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The Bleaching of the Korean Beeswax

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Abstract

The objectives of this study are to determine the optimum process conditions of Korean beeswax and discuss the parameter of adsorption. Purification conditions, such as time, temperature and the type of adsorbents were investigated using the relationship between the properties of refined products and process conditions and the optimum bleaching condition of Korean beeswax were determined for the first time. The various bleaching conditions were examined by observing the result of Lovibond color, photometric color, methods provided by the American Oil Chemists' (A.O.C.S.). The optimum bleaching temperature was 80°C and the bleaching agents (5% of the weight of beeswax) which consisted of activated clay and activated carbon and a vacuum system were also necessary.

Key words: beeswax, bleaching, clay, carbon

INTRODUCTION

The first known use of beeswax was as a preservative for the remains of ancient Egyptian pharaohs about 4,200 B.C. It was used for making candles around 100 B.C. Between the 5th and 15th centuries, it was used as a form of currency (1). Although beeswax was the first substance of its kind to be used by humans, other matarials which shared certain characteristics with beeswax also became known as waxes.

Beeswax is produced by two types of bees, those classified as *Apis mellifera* and *Apis cerana*. Bees of the genus *Apis* alone produce beeswax refined to a white color. Because of its unique viscosity, emulsifying property, consistency regulating property and thermoplastic nature, beeswax is used in cosmetics, pharmaceuticals, candles, foods and polishes (2,3).

The honey bee, *Apis cerana*, secretes beeswax in order to build up a hexagonal cell in which honey is stored. Wax first secreted by the bee is a transparent colorless liquid, which turns into a semi-solid substance on contact with the atmosphere. Beeswax varies in color from yellow through brown to black, and it is believed that the pollen carried by the bee affects the coloration (4,5).

The chemical composition and analytical value of European and Asian beeswax are different, and most of the beeswax used in Korea is imported from Europe, China and the United States (6-8). No effort has been made to explore the industrial uses of *Apis cerana*-produced Korean beeswax, even though production volume can exceed 1,500 tons a year (9,10).

As an initial step in utilizing *Apis cerana*-produced Korean beeswax, we attempted to establish the optimum conditions for preparing beeswax using Korean beehives. The beeswax was collected from the beehives, isolated and then refined. The first step of producing beeswax was to separate the honey from the beehives. The sliced beehives were placed in hot water. The upper layer, which was crude beeswax, then was treated with phosphoric acid. The crude beeswax was purified through bleaching and deodorizing processes. To optimize our apparatus, several experiments were conducted, based on the basic principles of bleaching.

There are a lot of parameters affecting the bleaching process. We investigated the effect of each parameter on various adsorbents with respect to the adsorption of the pigments. The objectives of this study are to determine optimum process conditions of Korean beeswax and discuss the parameters of adsorption.

MATERIALS AND METHODS

Crude beeswax

Crude beeswax was obtained from waste honey combs supplied by Korean industry. The honey comb was weighed and charged on top of water in the glass flask. The amount of water was equal to the weight of beeswax to be processed. After the honey comb had been charged, heat was applied until all of the honey comb was melted. The melted crude beeswax floating on the surface was strained with water through a wet cloth to remove bee and cocoon fragments and other foreign matter. Upon cooling, the wax solidifies into a cake on top of the water; dirt was removed by scraping the bottom of the cake. Glass makes an excellent container for the manipulation of wax, while the use of iron equipment may generate problems.

Acid treatment

0.5% phosphoric acid was added to the molten crude beeswax and kept at 90°C for 2 hr. After agitation, the crude beeswax was subjected to a thorough washing with deionized water, which removes undesirable products and leaves the beeswax with a mild, bland and pleasant odor. The deionized water, an amount equal to 40% of the batch of processed beeswax, was heated to 90°C in a separate kettle of washed acids (11).

Adsorbents

Activated bleaching earth, unknown activated clay;clay A and Bentonite-CAS 1302-78-9 (sample # 343; B, 408; C, 456; D) were used. Activated carbon, Chalcoal Activate (SHOWA Chemical INC); E, unknown activated carbons; F, G, H, were used. Non-montmorillonite minerals, such as shacnite; I, synthetic minerals, such as shacnite-white carbon; J, K, L, were used. The BET analysis of whole adsorbents are given in Table 1. Surface areas and average pore diameters were determined using a BET apparatus. Adsorption/desorption isotherms were measured by a method provided by Coulter Electronics Ltd. using a Micrometrics ASAP 2000. The computer of this instrument confirmed surface area and average pore diameter. Whole adsorbents was sieved to remove particles larger than 100 mesh to facilitate observations on the microscope, especially to avoid confusing larger structures formed during the bleaching process with large particles of the bleaching agents. This was dried for 10 hr at 250°C.

