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MICROCOPY RESOLUTION TEST CHART NATIONAL BUREAU OF STANDARDS-1953-A MICROCOPY RESOLUTION TEST CHART NATIONAL BUREAU OF STANDARDS-1963-A

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Technical Bulletin No. 716

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March 1940

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UNITED STATES DEPARTMENT OF AGRICULTURE WASHINGTON, D. C.

# INVESTIGATIONS ON THE PHYSICAL AND CHEMICAL PROPERTIES OF BEESWAX<sup>1</sup>

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United States Department of Agriculture, Bureau of Entomology and Plant Quarantine, in cooperation with the University of California Agricultural Experiment Station.

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### INTRODUCTION

The general trade has discriminated against certain western types of beeswax in favor of beeswax from other regions, both within and outside the United States. The basis for such discrimination obviously lies in differences in the properties of the waxes, but since virgin beeswax, or scale wax as produced by the bee, seems to have uniform physical and chemical properties, the differences are due to changes to which it is subjected after secretion. The color and texture of the white virgin wax are altered in the combs by contact with certain pollens and with metals used for wiring frames, as well as by contamination with propolis, which is abundant in some sections

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of the West. The chemical characteristics, especially acidity and iodine number, are decidedly altered by the admixture of propolis, and the various methods of rendering produce further changes. There are many more major honey plants in the Western States than in the East, and these natural sources offer a great variety of material for contaminating beeswax. Because of the many impurities that may contaminate scale wax, crude beeswaxes produced in the West have extremely variable composition. Obviously, therefore, they may be expected to respond differently to the various refining processes, and the refined waxes will differ in properties and possible uses.

Since the trade's present classification of crude beeswaxes as desirable or undesirable products is based on rule-of-thumb methods, a more definite basis for evaluation is needed. To determine the feasibility of establishing such a basis, a study was made of the physical and chemical properties of numerous crude beeswaxes, together with the kinds of impurities and some of their physical and chemical properties. The response of the crude waxes to miscellaneous tests with metals and to several bleaching tests was also observed.

### COLLECTION AND PREPARATION OF SAMPLES

### CRUDE WAXES

Most of the samples of waxes for general investigations were obtained from a large number of beekeepers located over a wide range of territory. Arrangements were usually made in advance so that the time of secretion, the plant source of incoming nectar, the method of rendering, and other variables could be recorded, and their history was, therefore, definitely known. Special samples were obtained from the writers' own bees through feeding and by moving the colonies to favorable locations as conditions warranted. Many open-market samples were also used for preliminary tests and for investigations on their behavior with metals and upon bleaching. Sixty samples were selected from the collection of crude waxes to be used for analyses and tests. They are referred to by number in the tables and text, and data on their history are given in table 1.

Sample No.	Geographical origin <sup>1</sup>	ical origin <sup>1</sup> Pisat source Co		Piekl Ireynration		
1	Davis		Yellow.	Cappings wax, water-ren-		
23		A 'falfs	do	deted in stainless steel. Do. Water-rendered in old honey		
 4		thistle.	Pale vellow	Nater-rendered in old honey can. New-combs wax, water-ren-		
5	Sacramento Valley	Star-thistle	Dingy yellow.	Cappings wax, solar-ex-		
			Black	tracted, remetted in old galvanized tang Old-combs wax, Hershizer press.		
7	Placerville	Manzanita	Dingy yellow	Cuptings way, water-mailed		
8 9 11	do 	Creeping sage Chamarbalia Honeydew and in- cense cedar.		Do. Do. Do. Do.		

TABLE 1.-Description of waxes used in the analyses

### CRCDE WAX

Where a State is not specified, the location is in California.

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## TABLE 1.—Description of waves used in the analyses—Continued

### CRUDE WAX-Continued

Sample No.	Geographical origin	Plant source	Color	Field preparation
11	Yerington, Nev	clover.	Yellow	Cappings wax, solar-e: tracted.
12	Glenn	Star-thistle	Dingy yellow	Cappings wax, solar-e: tracted, remelted in ga vanized iron.
13 14	do Shastn	Alfalfa and sweet- clover.	Black Pale yellow	Refuse wax, Hershizer pres Cuppings wax.
15	Pineridge	Honeydew, in- cense cedar.	do	Cappings wax, solar-e: tracted.
16 17	Colusa Chico	Star-thistle General mixture	Dingy yellow Brown	Do. Bee-supply manufacturer general mixture.
ıs	Lathrop	Lima bean	Yellow	Cappings wax, solar e tracted, remelted in ga vanized cappings melter.
19	Antelope Valley	Desert buck wheat.	Dingy yellowish brown.	dered in galvanized iton.
20 21	Ripon Oakland	Spikeweed Eucalyptus, mis- cellaneous.	Brilliant yellow Dingy yellow	Cappings wax. Do.
22 23	ldo 1:0s Molinos	Eucalyptus	Pale yallow Dingy yellow	Do. Cappings wax, solar-c tracted, remelted in gr vanized fron.
24	Bakersfield		Slightly dingy yellow.	Cappings wax.
25	San Joaquín		Yellow	Cappings wax from copp cappings melter. Refuse wax, Hershizer pre-
26 27	Corona		Black Dingy yellow	Cappings wax, water-re dored in gaivatilzed irou.
28	Imperial Valley			Cappings wax, solar- tracted. Do.
$\frac{29}{30}$	do Santa Ana	Orunge	Dingy white Creamy	New-combs wax, water- re dered in gaivanized fron.
31		Alfalfa and sweet- clover.		Open-market sample. Do.
32	do		Bright yellow	D0.
34		do.	Brown yellow	Do.
35	, do		Nearly black	Do.
36	do	do	Bright yellow	Do.
	do			Cappings wax, water-melt in rusty galvanized iron. Open-market sample.
00 80	**************************************		Dive	open marker semple.
	' dù	do	I Dark brown	Da.
39 40	do	do	Dark brown Dingy yellow	Da. Do.
41	do	í	DIRCK.	Do. Do.
41	1	í	DIRCK.	Do. Do.
41	1	í	DIRCK.	Do. Do.
41 42 43 <del>14</del>	do Mason Valley, Nevdo	do Miscellaneous do	Dingy yellow Smoky yellow do	Do. Do. Comb-honey-scrapings wa Do.
41	1	do Miscellaneous do	DIRCK.	Do. Do. Do. Comb-honey-scrapings wa Do. Cappings wax, solar-o tracted, remeited in g
41 42 43 44 45		do Miscellaneous do Alfalfa and sweet- clover.	Dingy yellow Smoky yellow do Dingy yellow Black	Do. Do. Do. Comb-honey-ecrapings wa Do. Do. Cappings wax, solar-t tracted, remeited in g vanized iron. New-brood-combs wax, H shizer traces.
41 42 43 44 45 46 47 48	do Mason Valley, Nev do Fallon, Nev do Masou Valley, Nev	do Miscellaneous do Alfalfa and sweet- clover. do do do	Dingy yellow Smoky yellow do Dingy yellow Binok Bright yellow	Do. Do. Do. Do. Do. Comb-honey-scrapings wa Do. Cappings wax, solar-t tracted, remeited in g vnnized iron. New-brood-combs wax, H shizer press. Cappings wax, sola extincted.
41 42 43 44 45 46 47	do Mason Valley, Nev do do do Mason Valley, Nev Cedarville	do do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion.	Bingy yellow do Dingy yellow do Dingy yellow Bingy yellow Bright yellow Brilliant yellow	Do. Do. Do. Do. Comb-honey-scrapings wa Do. Cappings wax, solar-e tracted, remeited in g vanized iron. New-brood-combs wax, Hu shizer press. Cappings wax, sola extracted. Comb-honey-scrapings wa Cappings wax, sola extracted.
41 42 43 44 45 46 47 48 49 50 51	do Mason Valley, Nev do Fallon, Nev do Mason Valley, Nev Cedarville Medina, Ohio	do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion.	Binck yellow do do Dingy yellow do Dingy yellow Binck Bright yellow Bright yellow Brilliant yellow Yellowish red	Do. Do. Do. Comb-honey-scrapings was Do. Cappings wax, solar-e tracted, remeited in g vanized iron. New-brood-combs wax, Ho shizer press. Cappings wax, sola extracted. Comb-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax."
41 42 43 44 45 46 47 48 49 50 51 52	do Mason Valley, Nev do Fallon, Nev do Mason Valley, Nev Cedarville Medina, Ohio	do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion.	Black Bright yellow do Dingy yellow Binck Bright yellow Brillant yellow Brilliant yellow Yellowish red	Do. Do. Do. Do. Comb-honey-scrapings was Do. Cappings wax, solar-e tracted, remeited in g vanized iron. New-brood-combs wax, Ho shizer press. Cappings wax, sola extracted. Comb-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax." Do.
41 42 43 44 45 46 47 48 49 50 51 50 51 52 53		do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- llon.	bingy yellow bingy yellow do Dingy yellow do Dingy yellow Black Bright yellow Brilliant yellow Yellowish red do Yellowish red	Do. Do. Do. Do. Comb-honey-scrapings wa Do. Cappings wax, solar-e tracted, remeited in g vanized iron. New-brood-combs wax, Hi shizer press. Cappings wax, sola extracted. Comb-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax." Do. Cappings wax.
41 42 43 44 45 46 47 48 49 50 51 52	do Mason Valley, Nev do Fallon, Nev do Masou Valley, Nev do Cedarville Medina, Ohio do Vernonia, Oreg Silverton, Oreg	do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion. Fireweed and scial Fireweed and scial Fireweed and scial	bingy yellow Smoky yellow do Dingy yellow do Dingy yellow Black Bright yellow Bright yellow Smoky yellow Brilliant yellow Yellow Yellow Yellow	Do. Do. Do. Do. Comb-honey-scrapings wa Do. Cappings wax, solar-o tracted, remeited in g vanized iron. New-brood-combs wax, H shizer press. Cappings wax, sola extracted. Comb-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax." Do. Cappings wax. Do. Do. Do.
41 123 133 145 46 47 48 49 50 51 52 53 53 53		do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion. Fireweed and sriel. Fireweed shock- berry mixture. do	bingy yellow bingy yellow do Dingy yellow do Dingy yellow Black Bright yellow Brilliant yellow Yellow Brilliant yellow Brilliant yellow Brilliant yellow Bright yellow	Do. Do. Do. Do. Comb-honey-scrapings wa Do. Cappings wax, solar-e tracted, remeited in g vanized iron. New-brood-combs wax, Hi shizer press. Cappings wax, sola extracted. Comb-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax." Do. Cappings wax. Do. Do. Cappings wax melted
411 422 433 445 445 445 445 447 449 50 51 52 53 55 55 55 55 55 55 55	Mason Valley, Nev do do Fallon, Nev do Mason Valley, Nev do Cedarville Medina, Ohio do Vernonia, Oreg Silverton, Oreg do Laramie, Wyo	do do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion. Fireweed and s- Fireweed berry mixture. do Alfalfa and sweet- clover.	bingy yellow bingy yellow do Dingy yellow do Dingy yellow Black Bright yellow Smoky yellow Yellowish red do Yellow Bright yellow Yellow	Do. Do. Do. Do. Do. Camb-honey-scrapings was Do. Cappings wax, solar-e tracted, remeited in g vanized iron. New-brood-combs wax, Ho shizer press. Cappings wax, sola extracted. Comh-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax." Do. Cappings wax. Do. Do. Cappings wax. Do. Do. Cappings wax melted enamelware.
41 42 43 44 45 46 47 48 49 50 51 52 52 53 55 55 55 55	do Mason Valley, Nev do do Fallon, Nev do Masou Valley, Nev do Cedarville Medina, Ohio vernonia, Oreg Silverton, Oreg Woodinville, Was Laramie, Wyo Hrush, Colo	do Miscellaneous do Alfalfa and sweet- clover. do Miscellaneous Alfalfa, sweet- clover, dande- lion. Fireweed and sweet- berry mixture. do Alfalfa and sweet- clover. do	bingy yellow bingy yellow do do Dingy yellow do Dingy yellow do Dingy yellow Bright yellow Smoky yellow Brilliant yellow Yellow Bright yellow Bright yellow Bright yellow Bright yellow Bright yellow	Do. Do. Do. Do. Do. Camb-honey-scrapings wa Do. Cappings wax, solar-o tracted, remelted in g vunized iron. New-brood-combs wax, H shizer press. Capping wax, sola extracted. Comb-honey-scrapings wi Cappings wax, sola extracted. Commercial "red wax." Do. Cappings wax. Do. Do. Do. Cappings wax. Do. Do. Cappings wax. Cappings wax. Cappings wax. Cappings wax. Cappings way. Cappings

