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ISOLATING CARAMEL COLORING COMPOUNDS

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8 Claims. (Cl. 99—148)

1

This invention relates to the isolation of the essential coloring compounds from caramelized sugars.

This application is a continuation in part of application Serial No. 753,054, filed June 6, 1947, now Patent No. 2,533,221.

In general the process comprises the separation of the compounds which actually impart color from the unchanged or only slightly caramelized mass of sugars which act as more or less undesirable diluents in ordinary commercial caramel color. The separation of the coloring compounds is accomplished by precipitation of the colors by addition of alcohols whereby the uncaramelized sugars or slightly caramelized sugars remain in solution while the coloring compounds or caramelized portions precipitate.

The caramel colors of commerce are produced by well known caramelization processes in which heat is applied to concentrated sugar solutions which may contain various amounts of catalysts preferably of an alkaline nature, the most commonly used being compounds of ammonia. Caramelization or the production of coloring power cannot be carried beyond certain limits which are imposed by the instability imparted by "overburning" and attainment of excessive viscosity, humin formation, charring and other undesirable results. Consequently the commercial caramel colors ordinarily contain only about 25% of the weight of the sugar solids in the form of coloring compounds, the remainder of the solids being primarily unchanged or slightly modified sugars. The essential characteristic, therefore, that of color imparting power or as it is known in the trade, tinctorial power, has been limited in the past by the practical degree of caramelization realizable under the limitations of the processes available.

It has long been recognized in the art that caramel colors exhibit instability in certain low boiling alcohols which are miscible with them in certain proportions. When an ordinary caramel color solution is diluted with concentrated methanol or ethanol, for instance, the color compounds will tend to precipitate while the sugars remain in solution. This has been a troublesome property of caramel colors which are widely used to tint alcoholic extracts, liquors, etc., and it has been an endeavor of manufacturers of caramel colors to produce types of high stability in alcohol. Very few commercial types will remain stable in ethyl or methyl alcohol above 65% by volume when the concentration of caramel color is raised above 5%.

2

Attempts have been made to utilize this feature of instability of caramel color bodies in alcohols as an analytical tool for the separation of the coloring compounds from the sugar residues. These attempts have been more or less successful on a very small scale for analytical purposes only but the technique has never been applied on a production or commercial scale because of certain inherent limitations. This is demonstrated by the fact that all caramel colors of commerce are mixtures of coloring compounds with sugars and are thus limited to relatively low tinctorial or coloring powers.

The outstanding limitations of alcoholic precipitation of caramel color compounds have been the difficulty of handling the gummy mass of carbohydrates resulting and the inefficiency of the separation. When a single alcohol is used the usual result is precipitation of the color in an unfavorable or sticky form which discourages further application except in the laboratory where repeated operations are feasible on the small scale and where economic considerations are not of primary importance. Single alcohols such as methanol and ethanol, will, however, precipitate the major portion of the color bodies.

In application Serial No. 753,054, filed June 6, 1947 a process of precipitating the caramel coloring compounds from caramelized sugars by the addition of a mixture of a water soluble alcohol and a solubility regulating liquid has been disclosed. Dialkyl ethers and dialkyl ketones are disclosed as solubility regulating liquids.

The objects of this invention are obtained by precipitating the caramel color compounds with mixtures of alcohols, in certain critical proportions, one of the alcohols being highly soluble in water, and the second alcohol being a solubility regulating alcohol. The water soluble alcohols comprise the monohydric alcohols of 1 to 2 carbon atoms and the solubility regulating alcohol should be at least slightly water soluble with a higher carbon content than the first alcohol. Monohydric alcohols with 2 to 5 carbon atoms comprise the group of solubility regulating alcohols. Obviously three or more alcohols can be employed if desired.

