EFFECT OF SOME ALKALI SALTS UPON FIRE-HOLDING CAPACITY OF TOBACCO

CONTRIBUTIONS FROM THE HULL BOTANICAL LABORATORY 233

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Introduction

Of all the qualities which are essential in a good cigar tobacco no single one is quite so important as the burn. The general composition of the leaf and the salts which it contains exert a great influence upon the course of the combustion. It is a well established fact that chlorides tend to prevent complete combustion and thereby products are formed which are injurious to the flavor and aroma. On the other hand, the carbonates of the alkalies, particularly of potassium, aid the combustion and increase the fire-holding capacity.

The term "burning qualities" with reference to a cigar is general and includes many points. The most important of these points are evenness of burn, color of ash, firmness and coherence of the ash, and the fire-holding capacity. The fire-holding capacity refers to the length of time the leaf or cigar will continue to glow after ignition. A cigar tobacco must have primarily a good fire-holding capacity, and for this reason this has been the main criterion in judging the burn of cigar tobacco.

Historical

It was maintained early that the fire-holding capacity depended upon the content of nitrates. SCHLOSING (15) and later others have disproved this theory. SCHLOSING (15), NESSLER (12, 13), KISSLING (8), and VAN BEMMELN (17) have shown that in a good burning sample of tobacco potassium is present in excess of the amount equivalent to combine with the sulphuric and hydrochloric acids, while in a poor burning sample it is equal to this amount or less. This indicates that potassium salts of organic acids favor a good burn. GARNER (4) concludes that the fire-holding capacity is dependent primarily upon the content of potassium combined with organic acids.

NESSLER (12) concluded that potassium sulphate exerts a favorable influence upon the burn; while JENKINS (6) found that fertilizing with potassium sulphate increased the content of sulphuric acid in the tobacco so that in some cases it injured the burn. GARNER (4) concluded that sulphates in general are injurious to the burning qualities, but not to so great an extent when all of the sulphuric acid is combined with the potash; while PATTERSON (14) found no apparent relation of the content of sulphuric acid to the burn.

NESSLER (12, 13), KISSLING (7), BEHRENS (2), VAN BEMMELN (17), BARTH (1), PATTERSON (14), CARPENTER (3), and GARNER (4) agree that chlorides are injurious to the burn. KISSLING (8) considered the content of ash to have little influence upon the burning qualities; while PATTERSON (14) and CARPENTER (3) concluded that a high content of ash was conducive to a good burn. NESSLER (12) found that calcium and magnesium have little effect except to whiten the ash. KISSLING (7) found good burning samples of tobacco high in content of calcium and fairly high in magnesium. GARNER (4) concluded that calcium in general does not greatly affect the fire-holding capacity, but is essential in the production of a good ash, and that large amounts of magnesium injure the burn. BARTH (1) treated several kinds of paper with numerous salts and found that tri-potassium phosphate is injurious to the burn. GARNER (4) found di-potassium phosphate neutral in its effects upon the burn.

A consideration of the reason for the favorable action of the potassium salts of organic acids has led to several theories. SCHLOSING (15) attributes their favorable action to the fact that when heated they swell and yield a porous mass. NESSLER (12) says that the potassium salts are reduced and that potassium acts as an oxygen carrier; while GARNER (4) attributes their action to the fact that the salts are readily decomposed to yield carbonates. GARNER suggests that the carbonates may act favorably by alternately giving off and taking up carbon dioxide, or that small amounts of free potassium may be formed which may act as an oxygen carrier. MAYER (10) also attributes the beneficial effects of the alkali salts to the fact that they are easily reduced. BARTH (1) suggests that the salts may have a beneficial action by raising the temperature of the leaf; he also attributes the harmful effect of the chlorides to the fact that they fuse and coat over the material, thereby preventing complete combustion.

