

# **INFLUENCE OF SUGAR END pH ON OVERALL COLOR RISE IN THE SUGAR END AND COLOR OF MOLASSES PRODUCED**

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## **Introduction:**

In beet sugar factories employing chromatographic separation of sucrose from molasses, the color of the molasses feed to the molasses separator has a relatively direct influence on the color of the sucrose enriched extract produced and the overall efficiency of sugar recovery from the molasses separation process. The subsequent sugar end processing efficiency of the separator extract to granulated sugar is also, to a certain extent, dependent on the color loading of the extract being processed. Generally, the higher the color of the molasses feed to the separation process, the higher the color of the extract fraction from the separation process. Thus, the color of molasses produced in such factories or companies becomes an important process variable to be monitored and controlled to whatever extent possible.

This study evaluates the effect of manipulating and controlling the pH of the high green, intermediate green and molasses produced on sugar end color rise and final molasses color. In general, the results of the study show that the pH of the green syrups has a relatively direct influence on the overall color rise in the sugar end and the color of the final molasses produced. Thus, the deliberate control of green syrup pH in the correct range will produce molasses of the lowest possible color relative to the quality of the thick juice processed.

No explanation is given for the noted effect of pH on color production. However, it is noted that the Indicator Value (effect of pH on the color measurement itself) relative to the process pH and color changes noted, has relatively little effect on the measured process color value.

## **Background and Methodology:**

Historically, the Mini-Cassia Factory of the Amalgamated Sugar Company, LLC located in Paul, Idaho, has produced a relatively low color virgin molasses. Beginning with the 2008 beet campaign, there was a noticeable increase in molasses color and along with that increase a substantial increase in the color of extract produced from the Company's molasses separator operations. The noted color increase in molasses produced seemed to coincide with efforts to optimize thin juice alkalization related to the juice softening process and the elimination of significant color rise during juice concentration. Effectively, the factory had substantially reduced the use of soda ash and 50% caustic addition to the beet end of the factory. While the factory was now able to produce soft, low color thick juice to the sugar end, the sugar end color rise had increased substantially causing the production of high color molasses.

In the review of historical data, it was noted that molasses produced typically averaged in the 9.1-9.3 pH range in the previous two campaigns. For the 2008 campaign, the

molasses produced had dropped to an average of 8.2 pH along with a nearly 50% increase in molasses color from approximately 40,000 ICUMSA to over 65,000 ICUMSA. Given that very limited data history was available for molasses produced color at the factory it was not clear whether or not there was a direct association of molasses pH with molasses color. However, given the recent somewhat dramatic reduction in soda ash and caustic addition to the beet end unit processes, it was theorized that the introduction of alkalization agents to the sugar end syrups downstream of the white sugar operations might minimize color production in the sugar end and the color of the final molasses produced.

In order to test this theory, the following steps were taken to begin a system of pH management of the sugar end process syrups and evaluate the response of the process color to pH manipulation.

1. Equipment was installed to meter a controlled amount of 50% caustic solution to the high green syrup collection tank.
2. Routine analysis of sugar end process syrups for pH, color, sucrose and total dissolved dry substance was established in order to facilitate color and material balances with which to determine the location and degree of color rise in the sugar end unit process systems.
3. Process management guidelines were established for sugar end process syrup pH and the response of color to process pH was tracked.
4. Central laboratory analysis was initiated to provide comparative analysis on weekly molasses and separator extract composite samples along with additional analytical information (Indicator Value) on the weekly composites.
5. Indicator Value measurements were conducted at 4.0, 7.0 and 9.0 pH in order to determine the effect of measurement pH relative to the actual molasses pH and color values.

Beginning with the 33<sup>rd</sup> day of the 2009-10 Beet Campaign, the factory began monitoring the pH and color of molasses produced. Samples were collected every 6 hours for analysis. Portions of each sample were collected into a weekly composite sample and sent to the Central Testing Laboratory for comparative analysis. Samples collected and tested at the factory laboratory were not pH adjusted for color measurement. The composite samples sent to the Central Testing Laboratory were adjusted to pH 7.0 for color measurement and also to pH 4.0 and pH 9.0 to evaluate the Indicator Effect on color measurement.

