

**CHARACTERISTICS OF WATER ADSORPTION ISOTHERMS
FOR MATERIALS CONTAINED
IN A BOX OF A TOBACCO PRODUCT**

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ABSTRACT

An experimental study has been carried out on the characteristics of water adsorption isotherms for typical materials used in a box of tobacco products or cigarettes. Equilibrium moisture contents for different varieties of tobacco, papers, filters and activated carbons were measured with a flow-type adsorption system under the conditions of a constant temperature at 303 K and relative humidities ranging from 5 % to 80 %. A modified Dubinin-Astakhov equation was accurately applied to represent the water adsorption isotherms for all materials. These isotherms were characterized by three parameters contained in the equation and divided into three groups; i.e. 1)tobacco, 2)papers as well as filters, and 3)activated carbons, depending mainly on pore sizes as well as the degree of swelling of the materials used. Under a relative humidity of around 60 %, the main water migration was found to take place in the tobacco and the percentage of migrated water to the total was assessed to be more than 80 %. The results suggested that the

selection of film, which has a function of being a high vapor barrier, is important to maintain the constant moisture content of tobacco during storage and marketing.

INTRODUCTION

In the tobacco industry, the water adsorption isotherms (WAI) for tobacco and tobacco packaging materials are important physical properties for the operation and design of the cigarette manufacturing process with special reference to drying, flavoring, packaging and storage. Not only is a systematic measurement of equilibrium moisture content (EMC) for these materials needed but also an equation is necessary which can be applied to the measured data for expressing the characteristic behavior of the WAI.

However, the data of WAI for these materials have not been measured systematically, and the information on the mathematical models or equations as well as their applicabilities to represent the characteristics of WAI has not appeared to date in the literature. Especially, an optimum equation is desired which can be applied to all materials by simply determining its parameters.

Although many models based on the well-known isotherm equation of Brunauer-Emmett-Teller (BET) for the EMC of industrial and food materials have been presented, these models have been recognized to be difficult to apply to the data for tobacco as well as to tobacco packaging materials. For example, the Guggenheim-Anderson-De Bore (GAB) equation, which is commonly used for food materials⁽¹⁶⁾, can be applied when the amount of adsorbed water corresponds to more than two layers of the molecule, and then the heat of adsorption is less than that of condensation of pure water. Since the heat of adsorption for tobacco is known to become almost equal to that of water⁽¹⁰⁾, the GAB equation is not suitable for tobacco. For the WAI of tobacco, Kamei et al.⁽⁵⁾ applied a modified Langmuir equation expressed in the form of a quadratic denominator, and Yoshida et al. showed that a polynomial Dubinin-Astakhov (DA) equation, which is modified for the use of zeolite, was applicable. Kobari et al.⁽⁸⁾ reported that WAI for an artificial fibrous material which was made from the cell wall components of tobacco leaf could be expressed as a function of the adsorption potential.

Recently, Kameoka et al.⁽⁶⁾ carried out a theoretical investigation to modify the DA equation for universal application to food materials, and their modification method appeared to be useful for tobacco and tobacco packaging materials.

The objectives of this work were to measure the WAI for the materials contained in a box of cigarettes and present a model to predict the WAI of these materials, investigating the applicable potential of the DA equation for expressing the characteristic WAI.

THEORETICAL MODEL

In this study the DA equation was employed to express the characteristics of measured WAI after investigating the applicability of several models presented. The DA equation was originally developed for explaining the adsorption phenomena of porous solid materials such as silica gel, activated carbon, and zeolite. It was formulated by considering the relationship between the volume of adsorption space and adsorption potential as indicated as follows⁽²⁾⁽³⁾.

$$W = W_0 \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (1)$$

where n is a positive integer below 6.