TAULE 1.—Description of waxes used in the analyses—Continued

8ample Geographical origin Plant source Color Field preparation No. SW-1 Davis\_. White. Scale wax. WAX FROM SUGAR-FED BEES : CW-1 Davis\_ New-comb war, **Č**₩-2 ....do. Do, ŏw-3

SCALE WAX

<sup>2</sup> These samples were propared by J. E. Eckert, of the University of California. Except for the basic scale war, they represent the purest beeswax obtainable.

Slightly yellow.

Do.

Before any physical or chemical determinations were made, foreign materials, such as twigs, bees, and dirt, were scraped from the surface of the sample. Materials imbedded in the body of the beeswax were removed by filtering the melted wax at 80° C. in quantities of 200 gm. through qualitative filter paper into glass beakers. In every case the wax was lighter in color after filtering. These prepared portions of the crude waxes were then used as sample maferial for all subsequent analyses and tests, except for the lests on clarification and decolorization with acids.

### SCALE WAX

Wax scales were obtained fresh from the bees by removing their combs from the hives, thus forcing wax production. An eight-mesh screen placed below the bee clusters prevented the bees from picking up the scales dropped by them. These scales were collected, placed in covered glass containers, and transferred to the laboratory.

The wax scales as received were mixed principally with bee feces, pollen, broken wings, and insects. The small particles were removed by sifting through a 30-mesh screen. Particles as large as the scales, or larger, were removed by hand. The scales were then placed on a screen, washed with water, and dried in an oven at 40° C. They were next melted in a beaker at 80°, and the liquid wax was filtered through qualitative filter paper, where it left a light-brown residue representing the very small particles of foreign material that adhered to the surface of the wax scales. The wax cake (SW-1) obtained after cooling was clear, white, and brittle.

### WAX FROM SUGAR-FED BEES

Since the procedure for obtaining the basic pure wax from the wax scales was very slow and laborious, a sugar-feeding method was used for obtaining relatively large quantities of practically pure wax. The bees in open hives were fed very heavily with sugar sirup and were allowed to work the wax scales into combs. These combs were then removed and melted over hot water in glass beakers. Three samples, designated as CW wax, were prepared in this manner.

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\_do\_

### METHODS OF ANALYSIS

Samples of the prepared wax were subjected to the standard tests on waxes described below. These tests were on properties of the wax as a whole, not on properties of specific contaminants. The tests included melting point, solidifying point, density, refractive index, ash content, saponification number, acid number, and iodine number. Ester numbers and the ester-acid ratios were obtained by calculation.

The melting point and the solidifying point were determined as follows: An open capillary tube of 0.5-mm. bore and 50 mm. in length was dipped to a depth of 3 to 4 mm. in a melted sample of each wax, cooled, and then sealed in a flame. The tube was attached to a thermometer, and the two were placed in a large test tube, which in turn was suspended through a cork in a 500-cc. wide-mouthed Erlenmeyer flask. The flask and the test tube were partly filled with distilled water to the same level, and the assembly was heated slowly, the water in the test tube being kept agitated. Near the melting point the rate of heating was 0.5° C. per minute. The temperature at which the wax became liquid was recorded as the melting point. Then the thermometer, capillary tube, and test tube were removed from the bath and slowly cooled. At the solidifying point the wax suddenly became opaque, and the temperature at this point was recorded. The precision of this test was  $\pm 0.5^{\circ}$ .

For the determination of density, approximately a 2-gm. sample of wax was melted in a porcelain crucible and slowly cooled to room temperature. The wax cake was removed by warming the crucible slightly and then attaching it to a very fine tared silk thread. The wax sample and thread were weighed in air and then weighed again after suspension in 95-percent alcohol of known density at 20° C. From these data the density of the wax was calculated by use of the formula

$$D_{w} = \frac{(W_{1} - W_{s}) \times D_{a}}{(W_{1} - W_{s}) - (W_{2} - W_{s})} = \frac{(W_{1} - W_{s}) \times D_{a}}{(W_{1} - W_{s})}$$

in which  $D_w$  is the density of the wax in grams per cubic centimeter at 20°,  $D_a$  is the density of ethyl alcohol in grams per cubic centimeter,  $W_1$  and  $W_s$  are the weights of wax and string, respectively, in air, and  $W_2$  is the weight of the wax when weighed in the alcohol.