The precipitating mix of alcohols should also contain from 5–30% of water. At 68% of alcohols only partial separation of the coloring fraction is obtained. The color precipitated in the dilute range will be extremely high in tinctorial power indicating that only the higher molecular weight color bodies are insoluble in the concentration specified. On the other hand in high al-

cohol concentrations (90 to 95%) practically all of the polymerized sugar, including uncaramelized or partially caramelized sugar, will separate in the insoluble phase. This results in the dilution of the concentrate which is uneconomical because the uncaramelized and partially caramelized sugar should be retained in the soluble fractions which will be concentrated and recaramelized. Preferably the alcoholic mix is adjusted to contain about 15% water.

The ratio of the alcohol precipitating mix to the caramel color solution is between 1.5:1 and 3:1.

By the technique of this invention a practical and efficient separation and purification of the essential coloring compounds in caramel color is effected. The new product is of much higher tinctorial power than any caramel color hitherto known to commerce, being 3 to 5 times as powerful in terms of coloring ability. The product is of a bland flavor and essentially odorless. It is stable in all the tests to which caramel colors are ordinarily subjected, such as stability in acidified solutions, etc. The product is a mixture of substantially pure caramelan and caramelen.

Ordinarily a caramelized sugar comprises approximately 30% of water and has approximately 25% of its solids content in the form of coloring compounds. For sugars with a higher water content more of the precipitating alcohols must be added.

The process of this invention may be employed generally with any of the conventional caramelizations of sugar but with the difference the caramelization can be carried to a more advanced state in order to make more color. The resultant tendency toward instability is of less critical importance in the process of this invention as the color bodies are later removed from the system in which they occur by precipitation. Hence the sugar may be burned to a tinctorial power of 25–30 in contrast to the usual 18–25. The tinctorial power is determined according to the normal color standards of this art in which a solution of 0.1% is matched in a cell of 1" thickness against Lovibond (Series 52) caramel color slides. The tinctorial power of the dried color bodies isolated by the described novel process is of such intensity that the matching solution for Lovibond 52 series comparison is of 0.025% concentration. Hence to determine the degree of "color intensification" obtained by isolating and drying the color bodies in commercial caramel color, the Lovibond 52 series readings are multiplied by a factor

$$\frac{(0.1)}{(0.025)} \text{ or } 4$$

As an Example, a commercial liquid caramel color had a tinctoral power of 22 Lovibond 52 series color units when a 0.1% solution was matched in a 1" cell against the comparator's slides. The solvent isolated dried color bodies in 0.025% solution had a tinctorial power of 24, Lovibond 52 series color units when matched in a 1" cell. The degree of color intensification was therefore

$$\frac{0.1 \times 24}{0.025 \times 22}$$

or 4.36 fold increase.

The caramelized sugar solution from which the color bodies are to be precipitated should be cooled to a temperature of less than 80° F. and preferably to less than 50° F.

The pH of the caramelized sugar solutions should be on the acid side preferably of pH 2.5 to 3.5. This may require little or no adjustment of the pH of the caramelized solutions as usually the pH of the solution at the end of the burning step is on the acid side.

Preferably the caramel color solution from which the colors are to be precipitated is poured into the alcohol solution and the mixture is stirred constantly during the addition.

At least one of the alcohols added must be an alcohol having a miscibility with water such as methanol, ethanol or mixtures thereof. In addition, the precipitating mix should contain an alcohol which is at least slightly soluble in water. Aliphatic primary, secondary or tertiary alcohols containing 3–6 carbon atoms have been found satisfactory. Mixtures of these alcohols which are slightly soluble in water may also be employed and commercially available mixes, such as fusel oil, are also suitable. The ratio of the water miscible alcohol to the slightly water soluble alcohol should be between 5:1 and 3:1.

The product can be added to solutions or foodstuffs to be colored, as a solid or it can be dissolved in water just before addition to the foodstuff or liquid to be colored. It has been found that a very convenient way to add the solid color bodies to the material to be colored is to prepare a solution in water and propylene glycol.

The novel features characteristic of this invention are set forth with particularity in the appended claims. The invention, itself, however, both as to its organization and its method of operation, together with additional objects and advantages thereof, will best be understood from the following specific examples.