As noted in Figure 1 below, caustic addition to the high green syrup collection tank was begun on the 40<sup>th</sup> operating day and continued for the balance of the campaign. Caustic addition was steadily increased raising molasses produced from pH 7.0 to pH 10.0 in the 40<sup>th</sup> thru 70<sup>th</sup> campaign days while noting the color response. As shown in Figure 1, the color response was in general inversely proportional to the molasses pH increase. From the 70<sup>th</sup> to the 100<sup>th</sup> campaign day, the molasses pH was systematically reduced to a low of pH 8.5 with a corresponding increase in molasses color. From the 105<sup>th</sup> campaign day to the end of the campaign, the target was set for molasses pH 9.5-10.0. Difficulty in managing precise caustic addition during this period resulted in some “swinging” of the actual pH along with related “swinging” of the molasses color. The relatively constant downward drift in color during this period was not specifically

identified but did appear to coincide with a corresponding increase in thick juice pH being supplied to the sugar end.

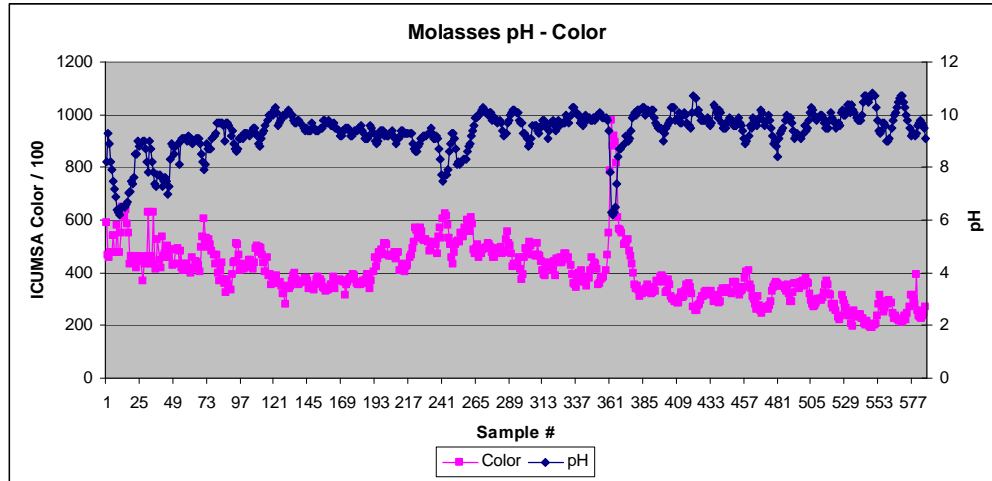


Figure 1

**Results and Discussion:**

As stated above, the color of the extract produced from the chromatographic separation of sugar from molasses is to a relatively large extent a function of the color of the molasses feed to the separator. Separator molasses feed and extract produced color for the 2009-10 processing season is shown in Figure 2. The color of extract has a fairly large dependence on the molasses feed color down to a molasses color of approximately 40,000 ICUMSA. With a relatively lower molasses feed color, extract produced color

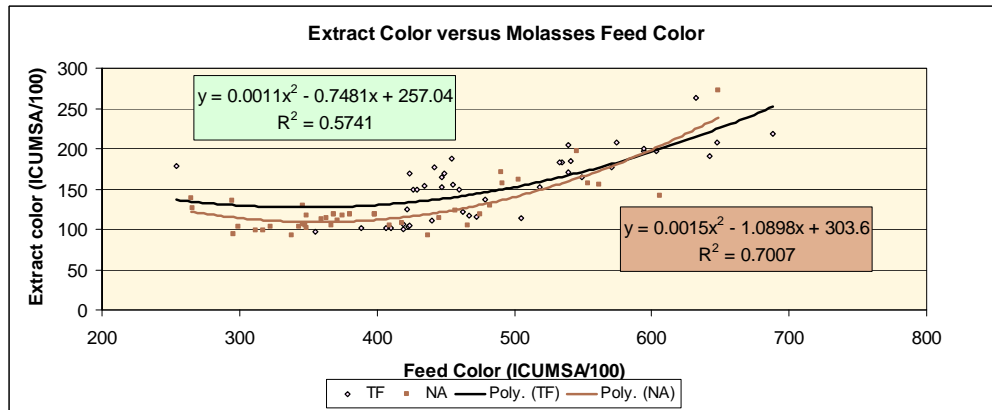


Figure 2

usually allows the efficiency of sucrose separation to be increased through an increase in the volume ratio of the extract cut from the separator thus retaining a greater percentage of color (and sucrose) in the extract product. Since 10,000 ICUMSA color extract is acceptable for processing to granulated sugar, sucrose recovery may be enhanced when molasses feed color is below 40,000 ICUMSA.