Object

The object of this work is to study the effects of various salts closely related to the salts of potassium with a view to obtaining some light upon the conflicting theories. It has been suggested that the effect of the various salts upon the colloidal state of the material of the leaf may bear some relation to the problem. It was thought that probably potassium possesses some peculiar chemical properties which may account for its action.

Effect of salts upon combustion of tobacco

METHOD

The method of experimentation consisted of treating leaves and filter paper with various salts and noting their effect upon the fire-holding capacity. The samples of tobacco used in this work were of a single strain of a cigar filler type of tobacco grown in Pennsylvania under definite fertilizer treatments. The leaves previously had been well sweated. In all cases the solutions of the salts applied were 28.9 per cent normal. In order to see whether the effect of the salts was upon the colloidal state of the materials of the leaf, some of the leaves were rendered acid by treatment with 0.5 normal acetic acid, and others were rendered alkaline by a treatment with 0.2 normal solution of sodium hydroxide. The salts were applied by means of an atomizer, and then the leaves were placed under a bell jar to allow the salts to diffuse throughout the leaf. Knowing that different portions of the same leaf have different fire-holding capacities, in each test a portion of the tip, middle, and base of the leaf were used, and similar portions were saved for a check upon each leaf. The strip of leaf was ignited by means of a fishtail burner and the time of holding fire was determined by means of a stop watch. As would be expected, due to variations in different leaves, the results were not always consistent in some cases where the comparative differences were small, but in each case a number of tests were carried out upon a number of different leaves until the average results were considered reliable for the purpose of comparing the effects of the various salts.

DATA

Because of the similarity in chemical behavior of the alkalies caesium, rubidium, potassium, sodium, and lithium, it was thought that a comparison of the effects of their salts upon the fire-

TABLE I

LEAVES FROM PLATS FERTILIZED WITH MANURE ONLY

Salt treatment	Other treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
Rb_2CO_3	0.2/N NaOH	50	71	60
K_2CO_3	"	60	40	24
Na_2CO_3	"	60	18	5
Li_2CO_3	"	50	19	4
Rb_2CO_3	0.5/N acetic acid	10	59	45
K_2CO_3	"	60	44	35
Na_2CO_3	"	60	18	10
Li_2CO_3	"	50	19	13
Rb_2CO_3	Nothing	90	101	88
K_2CO_3	"	90	68	43
Na_2CO_3	"	60	34	11
Li_2CO_3	"	20	20	12

holding capacity of tobacco might throw some light upon the problem under consideration. The data obtained are indicated in the accompanying tables. The rubidium carbonate and caesium carbonate used were tested spectroscopically.

Tables I and II show that caesium, rubidium, and potassium carbonates greatly promote the fire-holding capacity of tobacco. Rubidium carbonate is always more effective than potassium, and in the case where the three salts were compared upon the same kind of leaves caesium carbonate was more effective than rubidium. The relative behavior of sodium and lithium suggests the possibility that their effect upon the precipitation of colloids may enter in as a minor factor. According to HÖBER (5), the relative effectiveness of the alkalies in precipitating colloids in an acid medium is as follows: lithium > sodium > potassium > rubidium > caesium. In an alkaline medium the order is as follows: caesium > rubidium > potassium > sodium > lithium. In the cases where lithium is more

TABLE II

LEAVES FROM PLATS FERTILIZED WITH POTASSIUM CHLORIDE

Salt treatment	Other treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
K_2CO_3	0.2/N NaOH	60	54	49
Na_2CO_3	"	60	21	14
Li_2CO_3	"	60	16	10
K_2CO_3	0.5/N acetic acid	20	27	24
Na_2CO_3	"	20	8	5
Li_2CO_3	"	20	9	6
Cs_2CO_3	Nothing	20	61	57
K_2CO_3	"	30	40	36
Rb_2CO_3	"	20	48	44