A is the adsorption potential given as ;

$$A = RT \ln (p^0 / p) \quad (2)$$

The relationship between volume and the amount of adsorbed agent is

$$W = \frac{q \times M}{\rho} \quad (3)$$

The limiting condition of integer for the value of n in equation (1) was

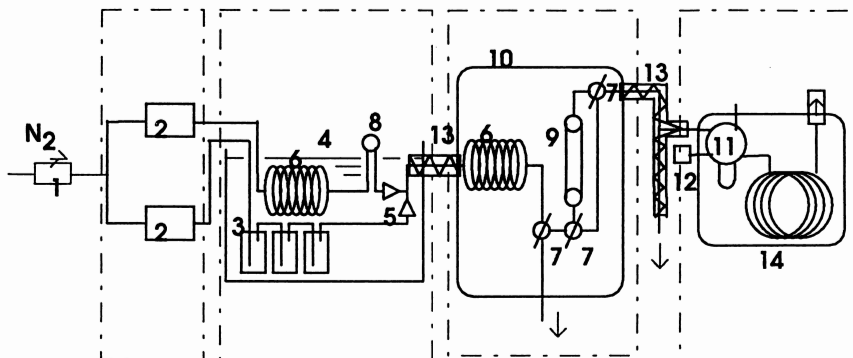
cancelled by the statistical considerations performed by Kameoka et al.⁽⁶⁾, and thus the real and positive values of n are valid in the equation. This extended condition promises the DA equation an increasing applicability, and for food materials they have reported the n values of real, positive, and below 1. Therefore, we tried to apply the DA equation to all the materials used in this study.

EXPERIMENTAL

Flow-type Adsorption System

A schematic drawing of a flow-type adsorption system is shown in Fig.1. The main functions of the system were the control of gas flow-rates, water-vapor supplying, operation of adsorption, and analysis of vapor concentrations.

Nitrogen dehumidified in a dryer (1) flowed through flow-rate controllers (2) at 0-100 cm³/min in each line. A part of it flowed into bubblers (3) to obtain saturated gas with water-vapor. The bubbler made of stainless steel was 300 cm³ in volume, and three bubblers were connected in a series and immersed in a water bath (4) at a constant temperature of 303 K. The desired relative humidity of gas was obtained by mixing the saturated gas from a bubbler line with a dehumidified and temperature controlled gas flowed through another line at a location after valve (5). The connection line (13) between water and air baths was heated and maintained at a temperature of 343 K to prevent it from undesirable condensation of water-vapor, and two coil-tube heat exchangers (6) were used to control the temperature of gas. Three-way cocks (7) and a by-pass line parallel to the cell line were used to monitor and ensure the desired adsorption conditions of flowing gas. Then the gas was injected into an adsorption cell (9), which was made of glass and about 10 cm³ in volume. During the adsorption processes, the cell was located in an air bath and its air temperature was maintained at a constant temperature of 303 K. To monitor the temperatures of the cell, the temperatures in both the inlet and outside of the cell were measured by using K-type thermocouples. At the outlet of the cell, the concentration of water vapor was analyzed with a thermal conductivity detector (TCD) of the gas chromatograph (14), using a six-way cock (11)



1. dryer 2. flow meter controller 3. bubbler 4. water bath
 5. valve 6. heat exchanger 7. three-way cock 8. valve
 9. adsorption cell 10. air bath 11. six-way cock
 12. flow controller 13. heater 14. gas chromatograph(TCD)

FIGURE 1 Flow-type adsorption system

and a sampling tube. The diameter of all pipe lines were 63.5 mm (1/4 in.) to lessen the frictional pressure drop of flowing gas.

Materials

A schematic drawing of materials contained in a box of cigarette is shown in Fig.2, and all materials used in this study are presented in Table 2. Typical two kinds of tobacco i.e. "bright yellow" and "Burley" for cigarette were prepared because their natures are different depending on their varieties and curing treatment methods employed during post-harvest processings.

The papers called as cigarette, tipping and wrapping are usually used to form the shape of a cigarette. Other papers of label, stamp and aluminum foil are used as packaging materials for outer packs or boxes. The aluminum foil consists of two adhered layers of a sheet of paper and aluminum and plays the role of a barrier against the movement of water-vapor.

