

While it is obviously impossible to reduce such values to a strict mathematical equation, this formula seems to afford a comparative estimate of the efficiency value of these three germicides.

SUMMARY.

In this study of the comparative germicidal values of phenol, mercuric chloride and potassium mercuric iodide, comprising determinations of the phenol coefficient, the toxicity coefficient, coagulation coefficient and the cost, it was found that potassium mercuric iodide, because of its remarkably high germicidal coefficient, its relatively low toxicity as compared to mercuric chloride, and its freedom from any coagulating or precipitating action on proteins, is far more efficient as a germicide than either phenol or mercuric chloride, and, notwithstanding its greater cost, its efficiency value is fifteen times that of mercuric chloride and is approximately one hundred and fifty times that of phenol.

REFERENCES.

1. John F. Anderson and Thomas B. McClintic: "A Method for the Bacteriological Standardization of Disinfectants," *Jour. Inf. Dis.*, Jan. 3, 1911, VIII, p. 1.
2. Worth Hale: "A Method for Determining the Toxicity of Coal-Tar Disinfectants," *Bulletin 88, U. S. Hyg. Laby.*, April 1913.
3. Douglas Macfarlan: "The Germicidal Value of Potassium Mercuric Iodide," *Am. Jour. Med. Sci.*, April 1920, CLIX, 4, p. 586.
4. Cassius H. Watson: "An Improved Substitute for Iodized Catgut Sutures," *Surg., Gyn., and Obstet.*, Jan. 1916, p. 114.
5. W. F. McKenna and H. A. Fisher: "The Use of Potassium Mercuric Iodide for Skin Disinfection," *Surg., Gyn., and Obstet.*, April 1920, p. 370.
6. Albert Schneider: "Bacteriological Methods in Food and Drug Laboratories," 1915, Blakiston, Phila., p. 252.

THE PREPARATION OF ACID-FAST CAMELS.*

BY GEORGE D. BEAL AND DONALD F. BOWEY.

This paper deals with the preparation of a caramel which will fully comply with the specifications used by up-to-date bottlers and others using the color and which will be sufficiently economical in preparation to compete with those already on the market. In 1913 it was pointed out by Brant that a desirable compound to be used in the coloring of beers should not suffer any change in tint when treated with a 0.5% solution of tartaric acid. Some varieties of caramel will retain their color indefinitely when used in the coloring of mildly acid beverages; others while withstanding the action of the acid will become discolored if the beverage is carbonated. Recently the demand for caramel to be used in the coloring of soft drinks has grown enormously.

An eastern manufacturer has succeeded by a secret process in preparing caramel which has been advertised as being acid-fast, and has been so successful in capitalizing this property that the majority of caramel users in the country demand an acid-fast caramel.

The specifications commonly adopted are as follows: Sixty grains of the concentrated caramel are dissolved in eight ounces of hot water. If one-half of this

* Contribution from the Chemical Laboratory of the University of Illinois. Read at the meeting of the American Pharmaceutical Association in Cleveland, Ohio.

solution on boiling with one drachm of commercial hydrochloric acid will remain clear for thirty minutes with no visible loss in tinctorial strength the caramel may be considered to be acid-fast. Ordinary sugar colors will make a very satisfactory coloring agent for soft drinks, bakers' supplies and candies, but the acid-fast color has become the standard of the industry.

The majority of commercial caramels are prepared from glucose, primarily because of the cheapness of the starting substance, although sucrose caramels apparently have a greater intensity. The method of manufacture usually consists in heating the glucose in a large iron kettle over a coal fire. Under these conditions the control of temperature, etc., becomes rather difficult. In our experiments all of the heats were made in a one-liter pyrex flask, heated in an oil-bath. Commercial glucose containing 85% of the sugar was used.

The general procedure followed was as follows: One hundred grams of glucose were melted in twenty-five cc of water. The empty pyrex flask was lowered into the oil-bath and the bath brought to the desired temperature. While maintaining this temperature, the melted glucose was poured into the flask, noting the time when added. At the end of the predetermined period of heating the flask was removed from the bath and five hundred cc of water added to the flask and allowed to stand for one hour to dissolve the color. The solution was filtered through asbestos in a Gooch crucible in order to determine the amount of insoluble char. The char adhering to the flask could be removed with ten per cent. sodium carbonate solution.

The caramels which were prepared by the above method were tested for acid-fastness, tinctorial strength and presence of char. The acid test was as modified by ourselves. Twenty-five cc of the filtered caramel solution were diluted with fifty cc of water and five cc of 6-normal hydrochloric acid. This solution was boiled in a small beaker. Ordinary caramels broke down in ten to fifteen minutes' time, but the acid-fast caramels remained clear even on prolonged boiling.

The caramel was tested for tinctorial strength by diluting five cc of the filtered caramel to one-hundred cc which solution was then compared in a colorimeter with one which had been arbitrarily prepared. The values obtained were for purposes of comparison only, and were not regarded as an actual measure of the absolute color value of the solution.