TABLE III

LEAVES FROM PLATS FERTILIZED WITH MANURE ALONE

Salt treatment	Other treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
Potassium oxalate	0.2/N NaOH	70	42	19
Sodium oxalate	"	70	19	−3
Lithium oxalate	"	70	14	−6
Potassium oxalate	0.5/N acetic acid	100	33	21
Sodium oxalate	"	100	11	0
Lithium oxalate	"	100	14	2
Potassium oxalate	Nothing	50	37	21
Sodium oxalate	"	50	16	1
Lithium oxalate	"	50	13	−2

effective than sodium in the precipitation of colloids, it is also more effective in promoting the fire-holding capacity, and vice versa. Potassium, rubidium, and caesium, however, do not show this relation. This casts some doubt upon this principle of the behavior of sodium and lithium. At any rate, this effect upon the colloidal state of the materials of the leaf could be of only minor importance. It seems very evident that of all the alkali carbonates only those of caesium, rubidium, and potassium materially aid the fire-holding capacity.

Table III shows that of the oxalates of potassium, lithium, and sodium, only the oxalate of potassium is effective in increasing

TABLE IV

LEAVES FROM PLATS FERTILIZED WITH MANURE ALONE

Salt treatment	Other treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
Potassium citrate....	0.2/N NaOH	30	29	13
Sodium citrate......	"	20	15	4
Lithium citrate......	"	20	16	6
Potassium citrate....	0.5/N acetic acid	20	39	19
Sodium citrate......	"	20	18	1
Lithium citrate......	"	20	19	1
Potassium citrate....	Nothing	20	24	18
Sodium citrate......	"	20	10	4
Lithium citrate......	"	20	11	5

TABLE V

LEAVES FROM PLATS FERTILIZED WITH POTASSIUM CHLORIDE

Salt treatment	Other treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
Potassium citrate....	0.2/N NaOH	50	28	18
Sodium citrate......	"	50	11	2
Lithium citrate......	"	50	10	0
Potassium citrate....	0.5/N acetic acid	20	37	30
Sodium citrate......	"	20	10	3
Lithium citrate......	"	20	5	−2

the fire-holding capacity. Here again in the cases where lithium is more effective than sodium in the precipitation of colloids, it is slightly more effective in promoting the fire-holding capacity.

From tables IV and V we see that potassium citrate is the only one of the 3 citrates which materially aids the burn. No correlation can be seen here between the effects of the salts upon the precipitation of colloids and their effect in increasing the fire-holding capacity.

Table VI shows a comparison of the results of a number of potassium salts. All of the potassium salts are very effective in promoting the fire-holding capacity, with the exception of the chloride, acid sulphate, and mono-potassium phosphate, which

TABLE VI

LEAVES FROM PLATS FERTILIZED WITH MANURE ALONE

Salt treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
K_2CO_3	90	68	43
KCl	50	9	−7
$KHSO_4$	40	7	−14
K_3PO_4	40	37	14
KH_2PO_4	40	16	−13
K_2HPO_4	40	42	13
K_2SO_4	30	53	29
Potassium oxalate	50	37	21
Potassium citrate	20	24	18
Potassium tartrate	50	64	48
Potassium acetate	50	45	29

TABLE VII

LEAVES FROM PLATS FERTILIZED WITH MANURE ALONE; LEAVES TREATED WITH 0.2/N NaOH, AND THEN WITH SALTS

Salt treatment	Number of tests	Average number of seconds holds fire	Average number of seconds increases fire-holding capacity
Na_2CO_3	60	18	5
$NaCl$	50	5	−1
$NaNO_3$	30	11	2
Na_2SO_4	20	6	1
Na_3PO_4	40	25	3
Na_2HPO_4	40	27	3
Sodium oxalate	70	19	−3
Sodium citrate	20	15	4
Sodium acetate	30	16	−5
Sodium tartrate	40	18	−5

are very injurious. Potassium carbonate and those salts which yield potassium carbonate when burned, tri-potassium phosphate, di-potassium phosphate, and potassium sulphate, improve the fire-holding capacity.