Above a molasses feed color of 40,000 ICUMSA, the volume ratio of the extract cut must be systematically reduced to maintain a reasonable extract color for processing in the sugar end at a reasonable processing rate and into granulated sugar of acceptable color. Thus, the sugar recovery efficiency of the separation process must be compromised sending a greater percentage of sugar in the molasses to raffinate when molasses feed color is high in order to maintain a relatively low extract color.

From this perspective, the color of molasses produced becomes an important process variable to be managed and controlled to whatever extent possible in order to optimize the sugar recovery and extract quality from the molasses separation process.

As noted in Figure 1, the color response to pH manipulation was essentially an inverse relationship during the 2009-10 campaign test period. As pH was increased, there was a corresponding decrease in molasses produced color. Regression analysis of all paired data for pH and molasses color collected at the factory laboratory, shown in Figure 3, give a regression coefficient of 0.512 indicating that about half of the color response is likely due to sugar end pH manipulation.

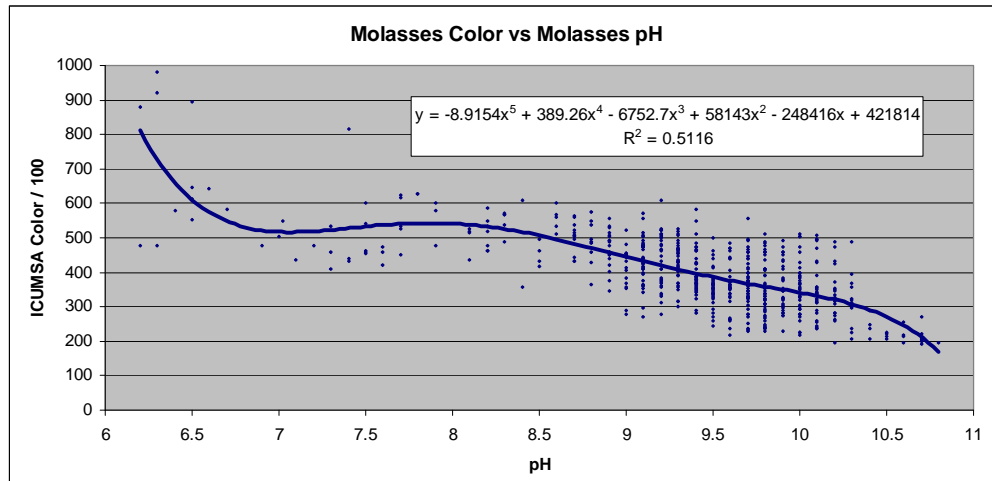


Figure 3

During the evaluation period several things were noted with respect to the deliberate change of molasses pH in the sugar end.

1. A change in pH was usually followed by an “attenuation period” where the molasses color seemed to trend downward over the course of several days. This effect was thought to be mostly related to the “back-mixing” effect of color in the process. This effect was more notable during extended periods of operation at a relatively constant molasses pH.
2. As the pH of the thick juice fed to the sugar end increased as a result of soda ash addition for lime salts control in the beet end, the color of molasses produced appeared to drop even when the molasses produced pH was held at a more or less constant value. This effect was noted particularly in the final weeks of the campaign when large amounts of soda ash are added and is seen as a continuous decline in molasses color during the final days of the campaign without a significant increase in molasses produced pH. In fact, as

this occurred, the amount of caustic addition required to the sugar end for pH control was reduced. Curiously, during this same period, the color of thick juice increased along with the increased thick juice pH yet the color of molasses produced trended towards lower values.

The weekly composite data pairs analyzed by the Central Testing Laboratory, as shown in Figure 4, show a roughly similar color response to pH with a higher regression coefficient of 0.76. To some extent, the variation in the shape of the curve and the noted color response may be in part due to the fact that the CTL color measurements were made on pH adjusted samples (pH 7.0) whereas the control laboratory measurements were not adjusted and measured at the molasses produced pH.