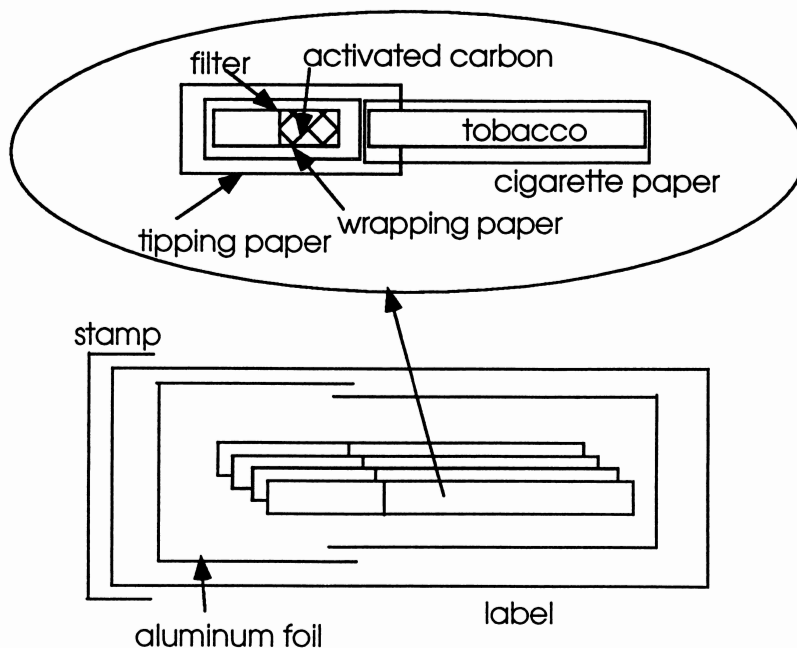


FIGURE 2 Schematic diagram of tobacco product

The cellulose acetate fiber, which is called tow, is 2.4/(1 molecular of glucose) in average acetyl degree, and a single fiber has a "Y" shape cross section. In the molding process of the filter, triacetin at about 6 wt% in concentration is added to the tow as a plastic agent, and then a part of the tow is melted during this process.

Three kinds of activated carbon were prepared, i.e., coconut (28-70 mesh), oil palm, coconut particle sampled from the filter, and their surface area as well as volume of pore (v_p) were determined by applying the Langmuir method to nitrogen adsorption isotherms, which had been obtained from the measurements with a "BEL JAPAN micrometrics BELSORP28"⁽¹¹⁾. The physical properties of activated carbon are listed in Table 1.

The accurate determination of a mass of dry material was required to get reproducible EMC from the measurements of adsorption. Then

Table 1 Physical properties of activated carbons

Activated carbon	Volume of pore $\times 10^3$ [m ³ /kg]	Specific surface area $\times 10^{-3}$ [m ² /kg]
Coconut	0.49	1255
Oil palm	0.39	1039
Coconut in filter	0.22	529

vacuum drying methods were used for this purpose, selecting an optimum drying condition for each material. The papers and filters were dried under the condition of a constant temperature of 373 K for 8 hours, and the conditions of 353 K for 8 hours were adopted to the tobacco. The former condition was determined according to the report by Kobari et al.⁽⁶⁾, which showed that fibrous materials such as pulp attained equilibrium within 4-5 hours when these materials were placed under an atmosphere of 10^{-3} Pa at a constant temperature of 373 K. For the latter conditions for tobacco, Sakamoto et al.⁽¹³⁾ reported that a dry material was obtained in an equilibrium state when it was treated by vacuum drying at a constant temperature of 353 K for 8 hours. The activated carbons were dried at a constant temperature and pressure of 473 K and 10^{-1} Pa, respectively, for 3 hours as was reported by Okazaki et al.⁽¹²⁾

Procedure

The amount of adsorbed water (q_w) was determined from the increase in mass of the cell after adsorption (ΔW) using the manner explained as follows; the volume of inner space of the cell (V_c) was determined by applying the gas displacement method, and an apparent density of materials (d) was measured by mercury porosimetry⁽⁷⁾. A dead volume of the cell (V_d) is

$$V_d = V_c - d \times W_s \quad (4)$$

The amount of water in the dead space (W_d) was calculated from the value of V_d and then q_w is given as

$$q_w = \frac{\Delta W - W_d}{W_s} \quad (5)$$

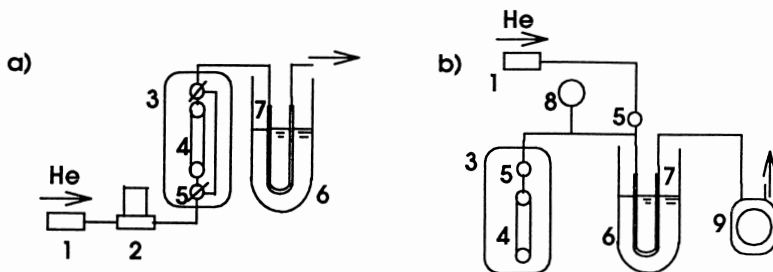
To determine the solid content, the material to be tested was put into the adsorption cell and then the cell was evacuated with a vacuum pump under the recommended conditions for temperature, pressure and drying time, as indicated previously. After vacuum drying, the cell was attached to the adsorption system and then the operation of adsorption was started. The time required to attain the equilibrium condition between the flowing gas and material was in the range of 2-8 hours.