Experimental conditions

Experiments on the effect of time and the vacuum were performed with a dosage of adsorbent 5% (w/w) of beeswax at 80°C and at a carbon/clay (w/w) ratio of 0.5.

The experiment on the effect of temperature was carried out for an hour and with a dosage of adsorbent 5% (w/w) of beeswax at a carbon/clay (w/w) ratio of 0.5.

The effect of increasing the dosage for adsorbent mixture was as follows. In this experiment, the variation in weight % of adsorbent during bleaching were examined in absence of oxygen. During bleaching, beeswax was heated to 80°C and stirred for 1 hr. Adsorbent was composed of a mixture of equal parts of clay and carbon. Aso, it was examined with bleaching of degummed beeswax using 0.5% phosphoric acid.

The effect for the adsorbent ratio and adsorbent types on bleaching was carried out under a vacuum at 80°C with a contact time of 1 hr. Adsorbent dosage of 5% (w/w) of beeswax was used.

Color

The assessment of color was carried out in the Lovibond Tintometer (Model E, England) and the recommended 5.25" cell was used. American Oil Chemists' Society provided for a determination of the optical density of the oil at 460, 550, 620, and 670 nm in a 21.8-mm cell, with the following equation being used for calculation of a photometric color that approximates color expressed in Lovibond red unit (12);

$$\text{Photometric color} = 1.29A_{460} + 69.7A_{550} + 41.2A_{620} - 56.4A_{670}$$

A: absorbance

Heating mantle in the spectrophotometer (JENWAY, Model 6100) was especially designed in order to inhibit solidification because the melting point of beeswax is higher than room temperature.

Table 1. BET analysis of whole adsorbents

Adsorbents		Surface area (m^2/g)	Average pore diameter (Å)
Activated clay	A	178	76
	B	109	144
	C	134	96
	D	162	167
Activated carbon	E	1256	24
	F	984	18
	G	1034	27
	H	866	19
Shacnite	I	207	70
	J	165	71
Shacnite-white carbon	K	312	84
	L	207	79

Apparatus

Bleaching experiments were done in a 100 ml cylindrical, pyrex glass vessel, which were maintained at the desired temperature by soaking in a hot water and oil bath (Fig. 1). The beeswax was mixed with the adsorbents by a magnetic stirrer. Without oxygen, the beeswax and the adsorbents were evacuated all the time and alternated with He gas admission before the adsorbents was added to the beeswax in a helium atmosphere. Then the mixture was evacuated before the experiment was started. Throughout the experiment a helium and vaccum atmosphere was kept above the process. After the bleaching reaction had finished, the bleaching apparatus was carried in a thermostat and turned up, then samples for filtration were taken with a glass filter holding a Whatman No. 2 paper in a cylindrical glass tube. The gallenkamp multispeed stirrer (model HS-360H, Japan) was found suitable for stirring at 350 ~400 rpm. A vaccum pump (SINKU KINO Co., GVD-05OA oil rotary vacuum pump, Japan) was connected to the bleaching system.

RESULTS AND DISCUSSION

Effect of time and vacuum

The effect of time during vaccum and atomospheric bleach-

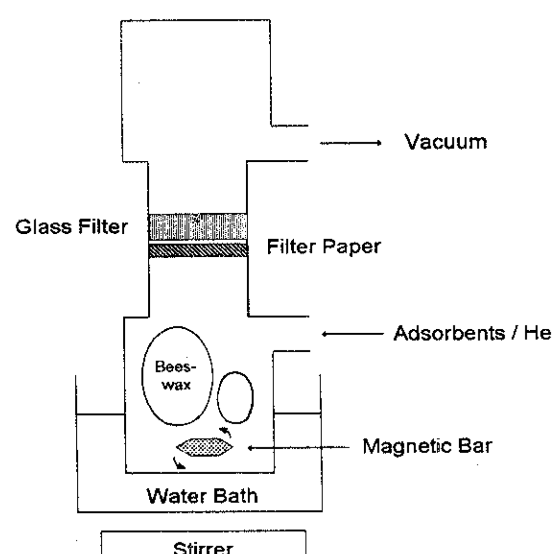

Fig. 1. Schematic diagram of bleaching apparatus.