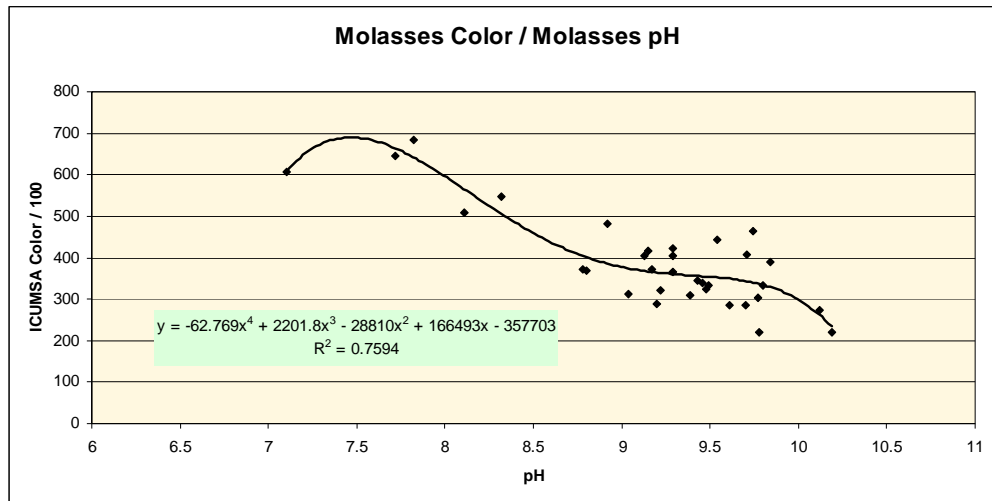


Figure 4

The major difference in the two response curves is the area where molasses color is most affected by pH. In the curves produced from the factory laboratory data, the color response appeared to be greatest beginning about pH 8.0 and having a relatively linear response through the highest pH values measure up to pH 10.5. For the weekly composite samples, the response of color to pH appeared to begin about pH 7.5 and be relatively linear through about pH 9.0 where the response appears to flatten somewhat through pH 10.0.

The question as to whether the difference in the response curves is due to the difference in the analytical methods between the two laboratories or due to the “averaging effect” of the composited samples is unclear. However, analysis of the Indicator Effect by the CTL does indicate that there is a small influence on the color measurement as a result of the pH at which the measurement is made. A total of 11 consecutive weekly composite molasses samples were analyzed at pH 4.0, 7.0 and 9.0 to determine the extent to which the color measurement was affected by the pH at which the measurement was made. All measurements, in both laboratories were made by absorbance at a wave length of 420 nm.

As shown in Figure 5, there is an average difference of about 50 color units (ICUMSA/100) between the color measurements at pH 4.0 compared to pH 7.0 and of about 20 color units between the measurement at pH 7.0 and pH 9.0. As the pH of the measurement is increased, the corresponding color measured is increased.