After finishing adsorption, the cell was attached to the desorption equipment, as shown in Fig.3. As shown in Fig.3(a), for materials except activated carbon, the water was desorbed by heating the cell at 403 K for 1 hour using the dehumidified helium gas as a carrier. For activated carbon, the water was desorbed by vacuum heating at a constant temperature of 473 K for 3 hours, using an apparatus as shown in Fig.3(b). Then, the desorbed water was collected with a liquid nitrogen trap in both equipments. The trapped liquid was diluted with ethanol, and the water content was analyzed by using the TCD of a gas chromatograph. The values of water content obtained were used for the conformity to that obtained based on the weighing method of the cell.

RESULTS AND DISCUSSION

Performance of apparatus

The water adsorption isotherms of bright yellow and Burley tobaccos are shown in Figs.4 and 5, respectively. To confirm the validity of the experimental apparatus and procedure employed in this study, the values of WAI obtained for "bright yellow" tobacco were plotted in Fig.4 comparing with a curve, which is shown as a dotted line, reported by



- 1. dryer 2. mass flow controller 3. air oven
- 4. adsorption cell 5. cock 6. liquid N₂ 7. cold trap
- 8. vacuum gauge 9. vacuum pump

FIGURE 3 Two types of desorption equipments

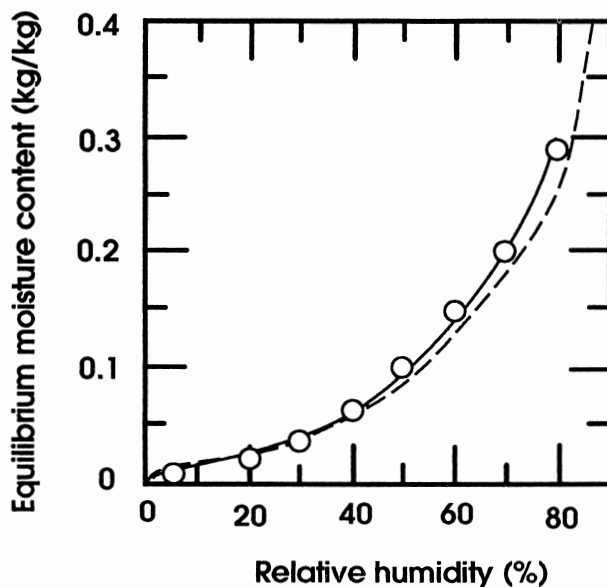


FIGURE 4 Water adsorption isotherm for tobacco "bright yellow"

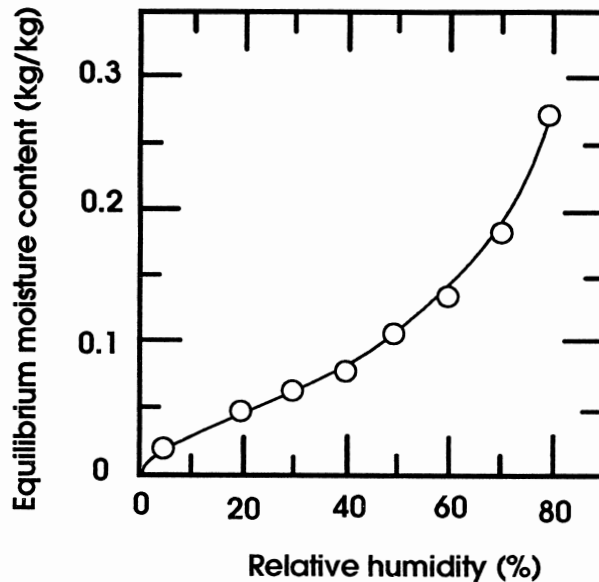


FIGURE 5 Water adsorption isotherm for tobacco "Burley"

Nakanishi et al. ⁽¹⁰⁾. Since good agreement between them was shown, our apparatus and procedures were appeared to be essentially valid for the objectives. From the comparison between the total amount of adsorbed water and the accuracy of the analyzing apparatus, we assessed that the experimental error of moisture content was sufficiently correctly within 0.5 % under the conditions of a constant temperature at 303 K and relative humidities ranging from 5 % to 80 %. The water adsorption isotherms for each packaging material are shown in Figs.6, 7, 8 and 9.

