the most sensitive wavelength at which to measure the level of color bodies present in a tallow sample. As expected, the transmission spectrum of edible tallow shows greater transmission than inedible at all wavelengths, but particularly for blue light (Figure 2).

During saponification, trace impurities in the tallow undergo transformations which contribute additional color bodies to the mass. Both tallows darken, as the transmission values for the saponified tallows show (Figure 2). This darker color is what affects the finished soap base, so values of saponified tallow at 440 nm should be most predictive of the finished soap base color.

However, as mentioned earlier, lot-to-lot variations in edible-grade tallow did not have the same correlation of unsaponified and saponified color. Figure 3 shows a comparison of transmission at 440 nm for tallow and saponified tallow measured on 378 lots of edible-grade tallow delivered to our plant from May 1989 through November 1992. The line x = y shows the 1:1 color ratio. All but four samples were darker when saponified than were the original tallows, indicating the presence of colorless compounds which convert to color bodies during saponification. The "shotgun blast" appearance of the plot indicates that the relationship between colorless compounds which become color bodies and the color bodies visible in tallow as received varies widely from lot to lot. Thus, the color of a tallow can only serve as a worst-case indicator for the color of the resultant soap. Yellow tallow will definitely produce a yellow soap, but water-white tallow may or may not make a white soap.

Color Measurements

Sap color test on fats: The so-called sap color test indicates the color of soap resulting from a particular oil or fat by saponifying a sample in alcoholic potassium hydroxide (72% SDA 40 alcohol, 14% KOH, 14% H_2O) and measuring the solution spectrophotometrically at 440 nm. The saponification ("sap") part of this test is important because of the contribution of originally colorless compounds to the resultant soap color. Although this test does not account for any mass action effects, or the washing steps which are an important part of commercial soap-making, the sap color test is an accepted quality control tool in the industry.

Yellowness index test on dried soap base: Dried soap base color was measured at our lab using the yellowness index [(YI) D1925] on a Hunter Lab Scan II Colorimeter. This index measures

$$YI = \frac{100 \cdot (1.28\,X - 1.06\,Z)}{Y} \quad (3)$$

where YI is the yellowness index per ASTM D 1925-70, and X, Y and Z are the CIE tristimulus values, which simulate the color-matching response functions of a human observer as defined by the 1931 2° Standard Observer or the 1964 CIE 10° Standard Observer. The YI of ground, dried soap base

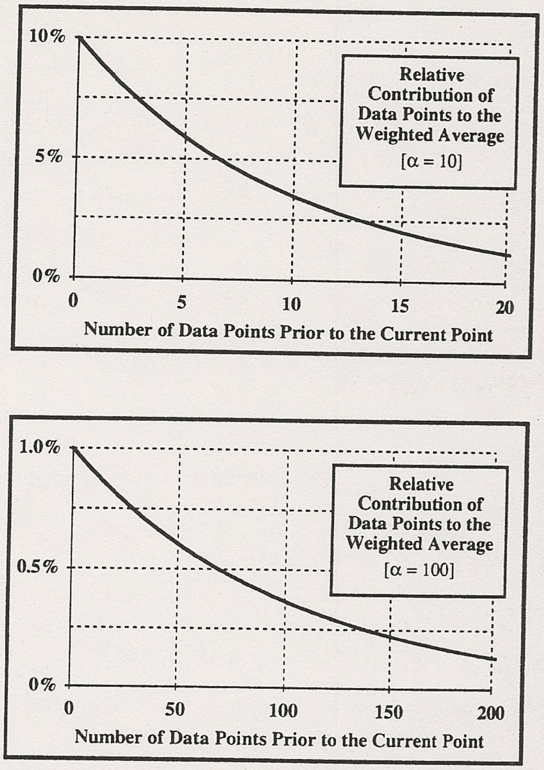

Figure 4. Number of data points prior to the current point, for α = 10 and α = 100

measured for reflected color in an optically pure petri dish indicates the degree of yellow color present due to scorching, soiling, degradation, reaction, or processing.

Correlating Test Results

With saponified tallow color and YI for the dried soap base, we were ready to begin mapping the color correlation. However, after pretreatment, tallow is usually emptied into a holding tank. Because the tank is rarely emptied completely, there may be tallow from several lots in the tank at a given time, which eliminates any one-to-one correlation between the two tests. Also, the rice-like pellets of dried soap are stored in large bins, to which several different kettles of soap may have contributed. Because the production process does not allow identification of a single tallow lot used to produce a single soap batch, we used an averaging technique to model the process over time.