The refractive index was read directly with a refractometer at a constant temperature of 80° C. Daylight, reflected from a sheet of white paper, was the source of illumination.

To find the percentage of ash, a 4-gm. sample of wax was placed in a platinum dish that had been ignited and cooled in a desiccator for 20 minutes and then weighed. The sample was slowly heated to 600° C. in a muffle furnace, to prevent the escaping vapors from igniting, at which temperature the sample was completely ashed within 15 minutes. The dish and contents were then cooled in a desiccator for 20 minutes and weighed. The difference between the final weight and the original weight gave the weight of the ash, and the percentage of ash was calculated from this value and the weight of the sample.

The saponification number was determined by the method given by Griffin.<sup>4</sup> Determinations were made in duplicate.

The acid number also was obtained by the method given by Griffin.\* The ester number was obtained by subtracting the acid number from the saponification number.

The iodine number was determined by the Hanus method.<sup>6</sup> Α 2-gm. sample was used, and 40 cc. of chloroform served as the solvent.

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These methods were employed whenever analytical data on waxes were required.

### CONTAMINATING MATERIALS

Wax scales are subject to various kinds of contamination immediately after they are produced. Within the hive contamination begins when the scale wax is manipulated into the comb by the mouth parts of the bees, to which dust and pollen adhere. The wax in the comb. furthermore, is constantly in contact with propolis, pollen, honey, dust, and brood or its food or decomposition products. Under such conditions solid particles become imbedded in the wax surface, and wax-soluble odoriferous substances, coloring matter, and the like diffuse into the wax. Further contamination occurs when comb or cappings waxes are rendered, because the hot wax dissolves propolis, pollen coloring matter, and foreign substances contained in the brood. Hot wax usually darkens when in contact with honey or water in vats made of certain metals.

The dispersed solids in crude wax have been found to consist chiefly of dust, insect remains, bits of straw and leaves, pollen grains, rust, and many other materials with which the wax has been brought in contact during handling and processing.

Deviation from either the physical or the chemical values of the scale wax, as observed in the crude or treated samples, indicates contamination.

### PROPOLIS

Many plants produce bud-coating gums, called propolis, which are insoluble in water and are collected by bees for various uses within the hives. Propolis is therefore a very common constituent of the impurities dissolved in beeswax. Some natural contamination of the wax occurs, because the bees use propolis to varnish surfaces and to fill spaces between the frames that are too small for them to enter. Much more propolis contamination results from mixing and rendering "scrapings wax" with crude wax from other operations.

Several samples of propolis were collected from beehives located in widely separated districts. At room temperature some of the samples were soft and sticky, whereas others were hard and brittle. The color ranged from light yellow through reddish brown to very dark brown. Janbert <sup>6</sup> reports that the vellow color of comb wax is due

<sup>&</sup>lt;sup>4</sup> GRIFFIN, R. C. TECHNICAL METHODS OF ANALYSIS AS EMPLOYED IN THE LABORATORIES OF ARTHUR D. LITTLE, INC., CAMBRIDGE, MASS. Ed. 2, 926 pp., illus. New York, 1927.

to the presence of chrysine (1,3-dioxyflavone) originating from propolis. Most of the samples had a spicy, pungent odor somewhat distinctive of the plant source, whereas others had very little odor. Most of them tasted bitter.

Propolis placed in melted beeswax dissolved partly or completely and imparted to the wax many of its physical and chemical properties. Samples of beeswax that were high in propolis, such as Nos. 43, 44, and 45, were distinctly sticky and possessed other abnormal characteristics, such as high density, index of refraction, and acid and iodine numbers (table 9).

Three samples of propolis were tested for melting point, density, and iodine number, with the following results: No definite melting points; densities at 20° C., 1.033, 1.121, and 1.145; iodine numbers, 19.6, 21.8, and 19.0. The saponification numbers for the first two samples were 28.9 and 69.3. The refractive index for the third sample was 1.45 and the acid number 125.0. These samples of propolis were obtained in different localities from the wax samples Nos. 43, 44, and 45.

Certain light-colored samples of propolis darkened greatly when heated in boiling water for 7 to 10 hours. The colored waxes known to contain propolis also darkened when heated for 7 to 10 hours in glass beakers at about  $75^{\circ}$  C. In some cases a lower layer of very dark reddish-brown liquid separated from the melted wax when it was allowed to stand undisturbed.

### POLLENS

Pollens constitute another important source of color in beeswax. Some highly colored pollens contain oil-soluble colored substances, usually yellow or orange, which are readily soluble in molten beeswax. If pollen grains containing these colored substances are brought into contact with white scale wax, the coloring matter in most cases diffuses into the wax, slowly at room temperatures but very rapidly at temperatures above the melting point of the wax. In several experiments white wax was exposed at 68° C, to fresh pollen grains from various sources. Table 2 records the results of these experiments. In some cases the wax became colored, whereas in others no color change occurred.

 
 TABLE 2.—Colors imparted to white liquid becauze by pollens when exposed at 68° C.

Plant source of pollen	Natural color of pollen	Color imparted to beeswax
Alfalfa (Medicago sotien) Algaroba (Prozopis chicensis) Asparagus (Arparagus officinalis) Black musuard (Brassica nigra) Broom (Cytisus scoparius) California-poppy (Eschecholizia californice) Daddeiton (Tarazacum officinale) Deciduous fruits. Fluree (Erodium cicutarium). Flure (Crodium cicutarium). Flure (Condit cicutarium). Gum plant (Grindelia canaporum) Hollyhock (Althaca rosci). Ladino clover (Trifolium repens) Orchard morning-vlory (Contok ulus arrensis. Perennial sunflower (Wichia).	Pale yellowish. Orange Light yellow Orange red Golden Rright yellow Yellow to brown Bright red Greeoist blig Creamy white Colden yellow White Brown White	ba, Fale yellowish orange, Light yellow. Trace of yellowish orange, Briliant orange yellow. Bricht yellow. Yellow. Do, Do, Do, Vellow, None. Trace of yellow, None.

Plant source of polien	Natural color of pollen	Color imparted to beaswax
Redmalds (Calendrinia caulescens) Spikeweed (Hemizozia fitchii) Star-thistle (Centeurea solstilialis) Sunflower (Heliamius belanderi) Willow (Salir sp.)	Colden yellow	Brilliant orange yellow. Bright yellow. Light yellow. Bright orange yellow. Vory light yellow. None. Do. Do.

TABLE 2.—Colors imparted to white liquid beeswax by pollens when exposed at 68° C.—Continued

### METALS

Since all comb wax has pollen grains imbedded in it, coloration is very likely to occur during the rendering process. Other substances not colored may also be dissolved by the wax and affect the chemical behavior of the rendered wax. In the process of rendering or remelting over water in iron trays, the yellow color of the crude wax is masked by a dark-brown or black appearance.

Experiments were performed to determine how contact with metals, in both the dry and wet states, affects the color of various waxes. The wax samples were melted either in beakers in contact with the metal or in pans composed of the metal to be tested. They were heated over a steam bath (100° C.) for varying periods of time, and the color changes noted by comparison with a portion of the original sample. Table 3 records some of the results of these observations.

TABLE 3.—Effect of meta	ls on th	e coloration	of	beesicar
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### IRON

Sample	Exposure		Color of wax			
Nó.	Wax in contact with—	Time	Original	Final		
25a 1 {2	Beaker + ferric oxide Beaker + ferric oxide + water Beaker + iron wire, dry. Beaker + iron wire + water. Iron skilet. Beaker + tin + iron filings + water. Tinned pan (scratched) + water. Beaker + iron filings + water. Skillet + water. Beaker + fron wire + water. Beaker + fron wire + water.	7 10 10 335 10 335 3 4 3 4 5 5 5	White	Brown, Do, Do, Do, Slightly darker, Grayfsi brown, Do, Slightly darker, Black, Black, Blackish brown, Brown, Do, Brownish yellow, Pinkish tinge.		