ing of beeswax is shown in Fig. 2. Lovibond red color and photometric color decreased most rapidly during the first 60 min. At both 80 and 100 min, the color passed through a minimum level and then increased with time. In experiments with exclusion of air the maxima of color were reached rapidly. These maxima are higher after a few minutes in the experiments with admission of air. This can be explained through the reaction of the conjugated compounds formed with the oxygen present in the experiments with admission of air, so that only after a longer time is the total amount of conjugated compounds greater. These reactions probably take place via newly formed hydroperoxides derived from the chemical properties of beeswax (13,14). With oxygen, the oxidation has an important effect on the color of fat and oils. While oxidation bleaches the carotenoid pigments, it develops the color of other types of coloring material and in some cases apparently even produces colored compounds of a quinoid nature. For instance, the partial oxidation of vegetable oil causes an increase in their red-yellow color, most of which is apparently due to formation of the chroman-5,6-quinone described by Golumbic (15). Cottonseed oil is particularly prone to darkening on oxidation (15). Some lots of cottonseed and soybean oil darken so readily that the darkening tendency is noticeable on bleaching (16). The poor bleach color are obtained due to new pigment that develops as the old ones are adsorbed.

Effect of temperature

The effect of temperature is shown in Fig. 3. During the experiment, the change in temperature was performed without oxygen. Lovibond color and photometric color increased with increasing temperature over the range of 85~120°C and was lowest at 80°C. It was assumed that as the bleaching temperature increased above 80°C, free fatty acid (FFA) content of the beeswax increased. Various reports in the literature are not in complete agreement as to the optimum temperature for use of the adsorbent. Van Den Bosch (14) reported that in the bleaching process, the higher the temperature, the more cojugated compounds that were formed.

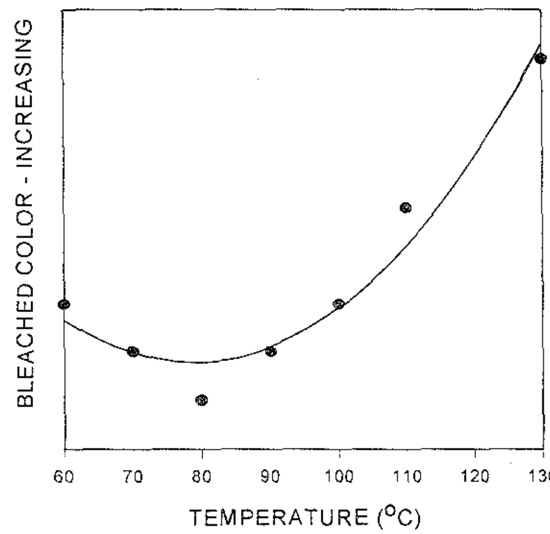

Fig. 3. Effect of temperature on bleaching of Korean beeswax.

Effett of adsorbent dosage and acid treatment

The effect of increasing dosage for adsorbent mixture is given in Fig. 4. Although larger doses removed more of each color, there were definite differences in decolorizing power at different dosages.

The activated clay and carbon retain more oil per unit weight than does the raw material, but their greater activity usually permits a lower dosage to be used. Thus, the overall

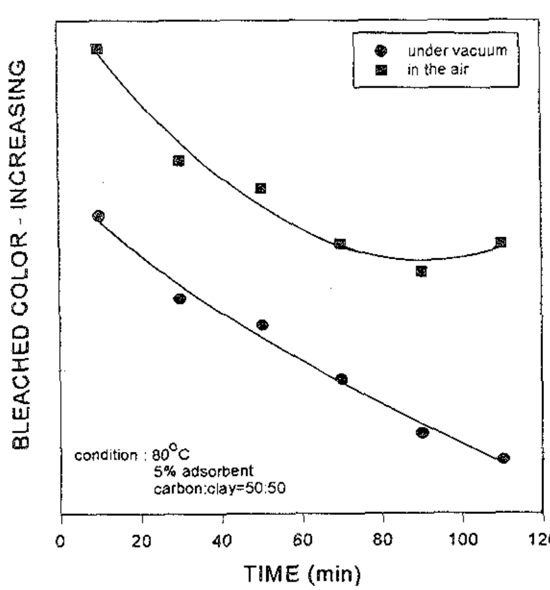

Fig. 2. Effect of time and vacuum on bleaching of Korean beeswax.