Table VII shows that sodium carbonate is the most effective of all of the sodium salts in promoting the burn. The other salts are either nearly neutral or exert a harmful effect. It is quite evident that none of the sodium salts exert the marked beneficial effects which some of the potassium salts exert.

Effect of salts upon combustion of lump sugar

The effect of various salts of the alkalies upon the combustion of different kinds of paper and lump sugar was also studied; although, as one would expect, due to the dissimilarity of materials, the results in these cases were not always parallel with those upon tobacco. The results with lump sugar are particularly interesting. In each case a small portion of the salt was placed upon the lump of sugar and then an attempt was made to burn the sugar by touching it to a gas flame. The results obtained are indicated in table VIII.

Discussion

SCHLOSING (15) attributed the favorable action of the organic salts of potassium to the fact that they swell up and yield a porous mass. NESSLER (12) combated this idea and showed that other salts of potassium which do not swell so much when heated also have a favorable action in promoting the fire-holding capacity of tobacco. GARNER showed that the carbonates of potassium are just as effective as the organic salts. From tables VI and VII we see that both potassium sulphate and tri-potassium phosphate, as well as potassium carbonate, promote the fire-holding capacity. These results confirm the conclusions of NESSLER and GARNER, and indicate that the good effects of the potassium salts of organic acids cannot be attributed to the fact that they swell and yield a porous mass when heated.

NESSLER (12) suggests that potassium salts are reduced and that small amounts of elemental potassium may act as an oxygen carrier. It is true that the salts of potassium which have a favorable action upon the fire-holding capacity are all salts of acids which are in a highly oxidized condition. Although no direct data could be found which would show the relative ease of reduction of the alkali carbonates, there are data upon the electrolytic solution tension of the alkalies. The order of the alkalies according to their decreasing electrolytic solution tension is as follows: caesium, rubidium, potassium, sodium, and lithium. The same order represents their increasing ease of reduction in solution. If we assume that this represents the order of the ease of reduction of the

TABLE VIII

EFFECT OF SALTS UPON THE COMBUSTION OF LUMP SUGAR

Salt	Effect
K_2C_3O	Lump of sugar burned with flame; sugar coaled
Rb_2CO_3	“ “ “ “ “ “ “ “
Cs_2CO_3	“ “ “ “ “ “ “ “
Na_2CO_3	“ “ “ “ “ “ “ “
Li_2CO_3	“ “ “ “ “ “ “ “
K_2SO_4	Lump of sugar burned slightly; sugar coaled slightly
K_2HPO_4	Lump of sugar burned; sugar coaled
KH_2PO_4	Lump of sugar burned slightly; sugar coaled slightly
K_3PO_4	Lump of sugar burned with flame; sugar coaled
KCl	“ “ “ “ “ “ “ “
KNO_3	Lump of sugar burned with flame, sputtered; sugar coaled
Potassium acetate	Lump of sugar burned with flame; sugar coaled
Potassium citrate	“ “ “ “ “ “ “ “
Potassium oxalate	“ “ “ “ “ “ “ “
Potassium tartrate	“ “ “ “ “ “ “ “
$LiCl$	“ “ “ “ “ “ “ “
Lithium oxalate	“ “ “ “ “ “ “ “
Lithium citrate	“ “ “ “ “ “ “ “
$NaCl$	Lump of sugar burned slightly; sugar coaled
Sodium tartrate	Lump of sugar burned with flame; sugar coaled
Sodium oxalate	“ “ “ “ “ “ “ “
Without salt	Lump of sugar melted, would not burn; did not coal
$LiSO_4$	Sugar melted; did not burn with flame; did not coal
Na_2SO_4	Lump of sugar burned slightly; sugar coaled slightly
$CaCO_3$	Sugar melted; did not burn with flame; did not coal
Pb_3O_4	Lump of sugar burned with flame; sugar coaled
$BaCO_3$	“ “ “ “ “ “ “ “
$KMnO_4$	“ “ “ “ “ “ “ “
Fine metallic iron	Lump of sugar burned with difficulty
Platinized asbestos	“ “ “ “ “ “
Zinc filings	“ “ “ “ “ “
Copper filings	“ “ “ “ “ “
Finely powdered glass tubing	Lump of sugar burned with flame; sugar coaled
Finely powdered charcoal	Lump of sugar burned with flame
Carbonized sugar	“ “ “ “ “ “

alkali carbonates, it would be difficult to explain by NESSLER'S theory why lithium and sodium carbonates are not effective, and caesium, rubidium, and potassium carbonates are effective.