Characteristics of WAI

The empirical equations for all the materials were obtained from the regression line by applying the least squares method. The values of constants estimated and determination coefficients are listed in Table 2, and the obtained curves are presented in Fig.4 to Fig.9. Since the values of the determination coefficients obtained were extremely high,

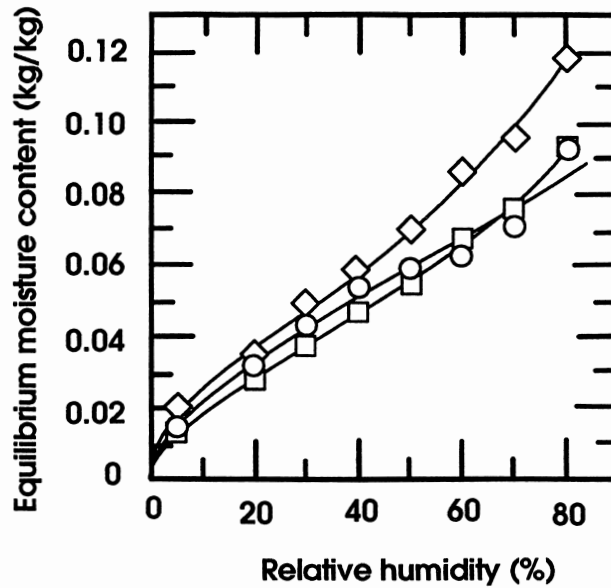


FIGURE 6 Water adsorption isotherms of papers used for cigarettes (○, cigarette paper; □, tipping paper; ◇, wrapping paper)

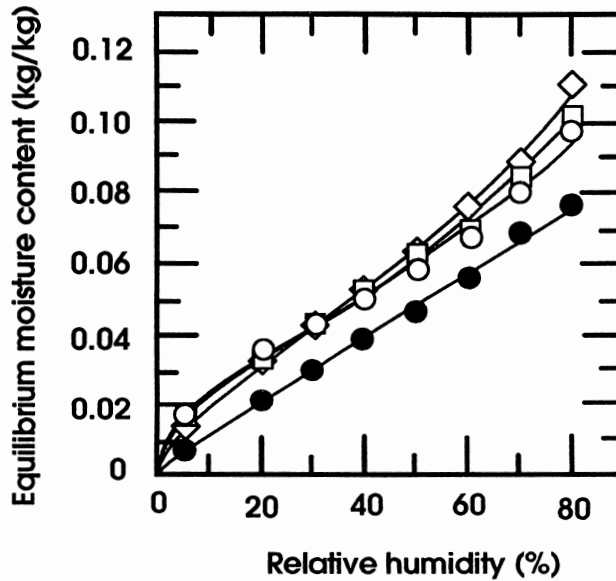


FIGURE 7 Water adsorption isotherms of papers used as packaging materials (○, label (soft); □, label (hard); ◇, stamp; ●, aluminum foil)

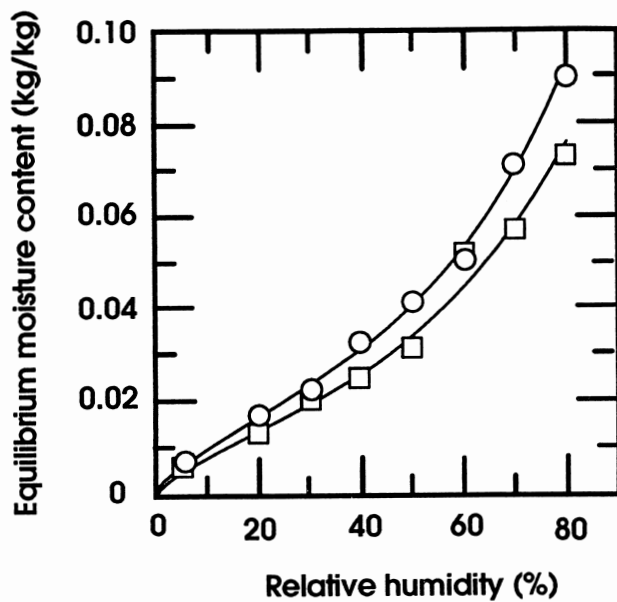


FIGURE 8 Water adsorption isotherms for filters (○, tow; □, filter)