Example 1

A solution of thirty-two (32) gallons of an alcoholic mixture of 85% total alcohols, by volume, and 15% water is prepared in which the alcohols are: 3.6 parts methanol or ethanol and 1.0 parts isopropyl. The temperature is reduced below 80° F. and preferably to about 50° F. and agitation is started by means of a mechanical stirrer. Caramel color of approximately 25 tinctorial power and 36° Bé. is added in fine streams by means of a nozzle until a total of 168 pounds has been included.

On allowing to stand quiescent the mixture separates into two distinct layers, in which the line of demarcation is easily apparent. Substantially all of the coloring power of the caramel will be in the lower dark colored layer and the sugars will be dissolved in the lighter colored upper layer. These layers can be separated readily by decantation or in a suitable separator equipped with valves which enable the top layer to be run down to the line of demarcation.

The upper layer containing the mother-liquor of sugars, is stripped of its alcohols and the latter recovered by conventional solvent recovery methods. The sugars are returned (sometimes blended with fresh sugars) to the burning process and recaramelized. The lower layer containing the coloring compounds, may be redissolved in a little water, stripped of its alcohol, redissolved again and dried by any of the conventional methods using heated rolls, spray dryers, etc. We have found spray drying to be economical and efficient and controllable to the extent of making a satisfactory dry powder of suitable par-

ticle size and solubility. The powder may, of course, be reground mechanically to any degree of fineness.

Example 1a

With ethanol and isopropyl alcohol the dried isolated color bodies had a T. P. of 24.1, (1) in 0.025% concentration, the color intensification, therefore, was:

$$\frac{4(24.1)}{25}=3.86 \text{ fold}$$

The dry substance recovery was 25%. The color units extracted were approximately 75% of the quantity originally present.

Example 1b

With the methanol and isopropyl alcohol the dried isolated color bodies had T. P. of 23.9, a 3.82 fold intensification and a dry substance recovery of 24.6%. The total original color units extracted were 77%.

Example 2

The mechanical manipulation cited above in Example 1 remains the same but the precipitating is varied, as follows:

An alcoholic mixture of 32 gallons of 85% by volume of total alcohols and 15% water is made and contains the following alcohols:

3.6 parts of methanol or ethanol and 1.0 part of secondary or tertiary butanol.

Example 2a

With methanol and secondary butanol the dried isolated color bodies and a tinctorial power of 24.2. The color intensification was 3.87. The dry substance recovery was 25.3%. The percent extraction of original color bodies was 83%.

The following examples further illustrate the variety of solvent mixtures and demonstrate the color intensification obtained thereby.

Example 3

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol to isopropanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color of 22.6 tinctorial power. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 24. Color intensification was

$$\frac{(0.1)}{(0.025)}\frac{24}{22.6}$$

or 4.25 fold. Twenty-five and nine tenths (25.9) percent of the starting dry substance having 76.5% of the original color units were extracted.

Example 4

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to normal propanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 0.025% solution had a tinctorial power of 24.7. The color intensification was

$$\frac{4(24.7)}{22.6}$$

or 4.37 fold. The dry substance recovery was 25.9 percent. The percent of total original color units extracted was 78.7.

Example 5

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol to ethanol of 3.5 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color of 22.6 tinctorial power. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 25.9. The color intensification was

$$\frac{4\times 25.9}{22.6}$$

or 4.58 fold. The percent recovery of dry substance was 17.2. Fifty-five percent of the original color units were extracted.

Example 6

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to normal butanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.6. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 24.7 The color intensification was

$$\frac{4(24.7)}{22.6}$$

or 4.38 fold. The dry substance recovery was 28.7 percent. The percent of total original color units extracted was 87.4.

Example 7

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to tertiary butanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.6. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 23.7. The color intensification was

$$\frac{4(23.7)}{22.6}$$

or 4.19 fold. The dry substance recovery was 31.6 percent. The percent of total original color units extracted was 92.2.