""a" designates chemically refined wax.

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### TABLE 3.-Effect of metals on the coloration of beswaw-Continued

MONEL

Sample	Exposure	į	Color of wax			
No.1	Wax in con-act with—	Time	Original	Final		
564	Beaker + monel filings +	6}2	White	Bluish green.		
4	water.	61-	Pale yellow	Paic brownish yellow.		
32{1	Beaker + monel plate Beaker + monel plate + water.	2149	Bright yellow	Brown. Do.		
	STAINLE	85 STE	EL	Ii		
β	Benker + dry plate Benker + plate + water	91 <sup>3</sup>	Bright yellow	bily derker.		
$32 - \frac{12}{3}$	Benker + plate + water	्रा		10.		
(4		5 534	do White	Slightly darker. White,		
12	da	5 1	do	100.		
25a	Beaker - dry plate	- a	. (10	' Do.		
5	do	ચુકે <u>ગ</u> ન	do			
45. White Filtrod wax .	do Beaker + plate + water Dry kettle	14	White	Brown. White.		
	ALUM	INUM	····	·· · · · · · · · · · · · · · · · · · ·		
	Maminum + water.		White	White.		
43	do	3	White Smoky yellow	Smoky yellow, a change except sepr		
tional samples.	Wet and dry	(?)	Variable	tation of resin. No change,		
	OTHER	метан	.3	·		
	Platinum dish + water	5	Smoky yellow	Smoky yallow, no change except sepa		
	:		1	change except sepa ration of resin.		
32	Brass + water	12	Bright yellow	Brownish vellow		
<b>4</b> 3	Copper + water Nickel + water	312 2	Smoky yellow	Change except sets		
Various samples	Zine, dry and wet.	(*)	Variable	Always change to dark		
Do	Powdered pure tin, dry and wet,	: رو. ا	də.	No change		
••••••••••••••••••••••••••••••••••••••	CHECKS (N	ю ме <sup>.</sup>		i		
Numerous samples of nonpropolised wayes.	Beaker, dry and with water	/¥)	White to yellow	No change.		
43		б ;	Smoky yellow,	Smoky yellow, resh separated out,		

The white waxes discolored much less than the crude. Probably the impurities in the crude waxes were responsible for the color changes. The crude waxes that contained much propolis, such as No. 43, discolored very rapidly in contact with iron, darkening slowly even when heated in glass. Part of the propolis changed to a very dark substance, which separated from the wax. This resinlike portion

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was hard and brittle after cooling. Crude wax containing little or no propolis showed practically no change in color when heated for a few hours in glass, platinum, aluminum, or stainless steel. The presence of water greatly accelerated discoloration of the crude wax by iron. The zinc coating on the galvanized iron in the tests in which water was employed was soon dissolved by chemical action of the solution, leaving the iron fully exposed to further chemical action. Heavily tin-plated iron was practically without effect as long as the tin coating was not abraded to expose the iron.

Several additional tests were conducted with filtered white wax from a commercial refining plant. These waxes became discolored by heating in the presence of water with iron, brass, zinc, or copper, the discoloration decreasing for the metals in the order named. No appreciable discoloration resulted from heating under similar conditions with aluminum, nickel, platinum, pure tin, and stainless steel. Monel metal had no effect on these waxes when dry, but when water was present a greenish discoloration developed after long exposure.

These laboratory tests, together with consideration of costs and practicability, indicate the desirability of using aluminum for commercial rendering and certain other processing equipment.

### CLARIFICATION OF CRUDE BEESWAX

Crude beeswax, whether it is to be refined or fabricated for use again in the bee industry, must be first melted in water and then strained or settled, or both, to remove honey and most of the suspenden matter. The wax is melted in insulated tanks by steam blown directly into the mass or by contact with steam-heated coils. The setthing requires many hours, depending primarily upon the quantity of wax, the efficiency of insulation, the maximum temperature to which the wax was heated, and the temperature of the surroundings. Some pacticles rise to the surface and form a scum, but most of them sink to the boundary between the water and the melted wax. The clear liquid wax is drawn off and cast into blocks. Sulfuric acid is sometimes added to the mixture of water and wax to hasten the clarification, and in such cases partial decolutization may also occur. Removal of suspended solids from the crude wax must be performed carefully to prevent chemical changes that would impart undesirable properties.

### DECOLORIZING PROCESSES

In the candle and cosmetic trades, and also in the preparation of models, a nearly white wax is required. Wax must therefore be bleached to make it acceptable for these trades. The processes for decolorization include the use of sunlight, finely divided adsorbing materials, and chemicals. Crude beeswax clarified and partly decolorized by a preliminary acid treatment responds more readily to decolorization or bleaching by sun treatment and adsorption than wax not so treated.

### PRELIMINARY ACID TREATMENT

Samples of crude beeswax from the writer's collection having a brown or black color were found to lose these colors when holled in glass beakers with solutions of oxalic, orthophosphoric, acetic, or citric acid (table 4). When cold, the treated waxes were usually a clear yellow. Qualitative tests on the acid wash solutions showed the presence of iron in most samples. Crude waxes that had become brown or black on treatment with iron or iron oxide in the presence of water (table 3) lost the discoloration when agitated with a 10-percent oxalic acid solution. The crude samples yellowed by acid treatment had apparently been discolored earlier by iron or iron salts. Colors imparted by other metals, such as copper, were also removed by the acid.

Sample No.	Acid (	Color of wax before treatment	Final color of wax
3	Citrie. Acetic (1 percent) Oxalic Citrie. Oxalic		Brownish yellow. Yellow. Brownish yellow. Yellowish brown. Yellow. Bright yellow. Brownish yellow. Light brown. Brownish yellow. Light brown. Brown. Yellow. Do. Somew hat lighter colors.

TABLE 4.—Effect of acid treatment on the color of crude beesicar

<sup>1</sup> The samples were boiled with 10-percent acid solutions for approximately 10 minutes unless otherwise specified. <sup>1</sup> A second lot of similar wax, as original supply was exhausted.

Conceivably the acid treatment might have affected the acid number of crude beeswax. To acquire data on this question, 50-gm. portions of the prepared samples of six crude beeswaxes were mixed with 200 gm. of 10-percent oxalic acid solution, and similar portions were mixed with 200 gm. of 1N sulfuric acid solution. After they had been boiled for 20 minutes, the mixtures were cooled and 15 gm. of each solid wax sample was removed for determination of the acid number. The remainder of each treated sample was then remelted over four times its volume of distilled water, and the mixture washed by agitation for 7 hours at 80° C. Again 15-gm. portions of some of the waxes were removed for determination of acid number. The results are recorded in table 5.

		Acid number					Aeld number				
Sample No.	Orig- inal	Immed folio treat wit	wing ment	wate after tr		Sample No.	Orig- inal	Immediately following treatment with-		wish	
	crude wax	Oxalic acld	Sul- furic seid	Oxalic acid	Sui- furic acid		crude wax	Oxalic acid	Sul- furic acid	Oralic acid	Sul- furic acid
B 35 50	17. 0 19. 5 17. 9	17.6 20.1 18.5	17.0 19.7 18.0	19. 2 18. 3	19. 0	52 53 56	19.6 19.2 19.0	20.0 19.4 18.3	19. <b>5</b> 19.4 19.6	19. 1	18.9

TABLE 5.-Acid numbers of crude waxes before and after acid treatment

Although the acid numbers of the waxes were almost always higher immediately after the acid treatment, after being remelted and washed with water two of the three samples so treated had acid numbers

slightly lower than those of the original waxes. The cause was very likely the retention of some free acids by the wax and their removal by washing.

### SUN BLEACHING

The sun has long been used to bleach beeswax. The ordinary procedure is to spread thin sheets, granules, or chips of the wax on sheets of canvas and expose them to the sun's rays. The mass is kept wet by sprinkling with water and is frequently turned over to expose new surfaces. This process is slow, the bleaching time varies with different waxes, and reflaking has proved necessary for some.

Sun bleaching of solid beeswax in any of the forms mentioned above was not possible during the summer in the vicinity of Davis, Calif., and in some preliminary experiments the wax was kept in the liquid state by the sun's heat.