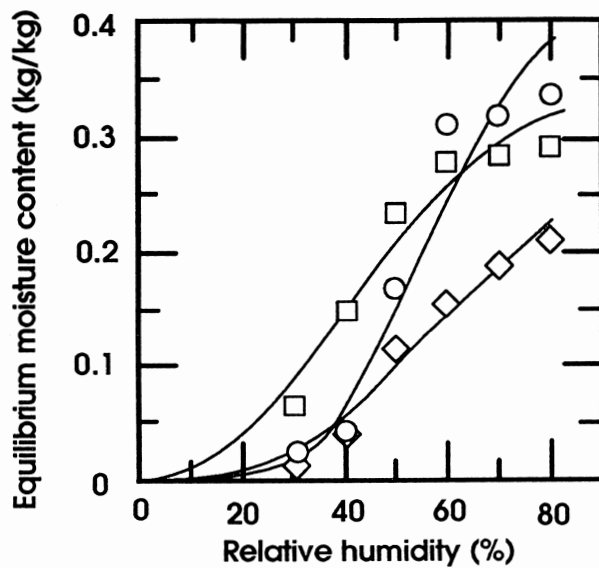


FIGURE 9 Water adsorption isotherms for activated carbons (○, coconut; □, oil palm; ◇, coconut in filter)

Table 2 Empirical constants and determination coefficients of the DA equation

Material	n	$w_s \times 10^3$ [m ³ /kg]	E [kJ/mol]	r^2
Tobacco				
bright yellow	0.43	2.15	0.12	0.997
Burley	0.33	1.86	0.07	0.996
Paper				
cigarette paper	0.86	0.10	3.57	0.990
tipping paper	0.60	0.16	1.66	0.999
wrapping paper	0.46	0.26	0.97	0.997
aluminum foil	0.94	0.10	2.54	0.999
label(soft pack)	0.61	0.14	2.23	0.995
label(hard pack)	0.58	0.17	1.74	0.999
stamp	0.66	0.17	1.82	0.999
Filter				
tow	0.42	0.34	0.30	0.999
filter	0.42	0.28	0.30	0.990
Activated carbon				
coconut	2.29	0.42	1.71	0.980
oil palm	1.82	0.34	2.60	0.978
coconut in filter	1.52	0.28	1.69	0.954

the DA equation was demonstrated to have high applicability to the materials used in this study.

It was found that the forms of WAI for the tobaccos, papers and filters were different from the activated carbons in the lower range of relative humidity of 0-30 %. Although the WAI for the former materials were increased showing the convex curves, those for activated carbons indicated the opposite behavior. From the measurements of structural parameters by the BET method, for the tobacco, papers and filters, it was recognized that drying of materials under vacuum or by the use of dehumidified agents such as diphosphorus pentoxide causes contraction of the material. From these results it was predicted that when these materials were in the dry state, the hydroxyl groups in the cellulose

molecules bonded with each other, and then, as water was adsorbed, these bonds were broken by the hydroxyl groups which existed in the water, leading to the gradual structural swell of the material⁽¹⁾. For the activated carbons, it is reported that water adsorption is caused not by adsorption on the surface but rather by capillary condensation within the material. Similar behavior is considered to take place in the material⁽⁴⁾⁽⁹⁾. Consequently, the EMC of activated carbon approaches a value of nearly zero in the range of lower relative humidity as shown in Fig. 9.

It can be seen that the EMC of the tobaccos is greater than those of papers and filters for a higher range of relative humidity. Especially, at a relative humidity of 60 %, the EMC of the tobaccos is twice as great as those of the papers and filters. This difference is considered to be caused by the nature of living plants, which contain hemicellulose, lignin and amorphous cellulose and so on.

Parameters in DA Equation

In connection with the physical significance of the empirical equations obtained, the constants of n as well as w_o involved in the DA equation have revealed useful information. For instance, the value of w_o shows the total volume of pores within the samples, and as the n value increases, the adsorbed pore diameter becomes smaller⁽¹⁴⁾.