GARNER (4) suggests that the carbonate might act favorably by alternately giving up and taking on carbon dioxide. We have seen that caesium, rubidium, and potassium carbonates are very much more effective than the carbonates of sodium and lithium. At 700° C. the order of the alkali carbonates according to their increasing ease of dissociation is as follows: potassium, rubidium, sodium, caesium, and lithium. Lithium carbonate is dissociated into carbon dioxide and lithium oxide to a much greater degree at 700° C. than any of the other carbonates (9). If potassium carbonate acts favorably by alternately giving off and taking up carbon dioxide, it is difficult to see why lithium carbonate should not be even more effective. It seems, therefore, that this theory will not explain the beneficial action of the caesium, potassium, and rubidium carbonates.

From table VIII we see that all of the salts which were effective in increasing the fire-holding capacity of tobacco will cause the lump of sugar to burn with a flame when ignited by means of a gas burner. Some of the salts which were only slightly effective in increasing the fire-holding capacity of tobacco, such as lithium carbonate and sodium carbonate, are effective also in promoting the combustion of sugar with the production of a flame. Here again caesium, potassium, and rubidium carbonates are particularly active. BARTH (1) has suggested that the salts present in the leaf may aid in the combustion by raising the temperature of the leaf, the effect being somewhat analogous to the effect of salts upon raising the boiling point of water. As shown in table VIII, such substances as metallic filings, powdered glass, and carbonized sugar when used in larger quantities also are effective in causing the lump of sugar to burn. From these results obtained upon lump sugar, it would seem as though their effect in raising the temperature might be of significance. But with this theory alone it would be difficult to account for the differences in degree of action of the various salts. Also it would be difficult to explain why some of the salts have no effect, while others have a very marked effect in promoting the combustion of tobacco. SLIGH and KRAYBILL (16) have determined the temperatures of burning cigars and have found some evidence which suggests that the moisture content as well as the composition of the cigar has an effect upon the burning temperature. It is planned to study this problem further with the object of determining the extent to which this hypothesis may be applied.

BARTH (1) considers the harmful effect of chlorides to be due to the fact that they fuse and coat over the material, thereby preventing complete combustion. SLIGH and KRAYBILL (16) found the temperature in the cigar varying from 813° C. to 925° C. during a puff, and from 584° C. to 803° C. at stationary temperatures between the puffs. It is doubtful whether the temperature of the burning strip of a leaf of tobacco would be as high as these stationary temperatures of the cigar. The temperature of the leaf then would not be high enough to fuse pure sodium chloride or pure potassium chloride. It would seem then as though the theory of BARTH would not account for the harmful effect of the chlorides. An objection might be raised from the standpoint that we have in the leaf mixtures of salts, and that their fusing points would be lower than that of the pure salts. The fusing point of sodium chloride is about 820° C., and that of rubidium carbonate is 837° C. (9). It would be difficult to understand why one salt should harm the burn by fusing and the other should not harm the burn when they fuse at almost the same temperature.

An attempt was made to tabulate and compare the chemical and physical properties of these salts with the hope of finding some explanation of their action. Among the properties compared were the melting points, specific heats, speed of vaporization, and dissociation pressure of the carbonates. A very careful comparison of the chemical and physical properties of the salts does not seem to offer any explanation of their action. It is true that the order of effectiveness of the caesium, rubidium, and potassium carbonates is the same as their increasing electrolytic solution tension, and also the same as their increasing atomic weights. The question might be raised as to whether their behavior might not be due in part to the alkalinity of the salts in solution. Such an explanation, however, would not account for the behavior of the sodium and lithium carbonates.