The first series of heats was made to determine the effect of time and temperature upon the three factors by which the product was judged. No catalytic agents were used.

It was apparent from the above that an acid-fast caramel could not be prepared by dry distillation of the sugar alone. The resulting caramel broke down on boiling with the acid and had a tinctorial value far below that which should have been obtained with the period of heating. The caramels which were formed with the highest percentages of char had the highest tinctorial values and were most resistant to acid.

Some authors have stated that the color strength would be improved if the sugar were caramelized in the presence of a little alkali. Four heats were run with the addition of ten cc of ten per cent. sodium carbonate solution at the beginning of the heating, other conditions being unchanged.

TABLE I.
EFFECT OF TIME AND TEMPERATURE UPON CARAMELIZATION.

Time, min.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
25	210°	2.68	22	8
30	210°	3.01	26	10
35	210°	3.24	35	10
40	210°	3.39	34	10
45	210°	3.53	33	10
50	210°	3.81	39	10
55	210°	4.00	26	17
60	210°	6.45	33	15
65	210°	5.18	36	15
70	210°	7.84	40	18
25	220°	3.00	25	12
30	220°	6.67	36	15
35	220°	5.59	28	15
40	220°	3.07	28	13
45	220°	4.78	31	16
50	220°	7.43	35	16
55	220°	6.61	33	15
60	220°	4.60	35	15
65	220°	7.18	38	16
70	220°	8.20	42	17
25	230°	3.15	26	13
30	230°	3.36	33	13
35	230°	5.19	36	15
40	230°	4.95	31	15
45	230°	6.31	36	15
50	230°	7.55	38	16
55	230°	7.85	41	18
60	230°	6.19	38	17
65	230°	5.50	36	15
70	230°	8.55	43	18

TABLE II.
CARAMELIZATION IN PRESENCE OF 10 Cc of 10% SODIUM CARBONATE.

Time, min.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
30	210°	3.58	31	10
40	210°	4.63	35	12
50	210°	6.95	45	15
60	210°	8.30	48	15

Only the tinctorial strength of the caramel was improved in this way, there being little or no effect upon the acid-fastness.

TABLE III.
CARAMELIZATION IN PRESENCE OF DILUTE HYDROCHLORIC ACID.

Time, min.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
30	210°	2.68	28	12
40	210°	2.98	29	12
50	210°	5.46	35	12
60	210°	5.65	43	15

A claim has been made that an excellent caramel could be prepared if a small amount of acid was added at the beginning of the operation. In the next four

heats five cc of hydrochloric acid solution, one part of 6-normal acid to sixteen parts of water, were added at the beginning of the heating.

The use of hydrochloric acid reduced the percentage of char but had no effect upon the tinctorial strength or acid-fastness. Similar experiments with sulphuric, nitric and phosphoric acids showed no improvement in the quality of caramel formed.

In cooking the test batches the caramel when just at the cracking stage rose rapidly to the neck of the flask. No stirring device to keep down the frothing was satisfactory. With the idea of securing a stirring effect which would progress with the degree of heating the addition of volatile salts was tried. Herzfeld (*Deut. Zuckerind.*, 35, 617) has prepared caramel by heating an 80% invert sugar syrup in an oil-bath at 170–180°. He finds that the time required is materially reduced by the addition of ammonia from time to time, although he is uncertain as to the action of the ammonia. A series of heats was made with the addition of five cc of a ten per cent. solution of ammonium chloride to the glucose.

TABLE IV.

CARAMELIZATION WITH AMMONIUM CHLORIDE SOLUTION.

Time, min.	Temperature, Centigrade.	% of char.	Tinctorial No	Acid test, min.
15	200°	8.63	121	30
16	200°	8.95	126	30
17	200°	9.54	127	30
18	200°	11.65	135	30
19	200°	12.48	132	30
20	200°	15.63	133	30

Only one-third of the time previously taken was required for the caramelization, the sugar did not froth, the caramel had a very much higher tinctorial value and was acid-fast. Apparently the best caramel was obtained in eighteen minutes' heating. Working at 200° and holding the heat for eighteen minutes, the quantity of ammonium chloride was varied in the next series of heats.

TABLE V.

EFFECT OF VARIATIONS IN THE AMOUNT OF AMMONIUM CHLORIDE ON CARAMELIZATION, TIME AND TEMPERATURE CONSTANT.

10% NH ₄ Cl. Cc.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
10	200°	25.63	142	30
9	200°	24.03	140	30
8	200°	19.25	141	30
7	200°	16.48	138	30
6	200°	13.78	135	30
5	200°	12.89	138	30
4	200°	9.05	121	25
3	200°	3.35	96	15

The best results were obtained with five cc of ammonium chloride solution. By using this quantity of ammonium chloride in combination with dilute solutions of hydrochloric and phosphoric acids the only effect obtained was a slight but not significant increase in the tinctorial strength of the caramel.