As indicated in Table 2, the n values for the tobaccos, papers and filters were less than 1 and almost equal among them. This agreement can be explained in terms of almost the same pore radius for these materials. The values for activated carbons were nearly 2 and this value usually appeared when the DA equation was applied to the organic vapor adsorption by activated carbons⁽²⁾⁽³⁾. Therefore, the water vapor adsorbed by activated carbons is also considered to enter into the micropores the same as the organic vapor.

There were great differences in the value of w_o between the different types of tobaccos and papers as well as filters corresponding to the aforementioned difference in the EMC for the range of higher relative humidity, while the w_o values for the activated carbon agreed well with the values of v_p , as expected, which were obtained from the nitrogen adsorption isotherms, and are presented in Table 1. The value of w_o for activated carbon or coconut contained in the filter was smaller than that

for coconut because of the effect of triacetin, which was usually added together with it in the molding process of filter⁽¹⁵⁾.

These results suggest that the characteristics of water adsorption for the material used are divided into three groups; i.e., (1)tobacco (2)papers as well as filters, and (3)activated carbons.

Prediction of water migration

The adsorption and desorption phenomena were considered for each material during the storage of the product by utilizing the WAI obtained. To predict the effect of various levels of relative humidity on water migration, the three levels of relative humidity were selected as 30, 60, and 80 % , and fluctuation in water migration was estimated at these levels by applying the following differential equation obtained from equations (1)-(3).

$$\frac{dq}{dp} = -q \frac{n (RT \ln \frac{p^o}{p})^{n-1}}{E^n} \frac{RT}{p} \quad (6)$$

Table 3 indicated the estimated values for increases in the EMC when the vapor pressure increased to 1 % of saturated vapor pressure (p^o), i.e., $0.01 p^o$, at each humidity level. As shown in these values, the EMC of activated carbons and tobaccos are increased in the range of less and more than 60 %, respectively. For the papers, the effect of fluctuation in relative humidity on the EMC did not appear definitely under a condition of relative humidity ranging less than 80 %.

The material, which was stored under a condition of relative humidity of 60 %, is usually used in the manufacturing process, and the final product is also recommended to be maintained under the same condition. So, the amount of water migration for each material was predicted when the relative humidity of air in the storage room for the final products was changed from 60 % to 50 % or 70 %. We assumed that a box of tobacco products contained tobacco columns of 25 mm in circumference, 70 mm in length and 700 mg/cig. in weight using equally mixed tobacco varieties of bright yellow and Burley, and a filter made from charcoal and cellulose acetate with a length of 10 mm and 15 mm,

Table 3 Estimated values for increases in the EMC when the vapor pressure increased to 1 % of saturated vapor pressure

Material	Relative humidity		
	30% [wt%]	60% [wt%]	80% [wt%]
Tobacco			
bright yellow	0.2	0.6	1.4
Burley	0.2	0.4	1.0
Paper			
cigarette paper	0.1	0.1	0.1
tipping paper	0.1	0.1	0.2
wrapping paper	0.1	0.1	0.2
aluminum foil	0.1	0.1	0.1
label(soft pack)	0.1	0.1	0.1
label(hard pack)	0.1	0.1	0.2
stamp	0.1	0.1	0.2
Filter			
tow	0.1	0.1	0.3
filter	0.1	0.1	0.2
Activated carbon			
coconut	0.3	1.2	0.3
oil palm	0.4	0.5	0.2
coconut in filter	0.3	0.5	0.3

respectively. Fig.10 illustrates the amount of water migration during (a)desorption and (b)adsorption processes. The materials were grouped into 3 categories and the values indicate the amount of water migrated into/from each category. The values in the blankets show the percentages of migrated water to the total. Under the relative humidity of around 60 %, the main water migration takes place in the tobacco and its percentages are assessed to be 82 % and 85 % in the desorption and adsorption processes, respectively. For other materials, the corresponding values are assessed to be in the range of less than 18 %.