These experiments were then transferred to Wabuska, Nev., where conditions for sun bleaching the liquid wax were more satisfactory. Portions of 46 of the crude-wax samples were exposed simultaneously in shallow aluminum pans mounted in a trough in contact with hot water (83° C.) from the hot springs at Wabuska. The molten wax layer in the pans was about 1.5 cm. deep. When a wax became white or nearly white, it was removed and the time of exposure to the sun noted. At the end of  $42\frac{1}{2}$  hours (1:30 p. m. on August 7, 1935) the remaining samples were removed.

Table 6 shows the results of these observations. The color disappeared entirely from several waxes and became much less intense in the others. Not only did the waxes bleach, but they also became very clear by coagulation and settling out of floating particles. No relation has been found between the properties of the crude wax and the effect of sunlight on color.

Sample	Expo-	Color before	Color after	Sample	Expo-	Color before	0.1
No.	sure		EXDOSULE	No.			Color after
	3010	capoguia	ezhotuta		sure	L criposure	exposure
		· · · · · · · · · · · · · · · · · · ·	· ••	·		· · ·	·
	Hours			1	Hours		ł
60	9	Nearly white	White	37			
18	IS	Yellow	E)o	3/		Dingy yellow	J White,
30	18	Cooperation	10	46	1215	do do	Do.
	20	Creamy	Do.	21	4245		Do.
4		Pale yellow	$D_0$ ,	12	4213		Do.
2	2014	3.0100	100.	17	4213	Brown	i Da.
14	$20\frac{1}{2}$	dot	Do.	56	4216	Bright yellow	Pale brown
15	21	Pale yellow	Do,	25	421.5	Yellow	Pale vellow
23	21 ,	Dingy yellow	Do.	6	4215		Pole brown
5	21 1	do	Do.	34	4212	Brownish yel	Do.
53	2514	Yellow	Do.		3-72	low.	D0'
9	2513	Dingy yellow i	Do.	57	101.1	Yellow	That we have a
481	26	Bright yellow	Do.	49		Provide and the	Pale yellow.
\$	26	Dingy yellow	Do.	35	1.1.2	Smoky yellow	. ')0.
28	26	Yellow	Do.	0.1	42.5	Nearly black	Pale brown.
11	27	Light yellow	Do.	. 17	4313	Black	Brown.
7	35 1			-14	424.2	Smoky yellow	Yallow
1		Dingy yellow	Do.	1	1		CTBATTL.
27	35	Yellow	Do.	33	121 2	Brown or gray	Dingy gray.
	30	Dinny vellow	Do.	. 39	421 5	Near black	Brown,
54	3516	Bright yellow	Do.	40	4236.	Dirty yellow	Brownish
10	351-5	Dingy yellow	Do.			•••	cream.
16	421/2	110	Do.	12	4214	Bright yellow	
31	421-5	Pale dingy yel-	De,	43	424.5	Smoky yellow	Yellow
	i	low.				Subject Sellow	cream.
33	421/2	Yellow	Do.	1 51	4912	Yellowish red	Vallandth
3	421/2	Brown	Do.			- one a man tett	brown.
19	421/2	Dingy yellowish	Do.	32	421.2	Brilliant yellow.	
	-/ -	brown.			1072	DITURNE ARIOM	Yellow,
				. 1		1	

TABLE 6.—Effect of sunlight on the color<sup>4</sup> of liquid crude becswar

It was difficult to describe the colors of waxes satisfactorily. In some waxes the shade changed between time of collection and use. None of the sun-bleached wax was mow white, and no 2 samples were identical its whitemess. After the removal of the material that had settled to the bottom of the wax, 100 gm, of each sample was placed in a glass beaker, melted at 80° C. in a drying oven, and then filtered through qualitative filter paper. The physical and chemical determinations were made on the filtered waxes (table 9).

### USE OF ADSORBING AGENTS

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Another process used for decolorizing crude beeswax consists essentially in bringing the molten crude wax into contact with small particles of adsorbing solids, such as infusorial earth, fuller's earth, or bone charcoal. Processes of this class are used in wax-refining plants in many parts of the United States. Since some waxes will not respond to this treatment, waxes that are to be bleached must be selected. Apparently this selection is merely by rule-of-thumb method. Several experiments were therefore performed to determine some of the factors involved in decolorization.

In the first experiments several adsorbent materials were tested for effectiveness in decolorizing two samples of crude wax. Of Filtrol, Nuchar, fuller's earth, Supercell, and bentonite, Filtrol proved most effective. The time of contact, the temperature, and also the relative quantities of Filtrol and crude wax influenced the degree of decolorization. Treatment at 80° C. was preferable to treatment at 130° because of darkening at the higher temperature. Treatment with Filtrol for 15 minutes proved as effective as treatment for much longer periods. The percentage of Filtrol required for different waxes ranged from 5 percent up; sometimes even 60 percent failed to decolorize the wax.

Physical and chemical analyses were made on 12 waxes that had been treated with Filtrol for one-half hour at 80° C. to determine which properties were affected by the process. The mixture of Filtrol and wax was stirred with a glass rod every 10 minutes. Approximately 50 gm. of wax was used for each sample, and the percentage of Filtrol ranged from 5 to 50. Several of the samples were treated with more than one concentration of Filtrol to determine the maximum effect. The effect of the Filtrol treatment on the color of these waxes is shown in table 7.

Filtrol Sample No. concen- tration	inal color Final color	Sample No.	Filtroi concen- tration	Original color	Final color
3	wn     Nearly white.       do     Whito.       gy yellow     Noarly white.       linut yel-     Do.       do     Do.	21 34 35 39 42 43 45	{ 50 15 20	Dingy yellow	Pala yellow. Light brown. Nearly white. Do. Smoky yel- low.

TABLE 7.—Effect of Filtrol treatment on the color of erude beeswar

Some experiments were conducted to determine the effect of iron staining on decolorization with Filtrol. Five-percent aqueous solutions of ferric chloride and ferrous sulfate were made up, and 25 gm. of each of eight crude waxes was boiled for 5 minutes in 25-cc. portions of each of these solutions. After being cooled to room temperature, the waxes were separated from the solutions and treated with 10 percent of Filtrol at 80° C. for 1 hour. The results appear in table 8.

TABLE 8.—Effect of staining from iron salts on the decolorization of crude	wares
10ith Filtrol	

			Color	alter treatment v	vith	
Sample No.	Original color	Filtrol	Ferric chlorido	Ferric citioride and Filtrol	Ferrous sullate	Ferrons sulfate aud Filtrol
ő	Dingy yellow.	Grayish white	Dark gray	Pale brown		White.
18	Yellow	Light yellow	do	Yellowish	gray. Dingy yel-	Yellowish
20	Brüliant yel- low.	White	Light gray	white. Gray	low. Brown	whita. White.
43		Smoky yellow_	Black	Dark brown	Black	Rusty or orange yel- low.
45 51	do. Yellowish red.	do Brownish yel- low	Graydo	Dingy yellow. Light brown.	Brown Black	Yellow. Do.
53	Yellow	White with yellowish	do	White	Light gray	White.
55	do	tínt. Very light yel- low.	Dark gray	White with grayish tinge.	Dingy yel- low.	White with yellowish tinge.

From table 8 it can be seen that in some cases preliminary treatment of the crude wax with ferrous or ferric salts promoted formation of white waxes upon treatment with Filtrol, whereas without this decolorization treatment the iron salts were detrimental.

### CHEMICAL TREATMENT

Many chemical methods have been reported for the decolorization of crude beeswax. Some prescribe agitating the melted wax in contact with aqueous solutions of either oxidizing or reducing agents in dilute sulfuric acid solution. When several representative samples of crude beeswaxes were treated with such oxidizing agents as sodium dichromate, sodium permanganate, potassium permanganate, hydrogen peroxide, ammonium persulfate, or benzoyl peroxide, none were completely decolorized. Moreover, many of the treated waxes were more brittle than the original wax. In other experiments zinc, aluminum, magnesium, tin, and other metals in granular or powdered form served as reducing agents when suspended in dilute sulfuric acid solutions and agitated with the melted crude waxes. Very little decolorization resulted; in some cases the color became a brilliant yellow, probably from the action of the dilute acid, as shown in some earlier studies (table 4).