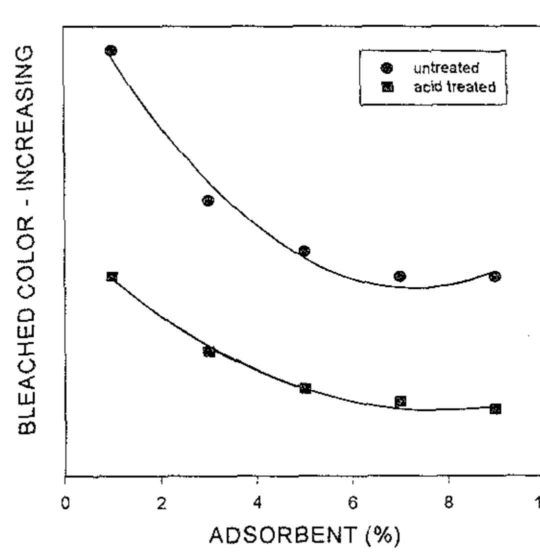

Fig. 4. Effect of dosage of adsorbent on bleaching of Korean beeswax.

loss of oil is often less. Because such loss of oil can be the most important cost factor, the edible oil processor's choice of adsorbent usually is a balance between activity, oil retention loss, and adsorbent cost (17). According to other reports, acid treatment leads to the production of unstable pigments and flocculation of colloids. Because of these characteristics, pigment in oil was settled down, which enhanced bleaching effect.

Effect of adsorbent ratio

The effect of changing adsorbent ratio is given in Fig. 5. When the activated carbon and activated clay was used alone, color of bleached beeswax increased in both sides. The result of this study showed that bleaching was best achieved when activated clay and activated carbon ratio is 0.5. Carbon is rarely used alone in the bleaching of most vegetable oils, but oil refiners frequently employ it in an admixture with bleaching clay. Such a mixture is often considerably more effective than bleaching clay alone. Carbon is also a superior adsorbent for traces of soap in refined oils. It is particularly effective in removing red, blue, and green pigment from coconut and palm kernel oil and better grades of animal fat, and it is popular for use in connection with diatomaceous earth in clarifying and mildly bleaching lard (18). Unlike bleaching earth, carbon imparts no foreign flavor or odor to the oil treated.

Effect of adsorbent type

The effect of adsorbent types on bleaching is given in Fig. 6. Bleaching efficiency was examined for four kinds of activated clay. Activated clays had higher adsorbing capacities than other adsorbents for the color bodies. It was assumed that the average pore diameter affect bleaching power. The data show that in activated clay the surface area is

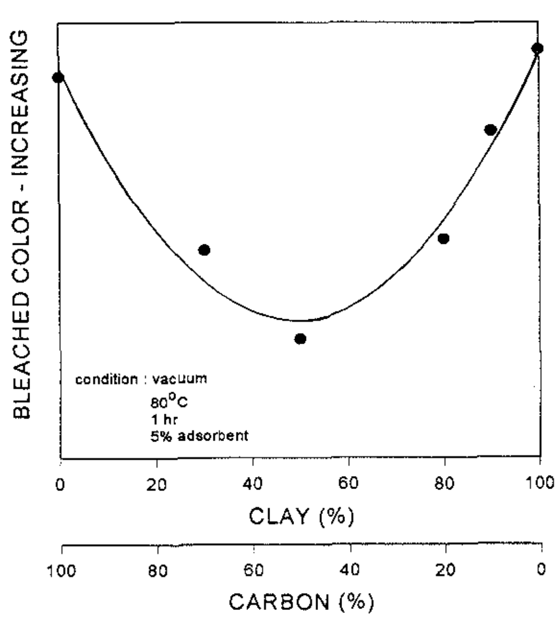

Fig. 5. Effect of adsorbent ratio on bleaching of Korean beeswax.

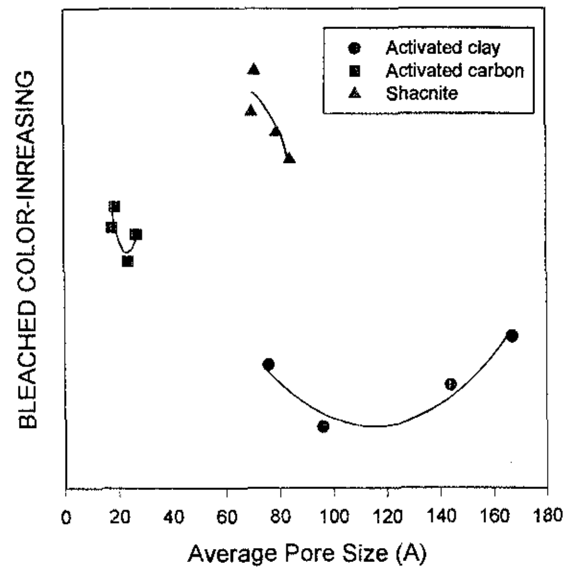

Fig. 6. Effect of adsorbent type on bleaching of Korean beeswax.

larger than 109 m^2/g and average pore diameter is larger than 76 Å, compared with that of activated carbon (Table 1). Considering the high surface area of activated carbon, we have attempted to establish the influences of pore size distribution and physical structure. Many other layer lattice clays related to activated clay have been examined by other workers as adsorbents (19,20)

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