Decaying Memory Averaging

The rationale behind this model is that the most recent event (tallow lot or soap batch, in this case) contributes proportionately more to the relevant character of the total mix than previous ones. This makes sense, since tallow (or soap base) is continually being removed between additions of new batches. The equation defining the decaying memory average at time n is

$$X_n = \frac{x_n + (\alpha-1)X_{n-1}}{\alpha} \qquad (4)$$

with S_n, the current deviation, defined by

$$S_n = \sqrt{\frac{(x_n - X_n)^2 + (\alpha-1)S_{n-1}^2}{\alpha}} \qquad (5)$$

and current time fraction out of specification, F_n, defined by

$$F_n = \frac{f_n + (\alpha-1)F_{n-1}}{\alpha} \qquad (6)$$

where $f_n = 0$, if x_n, the n^{th} (current) observation (in this case, lot or batch) is within specification; and $f_n = 1$, if x_n is out of specification. The $n-1$ term in these equations represents the immediately prior batch or lot, and α is the relaxation parameter [$\alpha > 1$]. (This is a measure of how far in the past we wish to consider.) If α is 1, then only the current, x_n information is considered. As α gets larger, characteristics of previous batches are weighed more heavily upon in the average.

The choice of α is process-dependent. In this case, it is a measure of how long the tallow remains in the holding tank and how long the soap rice remains in the bins. A value of 10 appears to best represent both processes. This means that the most recent batch or lot contributes 10% of the total in the weighted average, and the tenth most recent contributes 3.87% (See Figure 4).

Start-up: An important data point in the three previous equations is the $n-1$ value. For the first point, $n=1$, and the three above equations are not defined. The start-up equations are:

Average: $X_1 = x_1$

Deviation: S_1 is undefined

define $S_2 = \frac{|x_1 - x_2|}{\sqrt{2}}$

Fraction out of specification: define $F_1 = f_1$

Also note at start-up that the value for $n=1$ will have an overwhelming contribution to the *average*, *deviation* and *fraction out of specification*. For example, the decaying memory average at $\alpha = 10$ is:

$$X_1 = x_1$$

$$X_2 = \frac{x_2 + 9X_1}{10} = \frac{1}{10}x_2 + \frac{9}{10}x_1$$

$$X_3 = \frac{x_3 + 9X_2}{10} = \frac{1}{10}x_3 + \frac{9}{100}x_2 + \frac{81}{100}x_1$$

$$X_4 = \frac{x_4 + 9X_3}{10} = \frac{1}{10}x_4 + \frac{9}{100}x_3 + \frac{81}{1000}x_2 + \frac{729}{1000}x_1$$

so at $n = 4$, x_1 contributes more than 72% of the total value for X_4.

However, if the start-up algorithm is refined to substitute n for α until α is <n, the values for X_n takes the form of:

$$X_1 = x_1$$

$$X_2 = \frac{x_2 + X_1}{2} = \frac{1}{2}x_2 + \frac{1}{2}x_1$$

$$X_3 = \frac{x_3 + 2X_2}{3} = \frac{1}{3}x_3 + \frac{1}{3}x_2 + \frac{1}{3}x_1$$

$$X_4 = \frac{x_4 + 3X_3}{4} = \frac{1}{4}x_4 + \frac{1}{4}x_3 + \frac{1}{4}x_2 + \frac{1}{4}x_1$$

so the weighted average is simply the arithmetic mean until $n > \alpha$. There are similar effects on the deviation and fraction out of specification equations.

Data generation and collection: Decaying memory

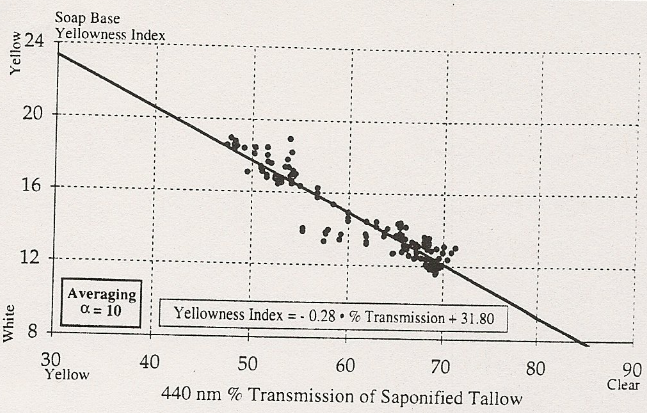

Figure 5. Relationship between soap base yellowness index and percent transmission at 440 nm of saponified tallow

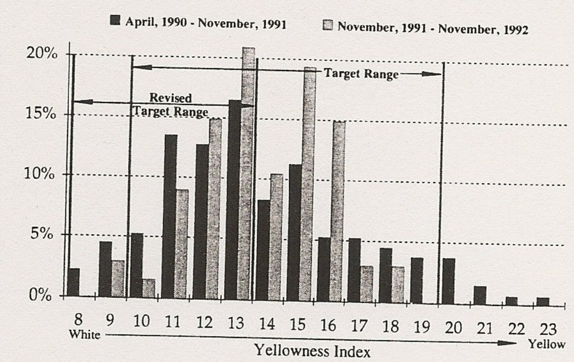

Figure 6. Histogram: Color of soap base

averaging statistics were collected in more than 100 databases on ten Macintosh computers in the laboratory network. Information is stored in MicroSoft Excel, if there are fewer than (or equal to) 1000 data points, or FoxBase+/Mac for databases larger than 1000 data points.