The action of some oxidizing and reducing agents was tested in slightly basic solutions. The wax was present in a highly emulsified state. Hydrogen peroxide and sodium hypochlorite proved to be effective, but the decolorization was not so rapid with hydrogen peroxide as with sodium hypochlorite, and not all the crude waxes decolorizable with sodium hypochlorite could be decolorized with hydrogen peroxide.

As these tests indicated that the use of sodium hypochlorite should be further investigated, 28 samples of crude wax were treated with this material and then tested for physical and chemical properties. The method consisted essentially in melting 100 gm. of crude beeswax in contact with four times its volume of hot distilled water. Solid sodium chloride was added to make a 6-percent aqueous solution, the mixture was vigorously agitated at  $70^{\circ}-75^{\circ}$  C., and just enough 6 M sodium hydroxide was added to emulsify all the wax.<sup>7</sup> Commercial sodium hypochlorite solution was then poured in slowly, with stirring, until the emulsion became white.

The bleached emulsion, while still being stirred, was cooled to separate the wax as a white wax paste from the aqueous solution, which was later decanted. The white pasty wax was remelted in direct contact with a 6-percent solution of sodium chloride, stirred for 10 to 15 minutes, and subsequently cooled and decanted. The mass was finally washed with hot distilled water and then placed over a dilute (0.05 M) hydrochloric acid solution at  $75^{\circ}$ -80° C. until the emulsion was broken. The white prepared wax was melted and washed three times with hot distilled water, cooled, and then sampled for analyses and tests.

### COMPARISON OF PROPERTIES OF CRUDE AND REFINED WAXES

The analytical data on the waxes, both before and after the various decolorization treatments, are assembled in table 9 to permit comparison of individual samples. To permit comparison of the properties of crude wax with those of pure beeswax (scale wax and wax from sugar-fed bees), the maximum and minimum values for crude waxes have been placed with those of the other two types in table 10. The maximum and minimum data for sun-bleached. Filtrol-treated, and chemically refined waxes are also included in this table to show the effects of decolorizing methods on the wax properties.

Bample No.1	Melting point	Solidify- ing point	Den- sity at 20° C.	Refrac- tive index at 80° C.	Ash	Sapon- ilica- tion num- ber	Acid nom- ber	Ester num- ber	acid	Todine number (Lianus)
1 1a 1s 2 2a 2b		<sup>6</sup> C. $(3, 1 \pm 0, 3)$ $(3, 4 \pm .3)$ $(3, 0 \pm .2)$ $(3, 2 \pm .3)$ $(3, 2 \pm .3)$ $(3, 2 \pm .3)$	Grams per cc. 0.061 .962 .960	1. 4403 1. 4395 1. 4411 1. 4400 1. 4395 1. 4396	Per- cent 0.017 .050 (1) .017 .050 .067	91.9 92.4 92.1 92.1	18.4 19.5 13.0 17.2 20.5 15.2	74.9 71.3	4.35	10.3 9.7 10.0 9.7 7 <b>5</b>

TABLE 9.— Physical and chemical properties of 60 sumples of crude becswax, and of the same samples after decolorizing treatments

See footnotes at end of table.

<sup>&</sup>lt;sup>5</sup> With a highly propolized wax the initial emulsion was an intense yellow. Such an emulsion was cooled while being stirred to separate the wax as a wax paste from the yellow aqueous solution. The solution was decanted and the wax paste washed with water, thus removing most of the color bilore treatment with sodium hypochlorite. In order to bleach this paste further it was necessary to liquefy it over a dispersion at 70°-75° C. The volume of the sodium chloride was the same as that originally used in melting the crude wax.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sample No. Maltin point	solldify- ing point	Den- sity at 20° C.	Refrac- tive index at 80° C.	Aslı	Sapon- Ifica- tion num- ber	Acid num- ber	Ester num- ber	Ester- acid ratio	Iodine number (Hanus)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ing point ing control in the second s	sily al 20° C. 20° C. 900 905 905 905 905 905 905 905	$\begin{array}{c} 1 \mbox{ five } 1 \mbox{ five } 1 \mbox{ five } 1 \mbox{ field} 1 \mbox$	Per- const 0.054 0.020 0.020 0.020 0.023 0.025 0.025 0.025 0.025 0.03 0.0300000000	$ \begin{array}{c} Iff cent for multiple for multiple$	$ \begin{array}{c} number \\ 16.5222.8 \\ 17.5.8 \\ 20.7.8 \\ 18.17.7.8 \\ 18.17.7.8 \\ 19.7.7.8 \\ 10.7.8 \\ 10.7.8 \\ 1$	$ \begin{array}{c} \text{number} \\ \hline \textbf{number} \\ \hline \textbf{r}, $	$ \begin{array}{c} \text{cold} \\ \text{cold} $	8.1 9.7 9.4 10.6

**TABLE 9.**—Physical and chemical properties of 60 samples of crude becswax, and of the same samples after devolorizing treatments—Continued

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See footnotes at end of table,

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Sample No.	Melting point	Solidify- ing point	Den- sity at 20° C.	Refrac- tive index at 80° C.	Ash	Bapon- ifica- tion num- ber	Acid num- ber	Ester num- ber	Ester- acid ratio	Iodine number (Hanus)
Sample No. 275. 28. 28. 28. 28. 28. 28. 28. 28	point		Grams Per cc. 0.964 .965 .965 .965 .965 .966 .961 .964 .964 .964 .964 .964 .964 .964 .964 .964 .965 .965 .965 .965 .965 .964 .955 .964 .955 .964 .955 .964 .955 .964 .955 .964 .955 .964 .955 .964 .955 .964 .955 .964 .955 .965 .964 .955 .965 .964 .955 .965 .964 .955 .965 .965 .965 .965 .965 .965 .965 .965 .965 .965 .965 .965 .964 .955 .965 .964 .955 .965 .965 .965 .965 .964 .955 .965 .955 .965 .955	at 80° C. I. 4415 I. 4403 I. 4403 I. 4403 I. 4403 I. 4405 I. 4405 I. 4405 I. 4405 I. 4405 I. 4405 I. 4405 I. 4405 I. 4406 I. 4414 I. 4405 I. 4416 I. 4405 I. 4416 I. 4405 I. 4416 I. 4417 I. 4406 I. 4416 I. 4	Ash Petrit 0.0040 0.020 0.022 0.025 0.	num-	ber 19.9 18.6 17.7 18.9 19.0 19.3 18.9 18.8 18.8 18.8 18.8 18.8 18.8 18.8 18.7 19.5 19.5 19.5 20.0 19.5 19.5 20.0 19.5 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 18.7 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 19.5 20.0 19.5 18.8 18.8 18.8 18.8 18.8 18.8 18.8 18.5 19.5 19.5 19.5 20.0 19.5 19.5 20.0 19.5 19.5 20.0 19.5 19.5 20.0 19.5 19.5 20.0 19.5 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.0 19.5 20.5 17.7 17.7 17.9 20.2 17.7 17.9 20.2 17.7 17.9 20.2 17.9 17.9 20.2 19.5 20.5 17.7 17.9 20.5 17.9 17.9 20.5 17.9 17.9 20.5 17.9 17.9 20.5 17.9 17.9 20.5 17.9 1			(Hanus) 8.844 8.86 9.44 8.86 9.68 9.68 9.68 9.68 9.68 9.68 9.68 9.68 9.68 9.68 9.68 10.27 11.16 8.43 9.99 9.36 9.12 9.88 9.12 9.88 10.53 9.12 9.88 10.53 9.12 9.88 10.53 11.16 1.1.38 9.9 9.88 10.53 11.16 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38 9.12 1.1.38
55	$\begin{array}{c} 64.2 \pm .4 \\ 63.6 \pm .3 \\ 64.5 \pm .3 \end{array}$	63.4±.4 62.7±.2 03.2±.3	. 961 . 963 . 960	1. 4411 1. 4389 1. 4403	(4) - 017 - 020	93.6 95.6 92.0	17.5 20.2 19.0	76.1 75,4 73.0	4.35 3.73 3.84	8.5 8.3 8.3 8.9

 
 TABLE 9.—Physical and chemical properties of 60 samples of crude becsucax, and of the same samples after decolorizing treatments—Continued

See footnotes at end of table.