Example 8

Thitry-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to normal amyl alcohol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.6 The dried isolated color bodies in 0.025% solution had a tinctorial power of 22.5 The color intensification was

$$\frac{4(22.5)}{22.6}$$

or 3.98 fold. The dry substance recovery was 28.7 percent. The percent of total original color units extracted was 79.6.

Example 9

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water,

made with a ratio of methanol or ethanol to isobutanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.6. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 23.3. The color intensification was

$$\frac{4(23.3)}{22.6}$$

or 4.12 fold. The dry substance recovery was 20.3%. The percent of total original color units extracted was 59.3.

Example 10

Thirty-two gallons of an alcohol mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to pentanol-3 of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.6. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 23.5. The color intensification was

$$\frac{4(23.5)}{22.6}$$

or 4.16 fold. The dry substance recovery was 26.1%. The percent of total original color units extracted was 76.9.

Example 11

Thirty-two gallons of an alcohol mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to isopropanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.6. All components of the system were cooled to 40° F. prior to the precipitation. The dried, isolated color bodies had in 0.025% solution a tinctorial power of 20.8. The color intensification was

$$\frac{4(20.8)}{22.6}$$

or 3.68 fold. The dry substance recovery was 37.4. The percent of total original color units extracted was 95.7.

Example 12

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to secondary butanol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.0. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 26. The color intensification was

$$\frac{4(26)}{22}$$

or 4.73 fold. The dry substance recovery was 20.3%. The percent of total original color units extracted was 66.2.

Example 13

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to tertiary amyl alcohol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.0. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 26.0. The color intensification was

$$\frac{4(26)}{22}$$

or 4.73. The dry substance recovery was 23.2%. The percent of total original color units extracted was 75.6.

Example 14

Thirty-two gallons of alcohol of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to primary active amyl alcohol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.0. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 25.4. The color intensification was

$$\frac{4(25.4)}{22}$$

or 4.62 fold. The dry substance recovery was 26.1%. The percent of total original color units extracted was 83.1.

Example 15

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to isoamyl alcohol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.0. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 25.7. The color intensification was

$$\frac{4(25.7)}{22}$$

or 4.67 fold. The dry substance recovery was 20.3%. The percent of original color units extracted was 65.4.

Example 16

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol or ethanol to secondary active amyl alcohol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.0. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 24.9. The color intensification was

$$\frac{4(24.9)}{22}$$

or 4.53 fold. The dry substance recovery was 26.1. The percent of original color units extracted was 81.5.

Example 17

Thirty-two gallons of an alcoholic mixture of 85% total alcohol by volume and 15% water, made with a ratio of methanol or ethanol to methyl amyl secondary alcohol of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having a tinctorial power of 22.0. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 19.1. The color intensification was

$$\frac{4(19.1)}{22}$$

or 3.47 fold. The dry substance recovery was 34.8%. The percent of total original color bodies extracted was 83.4.

Example 18

Thirty-two gallons of an alcoholic mixture of 85% total alcohols by volume and 15% water, made with a ratio of methanol to fusel oil of 3.6 to 1 were employed as in Example 1, to precipitate the color bodies in 146 pounds of 36° Bé. commercial caramel color having tinctorial power of 22.6. The dried, isolated color bodies in 0.025% solution had a tinctorial power of 24.7. The color intensification was

$$\frac{4(24.7)}{22.6}$$

or 4.37 fold. The dry substance recovery was 23.0 percent. The percent of total original color units extracted was 69.9.

We claim:

1. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising mixing the syrup with an alcohol mixture comprising 3–5 parts of an alcohol which is miscible with water and contains 1 to 2 carbon atoms to 1 part of a higher monohydric alcohol of 2–6 carbon atoms which is miscible with water, said alcohol mixture containing 5–32% by volume of water, permitting the mix to separate into two layers whereby the caramel color compounds are concentrated in the lower layer, separating the two layers of liquid, and separating the solid material from the lower layer.

2. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising mixing the syrup with an alcohol mixture comprising 3–5 parts of an alcohol which is miscible with water and contains 1 to 2 carbon atoms to 1 part of a higher monohydric alcohol of 2–6 carbon atoms which is miscible with water, said alcohol mixture containing 5–32% by volume of water, permitting the mix to separate into two layers whereby the caramel color compounds are concentrated in the lower layer, separating the two layers of liquid, and separating the solid material from the lower layer, stripping the solvent from the upper layer to recover a syrup suitable for subjecting to a further caramelizing treatment.

3. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising introducing the syrup into an alcohol mixture comprising 3–5 parts of an alcohol which is miscible with water and contains 1 to 2 carbon atoms to 1 part of a monohydric alcohol of 3–6 carbon atoms which is miscible with water, said alcohol mixture containing 5–32% by volume of water, thoroughly mixing the ingredients as the syrup is added to the alcohol mixture, permitting the mix to separate into two layers whereby the caramel color compounds are concentrated in the lower layer, separating the two layers of liquid, and separating the solid material from the lower layer.

4. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising mixing the syrup with an alcohol mixture comprising 3.6 parts of an alcohol which is miscible with water and contains 1 to 2 carbon atoms to 1 part of a monohydric alcohol of 3 carbon atoms which is miscible with water, said alcohol mixture containing 5–32% by volume of water, permitting the mix to separate into two layers whereby the caramel color compounds are concentrated in the lower layer, separating the two layers of liquid, and separating the solid material from the lower layer.

5. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising mixing the syrup with an alcohol mixture comprising 3–5 parts of an alcohol which is miscible with water and contains 1 to 2 carbon atoms to 1 part of isopropyl alcohol, said alcohol mixture containing 5–32% by volume of water, permitting the mix to separate into two layers whereby the caramel color compounds are concentrated in the lower layer, separating the two layers of liquid, and separating the solid material from the lower layer.

6. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising mixing the syrup with an alcohol mixture comprising 3–5 parts of an alcohol which is miscible with water and contains 1 to 2 carbon atoms to 1 part of a butyl alcohol, said alcohol mixture containing 5–32% by volume of water, permitting the mix to separate into two layers whereby the caramel color compounds are concentrated in the lower layer, separating the two layers of liquid, and separating the solid material from the lower layer.

7. The process of isolating the essential coloring compounds from caramelized syrups having a tinctorial power of 18–40 comprising mixing the syrup with an alcohol mixture containing 3–5 parts of an alcohol which is miscible with water and having 1 to 2 carbon atoms, to 1 part of a higher monohydric alcohol of 2–6 carbon atoms said alcohol mixture containing 5–32% by volume of water, permitting the mix to separate into two layers, separating the two layers of liquid, stripping both of solvent, returning the upper layer to further caramelizing process, and repeatedly precipitating the color bodies as above outlined as well as repeatedly returning the solvent stripped unprecipitated material to recaramelizing until the original raw material carbohydrate is substantially converted entirely to caramel color of high tinctorial power and no residual, unconverted sugar remains.

8. The process of converting sugars to caramel color of high tinctorial power and stability by means of successive caramelization steps after each of which the color bodies are separated from the residual sugars by precipitation in mixtures of at least two alcohols and water in certain critical proportions containing 3–5 parts of an alcohol which is miscible with water and having 1 to 2 carbon atoms to 1 part of a higher monohydric alcohol of 2–6 carbon atoms, said alcoholic mixture having 5–32% by volume of water; separating the layer of high sugar material from the layer of high color material, stripping solvents from the latter in a still and recovering the color therefrom; reburning the high sugar layer, after stripping of solvents, and subjecting it again to separation as above, the cyclic process continuing through at least four burning-precipitation-separation steps until all the original sugar is exhausted and substantially completely converted to color bodies of tinctorial power 20–25 units when a solution of 0.025% concentration is measured in a cell of ½'' depth

against Lovibond caramel color slides of series 52.

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