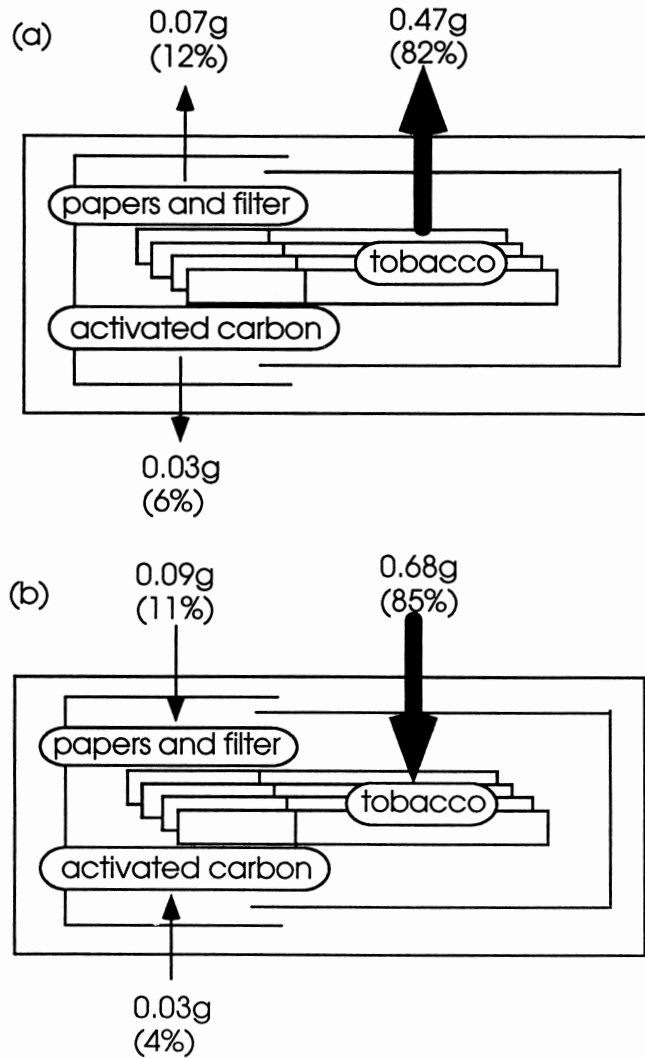


FIGURE 10 Calculated water migration, assuming that water is freely transferred between the product and the surroundings when the relative humidity is changed (a) from 60 to 50 %, and (b) from 60 to 70 %.

It is well known that one of the most important factors to guarantee the quality of cigarettes is to maintain the constant moisture content of tobacco during storage and marketing. For example, if the moisture content of tobacco changed about 1 % after manufacturing, the quality of the cigarettes is seriously damaged. In the desorption process, the EMC of bright yellow tobacco changes from 14.9 % to 10.0 % as indicated in Fig.4, the amount of water migration being estimated as about 5 %, indicating the inferior effects on the quality of the cigarettes. Thus the selection of film, which has a function of being a high vapor barrier, is important to maintain the relative humidity of air inside the box.

CONCLUSIONS

An experimental study has been carried out on the characteristics of water adsorption isotherms for typical materials used in a box of tobacco products. Tobacco products are composed of tobaccos, papers, filters and activated carbons. EMC for different varieties of tobacco, papers, filters and activated carbons were determined with a flow-type adsorption system under the conditions of a constant temperature of 303 K and relative humidities ranging from 5 % to 80 %. The DA equation was found to express the practical water isotherms over the whole range of relative humidities and provide the best isotherms for the interpretation of water adsorption. The results suggested that the characteristics of water adsorption are divided into three groups; i.e. 1)tobacco, 2)papers as well as filters, and 3)activated carbons, depending mainly on pore size as well as the degree of swelling. Under a relative humidity of around 60 %, the main water migration was found to take place in the tobacco and the percentages of migrated water to the total are assessed to be more than 80 % in both the desorption and adsorption processes.

NOMENCLATURE

A	=free energy of adsorption	[J/mol]
d	=apparent density	[kg/m ³]
E	=characteristic free energy of adsorption	[J/mol]

n	=constant in equation (1)	[-]
M	=molecular weight	[kg/mol]
p	=vapor pressure of water	[Pa]
q	=amount of adsorbed water	[mol/kg-dry material]
R	=gas constant	[J/K/mol]
r	=correlation coefficient	[-]
s	=specific surface area	[m ² /kg-dry material]
T	=temperature	[K]
V_c	=volume of adsorption cell	[m ³]
V_d	=dead volume of adsorption cell	[m ³]
v_p	=volume of micropore	[m ³ /kg]
W_d	=amount of water in dead space	[kg]
W_s	=mass of sample	[kg]
w_o	=constant in equation (1)(= volume of micropore)	[m ³ /kg]
ρ	=density	[kg/m ³]

<Superscript>

o =saturated

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