Sample No.     Melting point     Solidily- ing point     Den- sity at 20° C.     Refrac- tive at 80° C.     Sapon- iftea- tion ber       * C.     * C.     * C.     * C.     * C.     * C.	- Acid num- ber	Ester num- be	Ester- acid ratio	Iodine number (Hanus)
	-	1	·;	i
per cc. cent		1	1	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6     18.7       8     18.8       3     21.3       0     18.4       6     17.9       7     18.5       3     18.8       5     19.8	71,9 75,0 78,6 75,7 75,2 74,5 75,7	3.84 3.99 3.43	7.6 8.2 8.3 8.0 10.4 8.4 7.3

 
 TABLE 9.—Physical and chemical properties of 60 samples of crude becswax, and of the same samples after decolorizing treatments—Continued

<sup>1</sup> The sample number standing alone indicates the original crude sample; the letters following the sample numbers have the following significance: a, Chemically refined, batch 1; b, chemically refined, hatch 2; c, chemically refined, batch 3; d, partly chemically refined, batch 3; s, sun-blenched; F, Filtrol treated. The percentages indicate the percentage by weight of Filtrol used in the wax. <sup>1</sup> Trace.

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The maximum and minimum values of the crude waxes (table 10) show a very sharp difference from the values of the scale wax, especially the chemical values. Probably, therefore, the kind and amount of the soluble impurities in the wax produce a great effect on its properties.

 
 TABLE 10.—Physical and chemical properties of scale wax and waxes from sugar-fed bees, and maximum and minimum values (from table 9) for crude, sun-bleached, adsorbent-treated, and chemically refined becswaxes

Wax	Sample	Melting point	Solidify- ing point	Density at 20° C.	Refrac- tive in- dex at 80° C.	· Ash
		° C.	° C.	Grams per cc.		Percent
Scale	SW-1	64.4±0.6	;63. 5 <u>±</u> 0. 5	0,963	1. #02	
From sugar-fed bees	ICW-3	164.2±.4	(63.2±.4) (63.0±.4	. 959 . 959 . 954	1.4417 1.4403 1.4403	0 010
Crude	(Minimum	. 62.0	60.7	. 947	1.4388	(1)
Sun-bleached	Minimum	65.0		. 987	1.4527	. 037
bab-ba deneg i i i i i i i i i i i i i i i i i i i	)Maximum	65.2		987	1.4532	<u>) 014</u>
Filtrol-treated	{Minimum Maximum	61.8			1.4400	(4)
Chemically reflaed		62.7	61.4	. 930 . 964	1,4399	- 927
Wax	Sample	Saponi- fication number	Acid number	Ester number	Ester- acid rntio	Todine number (Hanus)
Scale				67,4	3.96	5.8
From sugar-fed bees	CW-1 CW-2 CW-3		18.5			6.5 6.2 7.0
Crude	(Minimum	59.3	16.5	71.1 113.0	3. 16 	
Sun-bleached	(Minimum	88.3	16.4	7L I	2 75	5.4
Filtrol-treated	Minimum	130.0	14.7		2,07	13.6
Chemically refined		640 A	15.6	99.1 71.1 87.1	5. 13 3. 43 5. 56	13.0 4,6 11-1
	1		•			

Trace.

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When the average values (not given in table) of each of the properties of the crude samples are compared with the corresponding values of the sun-bleached samples, only insignificant differences appear except for the percentage of ash, which is much lower for the sunbleached wax. Many of the values for individual samples, however (table 9), show marked differences, particularly in the chemical properties, after the bleaching. The saponification number showed no change in 2 samples, increased in 25 samples, and decreased in 19 samples. The acid number showed no change for 5 waxes, increased for 9, the decreased for 32. The ester number increased for 29 of the waxes and decreased for the remaining 17 samples. The iodine number increased for 5 and decreased for the remaining 41.

Figure 1 gives a numerical distribution of 60 samples of crude wax over the range of mininum-maximum values of some of their physical and chemical properties. Figure 2 gives a similar distribution for 46 samples of sun-bleached wax. The modes, or the values that occur most often, should indicate the approximate values to be expected in an average sample of crude or sun-bleached wax.

The method of sun-bleaching beeswax warrants commercial development. Many of the treated waxes have qualities, such as low ash content and nearly white color, that make them particularly desirable for candle manufacture. Where natural hot water and brilliant desert sunshine occur, a simple treating plant could be erected and operated at a low cost. High elevations are preferable because more sunlight comes through a rare atmosphere. Western crude beeswax could be collected and bleached into a fairly uniform product before it is moved to the large consuming markets in Illinois and New York.

moved to the large consuming markets in Illinois and New York. Upon decolorization with Filtrol, significant changes occurred in the chemical but not in the physical properties. With but few exceptions there was a decrease in ash content, saponification number, acid number, and iodine number. The variation in ester number is not significant, being dependent upon the magnitude of the changes in acid number and saponification number.

After treatment with chemicals, the increase in ash content was especially great. In most cases the ash was tested for chlorides; the chloride content, however, did not account for the total weight of ash. The iodine number was usually lower than that of the crude wax, but the values for saponification number, acid number, and ester number were about equally higher and lower.

For a few waxes (Nos. 2, 4, 37, 48, and 54) two batches of each, designated in table 9 as (a) and (b), were chemically treated. The analyses showed appreciable differences between batches of the same wax.

The color of the treated wax was generally a good white, but for a few samples it was light cream.

Four samples (Nos. 34, 39, 42, and 44) were tested to determine which properties showed the greatest change after the refining. Each sample was boiled for 20 minutes with four times its volume of 10percent oxalic acid and then chemically refined as follows: After treatment with the sodium chloride and sodium hydroxide, one-half of each sample (d in table 9) was removed and sufficient dilute (6 M) hydrochloric acid was added to break the emulsion; it was then washed twice with distilled water, tested, and analyzed. The other

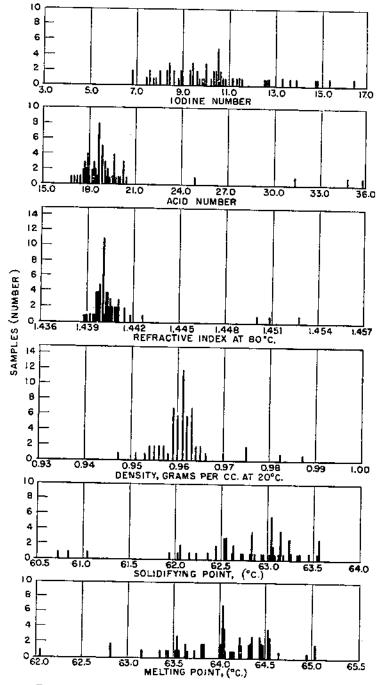


FIGURE 1.—Distribution of 60 samples of crude beeswax classified according to physical and chemical properties.

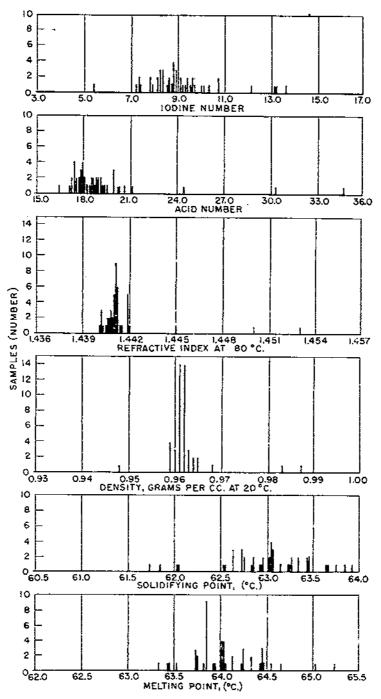


FIGURE 2.—Distribution of 46 samples of su-bleached beeswax classified according to physical and chemical properties.

half of each sample (c in table 9) was given the complete chemical treatment and three washes with distilled water before being analyzed. A comparison of these values with those of the crude waxes shows that the saponification number, the ester number, the percentage of ash, and the ester-acid ratio generally increased, whereas the acid number and the iodine number decreased, during the refining process.

Further investigations were conducted to determine where in the procedure the greatest increase in ash occurred. Samples of three crude waxes were chemically treated, and parts of each batch were removed at various points in the process for ash determination. The percentage of ash increased rapidly through the sodium hypochlorite treatment and then decreased rapidly as the number of washings with water increased. Washing the wax with 0.05 M hydrochloric acid proved much more effective than washing with water alone.