Extremely small amounts of caesium, potassium, or rubidium carbonates greatly increase the fire-holding capacity of the tobacco. A 2 per cent solution of potassium carbonate applied by means of an atomizer to the leaf was sufficient to produce the effect. Upon examining the ash left after the combustion, the potassium was found as the carbonate, that is, in the same form in which it was present before the combustion. It is possible, therefore, that certain salts, such as the carbonate, phosphate, and sulphate of potassium, and the carbonates of rubidium and caesium, act in a catalytic manner to promote the combustion of the tobacco leaf. In the combustion of lump sugar other salts are also effective, but the carbonates of caesium, potassium, and rubidium are more effective. Here the effect of the salts in raising the temperature may be important.

According to this assumption, caesium carbonate, potassium carbonate, rubidium carbonate, tri-potassium phosphate, di-potassium phosphate, and potassium sulphate have a catalytic action favoring the combustion of the tobacco leaf. The salts of sodium and lithium, potassium chloride, mono-potassium phosphate, and acid potassium sulphate do not have this catalytic action. The harmful effects of the chlorides seem to be due to a negative catalytic action.

It is possible that a careful study of the chemical action resulting when various organic materials, such as filter paper, and sugar treated with the salts, are subjected to temperatures close to the temperature of the burning cigar may help to explain the action. NEF (11) has studied the effect of alkalies upon the oxidation of sugars in solution at low temperatures. It may be that a study of the rate of oxidation of various organic salts of the alkalies when subjected to high temperature may furnish a better explanation of the effect of the potassium salts. Studies along these lines are planned. It may be that more than one factor plays a rôle in determining the action of the various salts, resulting in a complex situation.

Summary

1. The alkali carbonates of caesium, rubidium, and potassium have a definite marked effect in promoting the fire-holding capacity of tobacco, which sodium and lithium carbonates do not exhibit, the order of effectiveness being as follows: caesium, rubidium, potassium.

2. Of the oxalates tried, only potassium is effective. In the case of the carbonates and the oxalates in an alkaline medium, where lithium is more effective than sodium in the precipitation of colloids, it is slightly more effective also in promoting the fire-holding capacity. In the case of the citrates there is no such relation and, in the case of the carbonates, potassium, rubidium, and caesium do not behave in this manner. It is doubtful, therefore, whether the effect of the salts upon the colloidal state of the tobacco leaf is of any significance.

3. Only potassium citrate is effective in promoting the burn. The citrates of sodium and lithium are nearly neutral in their effect.

4. The organic salts of potassium, potassium carbonate, tri-potassium phosphate, di-potassium phosphate, and potassium sulphate improve the fire-holding capacity; while potassium chloride, acid potassium sulphate, and mono-potassium phosphate are injurious to the burn.

5. Sodium carbonate improves the fire-holding capacity slightly, while all of the other sodium salts are either neutral or injurious to the burn.

6. The data obtained do not confirm the idea that the reduction of the potassium salts will account for their favorable action.

7. Data are given which indicate that the harmful action of chlorides is not due to the fact that they fuse, as was suggested by BARTH.

8. Data are given which indicate that the alternately giving off and taking up of carbon dioxide will not account for the beneficial effects of potassium carbonate.

9. The effect of the salts in raising the temperature of the leaf may be of some significance.

10. The problem is probably complex, and the action of the caesium, potassium, and rubidium salts may be due to a number of complex factors.

11. It seems probable that caesium, potassium, and rubidium in the form of certain salts, such as the carbonates, sulphates, and phosphates, have a specific catalytic action in the combustion, and that the chlorides have a negative catalytic action. It is planned to study the rate of decomposition of various organic salts of the alkalies, and also the decomposition products of various organic substances treated with salts of the alkalies, when subjected to temperatures which are attained in the burning cigar.

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