The performance index technique discussed in George[2] can be used in conjunction with decaying memory averaging to provide a summary of current, recent and long-term performance.

Relationship Between YI and % Transmission: From April 1990 through November 1991, 179 shipments of tallow were received and 133 kettles of the premium soap base were produced, using an unchanged production process. The average production delay between receipt of tallow and final production of riced soap base was (and is) seven days. On a plot of percent transmission at 440 nm (%T440) of the tallow most likely to have been the major contributor to the soap batch against the soap, YI for saponified tallow showed no apparent trend. Figure 5 shows a very distinct trend when decaying memory averaging is used to relate tallow lots and soap batch yellowness. The least squares fit of the averaged data is:

$$YI = -0.28 \cdot (\%T440) + 31.80 \quad (7)$$

Application to Improve Quality

At the start of this study, the specification for acceptable upper limit of YI on our premium soap base was set at 20.

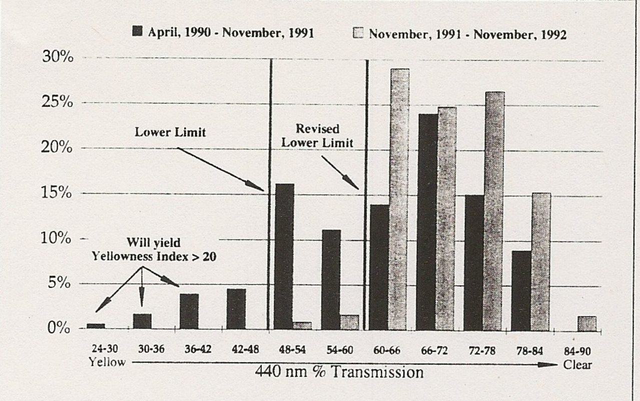

Figure 7. Histogram: color of saponified edible tallow

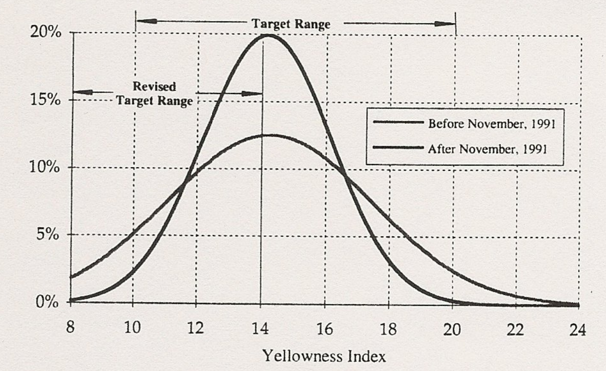

Figure 8. Normal distribution: yellowness index of soap base

However, Figure 6 shows that, during the period April 1990 through November 1991, nine batches (6.8%) exceeded this value. From equation 7, a YI of 20 or greater would result from saponified tallow %T440 of less than or equal to 42%. Figure 7 shows 11 tallow shipments, or 6.1%, below 42.

During this same period, we had set a "soft" limit of 48% transmission. Although we had insufficient data at that point to determine a relationship between sap color and YI, we believed such a relationship to exist, and the value of 48 was chosen based on shipments we were receiving at that time.

Starting in November 1991, we began to train our suppliers in the sap color test. Since the bulk of edible tallow is used by the food industry, with our use representing only a small fraction of the total, it was not a hardship for our suppliers to earmark lots identified by the sap color test as producing less yellowing for our use. With the cooperation of the suppliers, we were able to raise the lower limit on %T440 from 48 to 60. Figure 6 shows the effect of this change on the soap base color. Although 20% of the lots have YI more than the 15 calculated using equation 7, there are no YI values above 18.

Future Work

Although variation in the saponified edible tallow has been reduced, and the average %T440 value moved from 63% to 70% transmission, Figure 8 indicates that more work remains to be done. Although the variability of color within the premium soap base batches has been substantially reduced, as the height and steepness of the bell curve shows, the average YI has not been affected, despite a predicted average YI of 12.2 using our derived equation. Although our target YI range is now 8 to 14, 50% of our soap base production is clearly not within this range.

Now that limits have been set to minimize the color bodies contributed by the principle source—tallow—we need to explore whether cost-effective means exist to clean the other input streams identified in Figure 1. A close look at the YI prediction using equation 7, indicates that contributions from other sources are now significant.

Specific avenues to pursue include:

- Working with edible coconut oil suppliers to procure the lightest color raw material, as was done for tallow.
- Postprocessing the neat soap to remove remaining color bodies.
- Off-line processing of recycled materials to remove color bodies.
- Additional washing steps to remove color bodies.

References

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