### OBSERVATIONS ON WAX BLOOM

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On standing at room temperature, the surfaces of wax samples became coated with the white deposit called wax bloom or mold. This deposit was scraped off the surface of three samples and used for a number of observations. Under the microscope the bloom appeared as flat, transparent, refractive plates, without uniform symmetry. Melting-point determinations gave a reproducible value at 39° C, and the solidifying point was 37.5°. The samples of bloom were not entirely free from wax, but when melting occurred the wax remained on the walls of the melting-point tube.

Candles, of both crude and refined wax, covered with bloom were immersed in 1-molar solutions of hydrochloric acid or sodium hydroxide for 14 hours, with no evidence of solubility in either case.

The bloom from any source was very soluble in petroleum ether ((boiling point 30°-40° C.), benzene, carbon disulfide, xylene, and carbon tetrachloride, but insoluble in 95-percent ethyl alcohol and in water. It was completely combustible, leaving no ash, and is there-fore a mixture of organic compounds.

Possibly the production of wax bloom may be attributable to molecular rearrangements that occur's under optimum temperature conditions, causing changes in volume of the wax and extrusion of some of its low-melting and plastic components.

### SPECTROGRAPHIC OBSERVATIONS ON COLOR IN BEESWAX AND POLLENS

Since the physical and chemical properties determined for the crude waxes did not indicate the kind or quantity of the impurities, they do not constitute a satisfactory basis for classifying crude waxes. A suitable basis could be established, however, by determining certain properties of the wax-soluble impurities. Preliminary studies of the soluble colored substance in some of the crude waxes were therefore undertaken. It was found that certain of the colored impurities could best be extracted by leaching the wax shavings at room temperature

<sup>&</sup>lt;sup>8</sup> WOOG, PATL, and YANNAQUS, N. ORIENTATION DES MOLECCLES DE LA CIRE D'AREILLE, ET REPERCESSIONS SUR LA SOLIDITÉ DES MAYONS, Compt. Rend. Acad. Sci. [Paris] 202; 76-78, 1936. [Abstract in Bee World 18: 117-118, 1937.]

with ethyl acetate. The colored substances were removed almost completely, and when the extracting solution was chilled most of the dissolved wax precipitated out, leaving the colored substances in solution. Absorption-spectra measurements were then made on these solutions.

Since no data have been reported in the literature on the absorption spectra of the colored substances present in crude wax when dissolved in ethyl acetate, and since, furthermore, the position of absorption bands is dependent upon the solvent used for the solution, it was necessary to make a thorough study of the spectra of solutions in this solvent.

The color extracts were examined in two spectrographs, (1) a quartzprism spectrograph having a dispersion of about 50 Å, per millimeter in the visible region, and (2) a grating spectrograph employing a concave diffraction grating of 1 m, focal length and having a dispersion of about 17 Å, per millimeter in the visible range. The absorption cells used in all measurements were of quartz and were 1 cm, thick. The light source was a tungsten-filament lamp enclosed in glass; therefore the spectrum could not be measured below 3,200 Å, because of absorption by the glass.

In an attempt to determine optimum conditions, several photographs were taken of the spectra of solutions prepared from three crude waxes (Nos. 16, 20, and 43) at different exposure periods and concentrations of color extracts. To insure uniformity, a standard procedure was employed in developing the films. Time did not permit purification of the colored substances extracted. The results of these preliminary experiments showed, for all the extracts, that no absorption bands were apparent on the plates in the region studied, although all the spectrographs showed fairly sharp cut-offs whose position, as might be expected, depended on concentration and length of exposure.

Since pollens have proved to be an important source of the waxsoluble yellow substances, it seemed likely that some correlation might be found between the absorption spectra of extracts of certain crude waxes and those of certain pollens. At the time these experiments on wax colors were in progress only squash pollen was available. Extracts of this pollen in ethyl acetate and carbon disulfide were prepared, and their absorption spectra determined. The absorption bands in solutions of carbon disulfide did not coincide with those in ethyl acetate, and the bands for the ethyl acetate extract were somewhat sharper. The extract in ethyl acetate showed five well-defined absorption regions, occurring at 3,710-3,780; 3,900-4,000; 4,120-4,200; 4,450-4.550; and 4,600-4.690 A. Four of these bands were observed under greater dispersion, and the following zones were defined: 3,949 4,046; 4,194 4,306; 4,467-4,525; and 4,622-4,784 A. The carbon disulfide extract of the same dilution as the ethyl acetate solution showed bands at 4,840-4,980; 4,600-4,690; 4,320-4,400; and 4,140-4.210 A.

Further to check the absolute position of these bands, solutions of pure (B) carotene in carbon disulfide and in ethyl acetate were prepared, and the band position of this substance was determined. The absorption bands in carbon disulfide coincided well with those reported in the literature, while the bands in the ethyl acetate solution were displaced from their positions in the carbon disulfide solution and were somewhat sharper.

### SUMMARY

The physical and chemical properties have been determined on 60 samples of crude beeswax, obtained for the most part from beekeepers in California and other Western States, and these properties have been compared with those of freshly secreted scale wax and also with the properties of many of the same crude waxes after they had been decolorized by various processes.

For freshly secreted beeswax the properties are nearly constant, but with changes in the quantity and kind of contaminating impurities some or all of these properties change. The physical and chemical properties of the impurities, and not of the waxes as a whole, must therefore be used as the basis for classifying crude beeswaxes.

The impurities in crude beeswax consist of honey, suspended particles, or dissolved substances, and may or may not be colored. The soluble colored materials are attributable to substances extracted from pollens, to propolis, and to substances produced by contact of the wax with metals. Darkening of crude wax by contact with iron or oxides of iron is very common.

The crude waxes that were highly contaminated with propolis showed higher densities, indices of refraction, acid numbers, and iodine numbers than those containing little propolis but appreciable quantities of other soluble contaminants. Samples high in propolis could not be decolorized by sun bleaching or adsorption, and they were decolorized chemically only with difficulty.

When melted crude waxes were treated with certain dilute acids, brown waxes became yellow, but the yellow color was not removed.

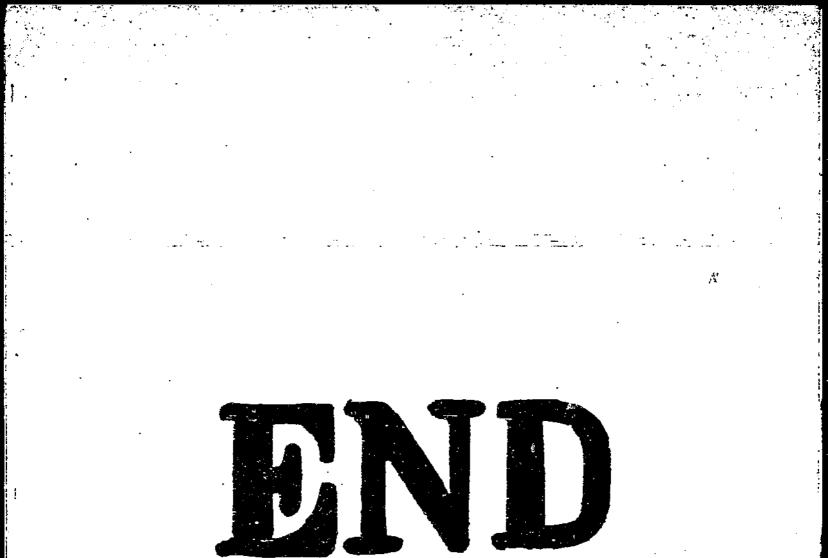
In tests of the complete removal or destruction of colored impurities by action of sunlight, adsorbent solids, and chemicals, the individual waxes differed greatly depending on the nature of the colored impurity. This fact indicates the necessity for establishing the chemical structure of these colored constituents and also their specific physical and chemical properties.

The effect of the method of decolorization on the composition of the wax is reflected to the greatest extent in the differences between the chemical properties of crude waxes and the corresponding refined waxes. The ash content was lowest in the waxes refined by sun bleaching. This process, however, was not so widely applicable to all waxes as the chemical method, which in every case produced a nearly white product with a relatively high ash content.

Wax bloom has been shown to be a mixture of organic compounds of low final melting point and narrow melting range.

Preliminary experiments on the absorption spectra of extracts of crude beeswaxes and of a pollen suggest the possibility of determining that the same colored substances may be common to some crude beeswaxes and pollens.

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