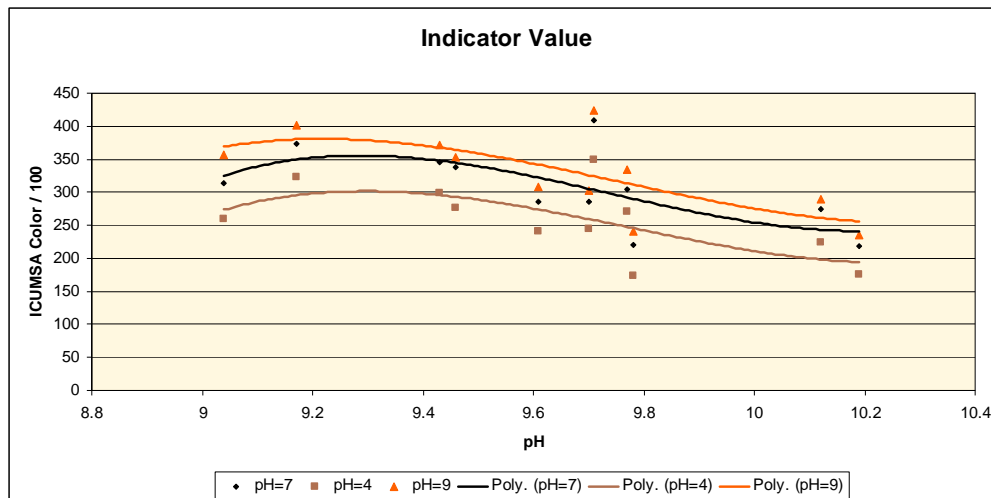


Figure 5

The evaluation of the Indicator Effect on molasses color shows that a higher measurement pH value will cause a higher indicated molasses color by about 20 color units in the pH range utilized during this evaluation. Thus, if a pH 9.0 molasses is adjusted to pH 7.0 for color measurement analysis, the color of the sample measured at the lower pH will be approximately 20 color units lower in value than if it were measured at pH 9.0. The difference in molasses produced color between a molasses having pH 7.0 and one having pH 9.0 is, on average, a difference of approximately 200-250 molasses color units (ICUMSA/100). Thus, the influence of the measurement pH on the color measurement value is less than 10% of the noted color change relative to the molasses pH and such measurement pH influence is in the opposite direction to the color response noted relative to change in the molasses produced pH value. From this it is concluded that the molasses color response to pH manipulation of the sugar end syrups is real and that pH manipulation can be effectively used to control the color of molasses produced.

Of further interest is the mechanism by which color is being inhibited by adjustment of the processing pH value as well as where in the process this inhibition is taking place. While during this test period no effort was made to evaluate the mechanism by which color inhibition was occurring, material and color balances were run at regular intervals during the test period to observe where in the sugar end unit processes color development appeared to occur and to what extent color development varied relative to both the molasses and thick juice pH.

The relative amounts of color development in the various sugar end unit processes are shown in Figure 6. It is noted that there is little notable change in color development in the sugar melters and the white crystallization relative to final molasses pH. The amount of color rise in the high raw and low raw crystallization unit processes appears to be primarily affected by the final molasses pH and also to some extent by the thick juice pH. Where molasses and thick juice pH are relatively higher, there appears to be an additive effect on the amount of color development experienced in these unit processes. By far, the greatest color inhibition is taking place in the low raw crystallization.

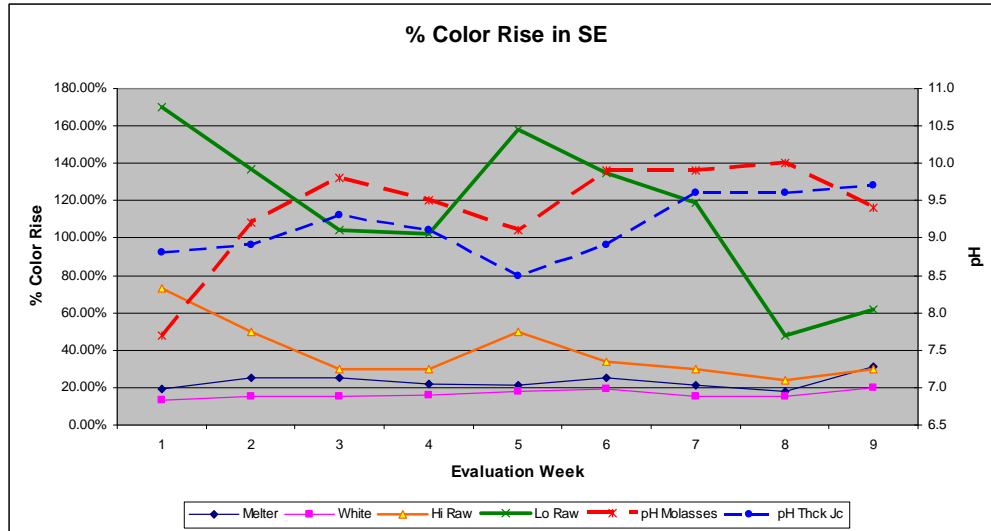


Figure 6

Close examination of Figure 6 reveals that molasses produced having pH 8.0, color rise in the high raw and low raw crystallization were approximately 70% and 170% respectively. With molasses produced having pH 9.5-10.0 and thick juice at pH 9.0, color rise in the high raw and low raw crystallization were approximately 30% and 100% respectively. With both molasses and thick juice at pH 9.5 or higher, color rise in the high raw and low raw crystallization were approximately 25-30% and 50% respectively. This very abrupt drop in color rise in the low raw crystallization with the increase in thick juice pH is quite interesting along with the fact that the color of thick juice was also from 50-100% higher at pH 9.5 or higher than at values below pH 9.0.