The chief objection to the use of the ammonium chloride being the cost of the salt, similar experiments were attempted with the substitution of a ten per cent. solution of commercial ammonium sulphate.

TABLE VI.

CARAMELIZATION WITH FIVE CC OF TEN PER CENT. AMMONIUM SULPHATE SOLUTION.

Time, min.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
15	200°	6.23	125	25
16	200°	7.86	128	25
17	200°	6.43	131	30
18	200°	6.64	142	30
19	200°	10.83	144	30
20	200°	15.65	149	30

Again the best results seemed to be obtained with eighteen minutes' heating. Accordingly the quantity of ammonium sulphate solution was varied in the next series of heats, keeping the temperature and time at 200° and eighteen minutes, respectively.

TABLE VII.

EFFECT OF VARIATIONS IN THE AMOUNT OF AMMONIUM SULPHATE SOLUTION; TEMPERATURE AND TIME CONSTANT.

10% (NH ₄) ₂ SO ₄ , cc.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
10	200°	21.61	153	30
9	200°	23.45	151	30
8	200°	19.82	146	30
7	200°	21.07	143	30
6	200°	15.92	139	30
5	200°	12.48	140	30
4	200°	8.52	136	30
3	200°	4.81	116	20

The caramel obtained by the use of ten cc of ammonium sulphate solution had the highest tinctorial value, but the per cent. of char was high. The experiment was repeated, adding three cc of the hydrochloric acid solution previously mentioned with the ammonium salt.

TABLE VIII.

EFFECT OF VARIATIONS IN THE AMOUNT OF AMMONIUM SULPHATE WITH THREE CC OF HYDROCHLORIC ACID ON CARAMELIZATION, TIME AND TEMPERATURE CONSTANT.

10% (NH ₄) ₂ SO ₄ , cc.	Temperature, Centigrade.	% of char.	Tinctorial No.	Acid test, min.
10	200°	16.05	162	30
9	200°	17.95	161	30
8	200°	15.31	158	30
7	200°	10.65	145	30
6	200°	12.77	151	30
5	200°	10.00	149	30
4	200°	8.78	145	30
3	200°	6.23	130	25

The presence of the acid reduces the quantity of salt required to about one-half the previous amount. The quality of the product remains unchanged. An attempt was made to substitute sulphuric and phosphoric acids for the hydrochloric acid, but a very poor product was obtained.

The following method is suggested for the preparation of an acid-fast caramel of high tinctorial strength. Place in a beaker or casserole one hundred grams of crystallized glucose and twenty-five cc of water. Heat the mixture upon a water-

or steam-bath until the sugar is liquefied. Add to this heavy syrup five cc of ten per cent. ammonium sulphate solution and three cc of a dilute hydrochloric acid made by mixing one volume of 6-normal acid with sixteen volumes of water. Place a one-liter pyrex or Jena flask in an oil-bath and heat to 200°. While retaining this temperature add the glucose syrup and heat for eighteen minutes. Remove the flasks from the bath and add, as soon as sufficiently cool, sufficient water to dissolve the caramel. Allow to stand until solution is complete and remove the char by filtration.

SUMMARY.

1. A satisfactory caramel can be prepared by heating commercial crystallized glucose in the presence of small amounts of ammonium sulphate and hydrochloric acid.

2. The ammonium sulphate and acid do not seem to enter into the composition of the caramel, but apparently act by facilitating the dehydration of the sugar molecule.

3. Dialysis of the caramel so prepared through a collodion membrane against water shows the absence of unchanged sugar.

4. The authors would suggest that the acid-fastness of a caramel depends upon the complete conversion of the sugar, the decolorization on heating with acid being initiated by the action of the acid upon the unchanged sugar.

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PHYTOCHEMICAL NOTES.*

No. 92. Constants of Cassia Leaf and Twig Oils.¹

BY I. NISHMURA.

The oils, the distillation of which is reported in the previous note,² were not examined at once owing to unavoidable delay. Their constants were determined a year later and are herewith reported. As an indication of the changes that took place during this interval, the densities of the leaf oils as originally determined and as redetermined a year later are here recorded side by side.

	Fall 1920 d_{20}°	Fall 1921 d_{20}°
1 Oil bale No. 1, original and cohobated.....	1.049
2 Original oil bale No. 5.....	1.0525	1.045
3 Original oil bale No. 2.....	1.0523	1.059
4 Cohobated oil (first) bale No. 1.....	1.0547
	1.0530
5 Cohobated oil (first) bale No. 5.....	1.0540	1.035
6 Cohobated oil (first) bale No. 2.....	1.0535	1.037
7 Cohobated oil (second) bales Nos. 1, 5 and 2.....	1.032

The differences are not great, but, what seems surprising, is that the densities taken about a year after distillation, are, for the most part, slightly lower than those first taken. Inasmuch as this is almost uniformly the case, this difference cannot

* From the laboratory of Edward Kremers.

¹ Scientific Section, A. Ph. A., Cleveland meeting, 1922.

² April JOURNAL A. PH. A., p. 294.