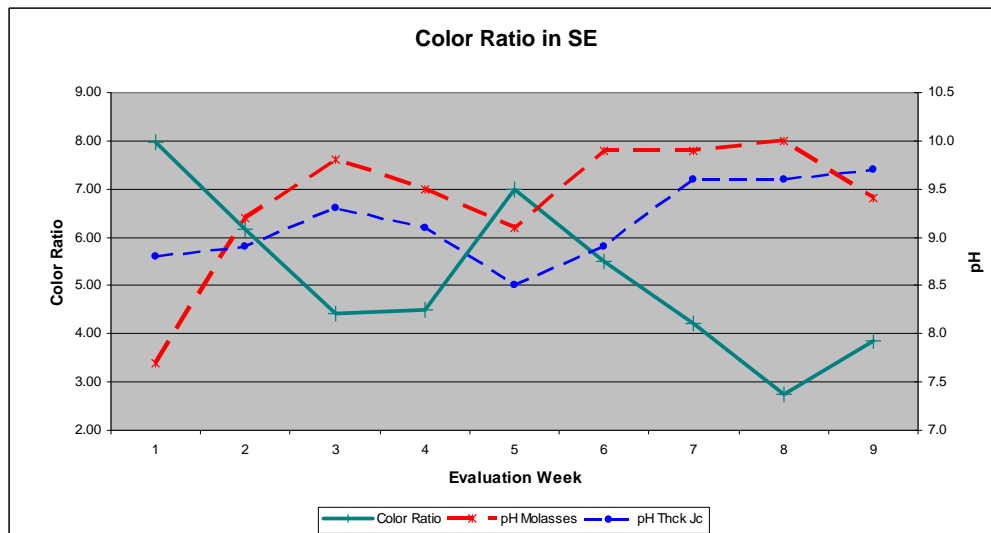


Figure 7

Overall sugar end color rise for the same operating period is shown in Figure 7. Generally, for a molasses produced pH 8.5-9.0, color increase in the sugar end was calculated to be 6-8 times the color weight entering in thick juice. With molasses produced in the range

of pH 9.5-10.0, color increase was calculated to be in the range of 4.5-5.5 times the color weight entering in thick juice. Both of these ranges were observed with thick juice in the range of pH 8.5-9.0. When thick juice of pH 9.5 or greater was introduced into the sugar end and the molasses pH held above 9.5 as well, the color increase in the sugar end dropped to the range of 3-4 times the color weight entering in thick juice.

Color Weight is defined as:

color \* weight dry substance

Color Ratio of color increase is defined as:

color \* wt. dry substance in thick jc / color \* wt. dry substance in molasses

Clearly, the data indicate that there is a relatively direct relationship between process pH and color formation and that the properties of the thick juice and sugar end syrups with respect to pH play an important role in the color behavior of the syrups in the sugar end. Interestingly, and also somewhat surprisingly, there was also noted that the color of thick juice bore an inverse relationship to the color of molasses produced with the color of thick juice generally increasing as the thick juice pH increased while the color of molasses generally trended downward with the rise in thick juice pH.

#### **Observations and Conclusions:**

1. The color of molasses produced was generally found to be an inverse relationship to the pH of the molasses. As molasses pH is raised, molasses color will be reduced.
2. As the pH of thick juice fed to the sugar end increased, a reduction in molasses color was noted. This observation confirmed that higher levels of alkalization in the beet end likely did have the effect of suppressing molasses color.
3. The pH at which molasses color is measured (Indicator Effect) was found to have no significant effect on the noted relationship between molasses color and pH.
4. The degree of color development in the sugar end is significantly affected by pH of the syrups in process. Most of the color development occurs in the low raw crystallization with a relatively smaller amount occurring in the high raw crystallization. No significant change in color development in the melter station or the white crystallization operations were noted at any of the thick juice or molasses pH levels encountered in this study.
5. Color ratio noted in the sugar end operations were found to be as high as 8 times the color entering in thick juice at a molasses pH below 8.0 and as low as 3 with molasses pH exceeding 9.5 along with thick juice pH at 9.5 or higher.